

Leaching behaviour of a complex zinc ore in a mixed citric-oxalic acid medium: Interaction effect and statistical modelling

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Abstract: Zinc leaching from a complex zinc ore using a mixture of citric and oxalic acids was investigated through response surface methodology (RSM) with a modified central composite design (CCD). The effects of solid content (2.5–12.5% w/v), citric acid stock solution concentration (0.25–1.25 M), oxalic acid stock solution concentration (0.05–0.25 M), leaching time (15–120 min), and temperature (30–70°C) were evaluated. Based on the F-values of the linear terms, the apparent order of influence was oxalic acid stock concentration > temperature > leaching time > citric acid stock concentration > solid content. This ranking represents linear main effects rather than overall variable importance, as significant interactions were also identified. Oxalic acid exhibited a strong negative linear effect, indicating that increasing its concentration did not improve Zn recovery. The highest experimental Zn recovery (67.98%) was obtained at 10% (w/v) solids, 1.0 M citric acid, 0.10 M oxalic acid, 30 min, and 60°C. Numerical optimization predicted a maximum Zn recovery of 81.42% at 10% (w/v) solids, 1.0 M citric acid, 0.10 M oxalic acid, 90 min, and 60°C. Three independent validation experiments yielded an average Zn recovery of $78.77 \pm 1.10\%$ ($n = 3$), corresponding to a relative prediction error of 3.25%. These findings demonstrate the effectiveness of RSM-based optimization and suggest that increasing oxalic acid concentration in the mixed-acid system may reduce Zn recovery.

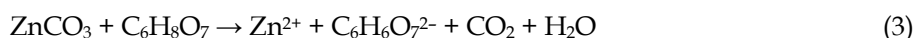
Keywords: zinc leaching, citric acid, oxalic acid, response surface methodology (RSM)

1. Introduction

Zinc (Zn) is an important industrial metal widely used in battery production, galvanizing steel, the automotive, and electronics industries (Pais and Rao 2021). Additionally, it is the third most widely used non-ferrous metal after aluminum and copper (Sahu and Agrawal, 2008). However, due to the increasing demand for zinc, the depletion of easily processable sulfide ores, and the generation of sulfur emissions during metallurgical processes, the beneficiation of oxide zinc ore has gained importance in recent years (Chen et al., 2009; Shi et al., 2012). Sulfide and carbonate ores are commonly used as raw materials in zinc production (Turan et al., 2004). In the beneficiation of smithsonite, flotation and leaching methods are employed (Ciccu et al., 1979; Pereira and Peres, 2005; Ehsani et al., 2019; Kaya et al., 2019; He et al., 2021; Chen et al., 2026). The flotation method is widely used in the beneficiation of sulfide minerals (Brest et al., 2021). In the flotation method, the target minerals are floated at specific pH values using anionic or cationic collectors and separated from the gangue (Top, 2021). Since oxide and carbonate minerals are generally suitable for atmospheric acid leaching, hydrometallurgical processes are preferred for the processing of complex metal resources containing disseminated lead and zinc. The processes do not emit hazardous dust or toxic gases and are highly suitable for small-scale operations (Jha et al., 2001; Sethurajan et al., 2017).

Leaching processes using organic acids have garnered attention in recent years not only for their environmentally friendly and biodegradable properties but also because they increase solubility by forming complexes with metal ions (Pathak et al., 2021; Golmohammadzadeh et al., 2018). In this context, citric acid and oxalic acid are two important organic acids that stand out due to their ability to form complexes with metal ions such as zinc (Gadd, 1999). Citric acid is a weak acid, and it is known

that citrate ions increase solubility by coordinating with zinc ions (Almbrok et al., 2025). The reaction between citric acid and smithsonite ore can be expressed as follows (Irannajad et al., 2013).



The corrosive properties of inorganic acids (such as sulfuric acid) used in leaching methods, their environmental impact, and the difficulties in managing the resulting waste have disadvantages from a sustainability perspective (Kishiko et al., 2025). However, among organic acids, oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) offers an advantage in selective leaching processes by facilitating the dissolution of metal ions through its complexation ability (Sheng et al., 2026).

The dissolution behavior of oxide minerals from different environments has resulted in numerous products. In their study, Hurşit et al. (2009) investigated the leaching behavior of smithsonite ore using gluconic acid. Deng et al. (2015) found that trichloroacetic acid follows the shrinking core model of surface reaction in the time-dependent dissolution tendency of smithsonite and that this acid is an effective and environmentally friendly extraction reagent. Irannajad et al. (2013) reported that approximately 82% zinc recovery was achieved under optimal conditions using citric acid on low-grade zinc oxide ores. Kumas and Obut (2021) reported that resistant phases formed at high temperatures during the leaching of smithsonite ore in a NaOH medium significantly reduced zinc dissolution. Kursunoglu et al. (2021) evaluated the selection of the appropriate acid type for zinc recovery from flotation tailings using the Analytic Hierarchy Process (AHP) and demonstrated that sulfuric acid offers the highest performance, while citric and oxalic acids could be preferred as alternatives in situations where environmental criteria take precedence. Ehsani et al. (2021) investigated the leaching behavior of zinc from smithsonite in aqueous ammonia solutions and reported that zinc recovery increased significantly with ammonia concentration, reaching up to 79.7%, while the process exhibited high selectivity; furthermore, subsequent thermal treatments enabled the production of high-purity ZnO. Chen et al. (2024) investigated the leaching of smithsonite in an ammonium citrate medium and reported that a zinc dissolution efficiency of approximately 83.5% was achieved under conditions optimized using the response surface method. Şahin et al. (2025) reported that approximately 98.85% zinc dissolution efficiency was achieved in smithsonite leaching using lactic acid following optimization via the Taguchi method. In their study, Xin et al. (2025) investigated the selective separation of Zn from zinc-containing industrial powder using hybrid malic acid-sulfuric acid leaching and reported a Zn separation efficiency of 97.70%. The results showed that the chemical properties and interactions of the component acids greatly influenced the performance of mixed acid systems. Although both citric acid and oxalic acid have individually been investigated as environmentally friendly leaching agents, they exhibit different chemical characteristics that influence zinc leaching behavior (Gadd, 1999; Pathak et al., 2021). Citric acid promotes zinc dissolution by forming soluble citrate complexes with dissolved Zn^{2+} ions (Irannajad et al., 2013; Almbrok et al., 2025). In contrast, oxalic acid facilitates mineral dissolution and exhibits strong complexation with dissolved metal ions (Sheng et al., 2026). However, because oxalate ions can form complexes with metal cations (Gadd, 1999), excessive oxalic acid concentrations may promote the formation of sparingly soluble metal oxalates. Therefore, the combined use of citric and oxalic acids may produce antagonistic effects on Zn leaching depending on metal complexation, mineral dissolution, and the possible formation of sparingly soluble metal-containing species. A systematic evaluation is necessary to determine the interaction of oxalic acid and citric acid under different operating conditions.

Studies investigating the combined use of citric and oxalic acids in the leaching of complex zinc ores are limited. These acids were selected for this study because of their metal-ion complexation behavior and their significance in chemical and bioleaching systems. Previous studies have indicated that citric and oxalic acids are used in combination in both bioleaching systems and chemical leaching processes. Ilyas et al. (2021) reported the simultaneous production of citric and oxalic acids by *Penicillium chrysogenum* in a bioleaching system, with concentrations depending on the experimental conditions. Citric acid levels of 12–63 mM and oxalic acid levels of 1–29 mM were detected in glucose-containing media. Kursunoglu and Kaya (2015) investigated the sequential use of 0.5 M citric acid and 0.5 M oxalic

acid in leaching. Studies in the literature indicate that citric and oxalic acids can be used in combination in chemical and biological leaching processes, and further research is required to investigate the behavior of these two acids within a mixed-acid system. However, the leaching experiments in the present study were not designed to model the organic acid concentrations produced during bioleaching. In the experiments, the interactive effects of solid-to-liquid ratio, leaching temperature, leaching time, and citric-oxalic acid concentrations on Zn recovery were evaluated using the Response Surface Methodology (RSM) based on a modified central composite design. This study presents a statistical evaluation of Zn leaching using a mixed citric-oxalic acid solution. Although the acid concentrations employed in the experimental work were higher than those in the referenced bioleaching study, the findings shed light on future research regarding leaching systems involving these organic acids.

2. Materials and methods

2.1. Characterization of sample

The ore sample obtained from the Kozan-Horzum region of Adana province, Turkey, was dried in an oven at 105°C until constant mass was achieved, crushed to a particle size smaller than 1 cm in a jaw crusher, and then ground to below 75 μm in a ball mill. Chemical composition analysis determined that the main components of the sample were 39.89% Fe_2O_3 , 12% Al_2O_3 , 11.18% ZnO , 9.10% SiO_2 , and 8.58% CaO . Low percentages of SO_3 , K_2O , TiO_2 , Cr_2O_3 , MnO , CuO , and PbO were also detected. The loss on ignition (LOI) of the sample was determined to be 14.25%. Citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \times \text{H}_2\text{O}$, CAS No: 5949-29-1) and oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \times 2\text{H}_2\text{O}$, CAS No:6153-56-6) used in the experimental studies were obtained in analytical grade pure form from Merck. The chemical composition of the ore sample was determined by X-ray fluorescence (XRF) analysis using a MiniPal 4 spectrometer (PANalytical). The mineralogical compositions of the raw ore and the leaching residue were characterized using a Rigaku MiniFlex II diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), operated at 40 kV and 30 mA. The XRD patterns were recorded over a 2θ range of 10–90° using a step size of 0.02°. For clarity, Fig.1 presents the measured data over $2\theta = 10\text{--}65^\circ$. No measured data are available below $2\theta = 10^\circ$. The clay mineral assemblage is not specified, as a fraction analysis was not performed. Phase identifications of the samples and leaching residues used in the experiments were evaluated by taking into account the chemical composition of the ore and the mineral assemblages expected for this type of ore. The corresponding JCPDS–PDF reference numbers obtained from the software are provided in parentheses for each identified phase. The EDS results were evaluated as semi-quantitative elemental data for the examined areas, with reported weight percentages calculated based on the elements included in the analysis. Leach residues were examined using a scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (SEM-EDS). SEM images were acquired using a ZEISS Sigma 300 microscope at an accelerating voltage of 5 kV. EDS analyses were performed at a voltage of 15 kV with a live count time of 30 seconds. In the SEM-EDS analysis, the Au used for coating purposes was excluded from the reported composition, and the weight percentages of the remaining elements were normalized to 100%. The EDS results were evaluated as the semi-quantitative elemental composition of the examined regions.

2.2. Organic acid leaching procedure and analytical methods

Leaching experiments were performed in a three-neck round-bottom glass flask equipped with a reflux condenser using a heated magnetic stirrer. The Reflux condensers were used in the experiments to minimize evaporation losses. The ore sample particle size was fixed at $\sim 75 \mu\text{m}$. The stirring speed was maintained at 600 rpm using a magnetic stir bar throughout the experiments. Citric acid and oxalic acid stock solutions were prepared separately at the concentrations specified in the experimental design. Equal volumes (100 mL each) of both solutions were then mixed to obtain a total of 200 mL of leaching solution. The nominal values of the citric acid/ore and oxalic acid/ore ratios were calculated separately by dividing the initial amount (mmol) of each added acid by the ore mass (g). The nominal Citric Acid-to-ore and oxalic acid-to-ore ratios are reported separately in Table 2. This represents the nominal amount of organic acid added per unit mass of ore; it should not be interpreted as the mineral-specific acid consumption. The experimental temperature was periodically monitored throughout the leaching

experiments. Throughout this study, the reported citric and oxalic acid concentrations refer to the concentrations of the separately prepared stock solutions used in the experimental design. For each leaching experiment, the solution was filtered using Whatman filter paper to separate the residue from the charged leaching solution. The Zn concentration in the charged leaching solution was determined by atomic absorption spectroscopy (AAS). Zn recovery was calculated according to Equation (4):

$$\text{Zn recovery (\%)} = \frac{C_{\text{Zn}} \times V}{m_{\text{ore}} \times w_{\text{Zn}}} \times 100 \quad (4)$$

Zn concentration in the solution is symbolized as C_{Zn} ; final solution volume as V ; mass of the sample used in the experiment as m_{ore} ; and initial elemental Zn mass fraction of the feed material as w_{Zn} . In experiments conducted according to the experimental design, the solid residues obtained in experiment number 18, 21 and 26 were washed with distilled water after filtration, dried in an oven, and then analyzed by XRD to determine the mineralogical changes that occurred. The Zn concentration in the leaching solution was determined by atomic absorption spectroscopy using a PerkinElmer AAS instrument (PerkinElmer Inc.) after appropriate dilution. The measurements were performed at an external analytical laboratory.

2.3. Experimental design

The effects of different solid ratios, temperatures, leaching times, and citric and oxalic acid stock solution concentrations on Zn recovery were investigated. Using the RSM-CCD approach, the acid concentration range for citric acid (0.25–1.25 M) was selected to be sufficiently broad to evaluate the main and interaction effects on Zn recovery. However, for oxalic acid, a lower concentration range (0.05–0.25 M) was investigated, taking into account the potential for the formation of sparingly soluble metal-oxalate species in oxalate-containing systems. This method combines experimental design with mathematical regression modeling to enable quantitative assessment and prediction of process responses within the examined factor ranges (Box and Hunter, 1957; Myers et al., 2016; Zhang et al., 2022; Elkelawy et al., 2022; Bhavani et al., 2022; Wu et al., 2022; Mung'au et al., 2024).

The statistical analysis in this study is based on a modified CCD consisting of 32 experiments. The cubic (factorial) part of the design is established as a 2^{5-1} half-fractional factorial using the E = ABCD generator (I = ABCDE defining relation). This structure corresponds to a Resolution V design that allows all main effects and binary interactions to be estimated independently, under the assumption that triple and higher-order interactions are negligible. This factorial core was expanded by adding 10 axial points and 6 center points, resulting in a design consisting of a total of 32 trials. The design is described as "modified" because the lower axial level of the time factor (D), which should theoretically be zero minutes, has been increased to 15 minutes since there is no physical equivalent.

This change causes the axial level of the D factor to introduce asymmetry, resulting in the modified design losing its rotatable capability in the D direction. Therefore, the prediction variance varies depending on the direction and distance from the design center at the lower limit of the experimental time interval. The reason for accepting this limitation is to exclude the physically meaning zero-minutes leaching condition and to create a viable design region. The upper and lower limit values and coded levels for the independent variables are given in Table 1. The experimental design, regression analyses, and ANOVA calculations were performed using Design-Expert® software (Stat-Ease Inc., version 13). Numerical optimization of the adapted second-order model was performed to maximize Zn recovery within the selected optimization region (A = 5–10% (w/v), B = 0.5–1.0 M, C = 0.10–0.20 M, D = 30–90 min, and E = 40–60 °C). Three independent experiments were conducted under the predicted experimental conditions.

The experimental data are expressed as a second-degree polynomial.

$$Y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k b_{ij} X_i X_j + \varepsilon \quad (5)$$

In this equation, Y represents the predicted response; b_0 is the intercept term; b_i , b_{ii} , and b_{ij} represent the linear, quadratic, and interaction coefficients, respectively; X_i and X_j are the coded values of the independent variables k denotes the number of factors and ε is the random error term (Alanazi et al., 2023). The model's fit and statistical significance were evaluated using analysis of variance (ANOVA). The significance of the models was determined using p-value (< 0.05) and F-values. The model's fit was analyzed using the coefficient of determination (R^2), adjusted R^2 , predicted R^2 , and the lack-of-fit test

(Pashaei et al., 2023). The experimental design included six replicated center points to estimate the pure experimental error and evaluate the lack of fit of the developed model.

Table 1. Minimum and maximum values of the independent variables

Code	Variables	Low axial	-1	0	+1	High Axial
A	Solid Ratio (%) (w/v)	2.5 (-2)	5 (-1)	7.50 (0)	10 (+1)	12.5 (+2)
B	Citric acid (M)	0.25 (-2)	0.5 (-1)	0.75 (0)	1 (+1)	1.25 (+2)
C	Oxalic acid (M)	0.05 (-2)	0.1 (-1)	0.15 (0)	0.2 (+1)	0.25 (+2)
D	Time (min.)	15 (-1.5)	30 (-1)	60 (0)	90 (+1)	120 (+2)
E	Temperature (°C)	30 (-2)	40 (-1)	50 (0)	60 (+1)	70 (+2)

3. Results and discussion

In this study, the effects of solid ratio (A), citric acid stock solution concentration (B), oxalic acid stock solution concentration (C), time (D), and temperature (E) on complex zinc ore were investigated using the response surface methodology. The experimental results were analyzed using ANOVA to assess the statistical significance of the model. Table 2 presents the experimental conditions used in the Zn runs and the corresponding Zn (%) responses.

The XRD patterns of the raw ore indicate the presence of smithsonite (ZnCO_3 , JCPDS card no: 08-0449), quartz (SiO_2 , JCPDS card no: 46-1045), calcite (CaCO_3 , JCPDS card no: 05-0586), hematite (Fe_2O_3 , JCPDS card no: 33-0664), dolomite ($\text{CaMg}(\text{CO}_3)_2$, JCPDS card no: 36-0426), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, JCPDS card no: 89-6538) and goethite (FeOOH , JCPDS card no: 29-0713). Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, JCPDS card no: 20-0231) was also identified in the leach residue from Run 21 (Figure 1). The XRD patterns of the leach residues exhibited diffraction peaks tentatively attributable to zinc oxalate dihydrate ($\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, JCPDS card no: 25-1029), suggesting the formation of a secondary zinc oxalate phase during leaching (Figure 1). However, zinc oxalate dihydrate and iron(II) oxalate dihydrate (humboldtine, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) exhibit similar diffraction patterns due to their isostructural nature. Given the Fe-rich composition of the ore and the similarity of the diffraction patterns, a contribution from humboldtine cannot be excluded (Echigo and Kimata, 2008). Fe was detected by EDS; however, the total Fe content of the residue was not measured. The data do not conclusively distinguish whether the oxalate phase contains Zn, Fe, or both. These findings suggest that Fe-bearing phases may also participate in oxalate-related reactions during leaching, although their specific contribution cannot be established from the present data. Figure 1 presents the XRD patterns for Run 18 (13.06% Zn recovery) which yielded the lowest Zn recovery Run 21 (67.98% Zn recovery) which yielded the highest Zn recovery within the experimental design and Run 26 (0.25 M; 35.27% Zn recovery) conducted at the highest oxalic acid stock solution concentration. When conditions regarding sample preparation, measurement parameters, and intensity scaling are comparable, variations in smithsonite reflection intensities can provide qualitative information about dissolution. However, quantitative phase analysis was not performed, and peak intensities were not used to calculate mineral abundance or mineral-specific dissolution percentages. The 67.98% Zn recovery obtained in Experiment 21 represents the total Zn recovery, not specifically the dissolution percentage of the smithsonite.

SEM-EDS analysis was performed on the leach residues from the experiments conducted within the scope of the RSM-modified CCD design, specifically those yielding the lowest (Experiment 18:13.06%), highest (Experiment 21:67.98%), and highest concentration of oxalic acid stock solution (Experiment 26) (Figure 2). The SEM image of the residue from Experiment 18 reveals plate-like structures and fine particles (Figure 2a). The corresponding EDS results indicate the presence of 39.72 wt.% C, 38.21 wt.% O, 2.49 wt.% Si, 1.56 wt.% Ca, 9.82 wt.% Zn, 1.73 wt.% Fe, 3.26 wt.% S, 1.59 wt.% Mg and 1.62 wt.% Al.

According to the EDS results for Run 21 residue indicated 52.15 wt.% C, 31.85 wt.% O, 2.03 wt.% Si, 1.33 wt.% Ca, 5.80 wt.% Zn, 1.73 wt.% Fe, 3.31 wt.% S, 0.89 wt.% Mg and 0.91 wt.% Al. In the SEM image of the residue from Experiment 21, cracks on the sample surface and fine particles adhering to the surface are observed (Figure 2c). EDS results indicate the presence of Zn, consistent with the fact that the Zn did not completely dissolve. As such, these observations fail to identify the cause of the cracks or to distinguish primary Zn-bearing minerals that have not dissolved from potential secondary

Table 2. Experimental design matrix and corresponding Zn recoveries for leaching

Run	A: Solid Ratio (%) (w/v)	B: Citric Acid stock solution Concentration (M)	C: Oxalic Acid stock solution Concentration (M)	D: Time (min.)	E: Temperature (°C)	Zn (%)	Citric Acid to ore ratio (mmol g ⁻¹)	Oxalic Acid to ore ratio (mmol g ⁻¹)
1	7.5	0.25	0.15	60	50	39.12	1.67	1.00
2	12.5	0.75	0.15	60	50	32.76	3.00	0.60
3	5	0.5	0.1	90	40	45.97	5.00	1.00
4	7.5	0.75	0.15	60	50	45.55	5.00	1.00
5	7.5	0.75	0.15	15	50	37.68	5.00	1.00
6	7.5	0.75	0.15	60	30	31.48	5.00	1.00
7	7.5	0.75	0.15	60	50	44.31	5.00	1.00
8	5	1	0.2	30	60	21.26	10.00	2.00
9	7.5	0.75	0.15	60	50	45.44	5.00	1.00
10	7.5	0.75	0.15	120	50	52.59	5.00	1.00
11	10	1	0.2	30	40	35.46	5.00	1.00
12	5	1	0.1	90	60	48.94	10.00	1.00
13	7.5	1.25	0.15	60	50	51.95	8.33	1.00
14	5	0.5	0.1	30	60	42.77	5.00	1.00
15	10	1	0.1	90	40	58.94	5.00	0.50
16	10	0.5	0.2	30	60	38.20	2.50	1.00
17	7.5	0.75	0.15	60	50	48.91	5.00	1.00
18	10	0.5	0.1	30	40	13.06	2.50	0.50
19	5	0.5	0.2	30	40	44.70	5.00	2.00
20	10	1	0.2	90	60	46.27	5.00	1.00
21	10	1	0.1	30	60	67.98	5.00	0.50
22	10	0.5	0.1	90	60	63.01	2.50	0.50
23	7.5	0.75	0.05	60	50	57.17	5.00	0.33
24	10	0.5	0.2	90	40	26.78	2.50	1.00
25	7.5	0.75	0.15	60	50	46.76	5.00	1.00
26	7.5	0.75	0.25	60	50	35.27	5.00	1.67
27	7.5	0.75	0.15	60	50	45.44	5.00	1.00
28	2.5	0.75	0.15	60	50	24.87	15.00	3.00
29	5	0.5	0.2	90	60	32.54	5.00	2.00
30	7.5	0.75	0.15	60	70	47.52	5.00	1.00
31	5	1	0.2	90	40	40.65	10.00	2.00
32	5	1	0.1	30	40	37.95	10.00	1.00

Zn-bearing precipitates. The SEM image for Experiment 26 shows elongated structures, with EDS results indicating 24.65 wt.% C, 55.61 wt.% O, 1.92 wt.% Si, 1.63 wt.% Ca, 9.32 wt.% Zn, 2.51 wt.% Fe, 3.12 wt.% S, 0.61 wt.% Mg and 0.63 wt.% Al; however, the composition and phase identity of these structures cannot be determined from these data. Fe was detected in the analysed leach residue. This constitutes qualitative evidence of the presence of Fe in the solid phase following the leaching process. However, these localized measurements do not determine the extent of Fe co-dissolution or reveal the total Fe content of the residues. C and O were detected alongside Zn in the leach residue regions. It was not possible to assess the potential contribution of the sample preparation stage to the C signal. The C, O, and Zn results from the residues provide supporting elemental information; however, on their own, they cannot confirm the carbonate phases or the potential formation of zinc oxalate dihydrate. Furthermore, SEM-EDS observations do not conclusively demonstrate surface passivation.

3.1. Model adequacy and diagnostic evaluation

The statistical significance and adequacy of the developed quadratic model were evaluated using analysis of variance (ANOVA), and the results are presented in Table 3. The model was statistically

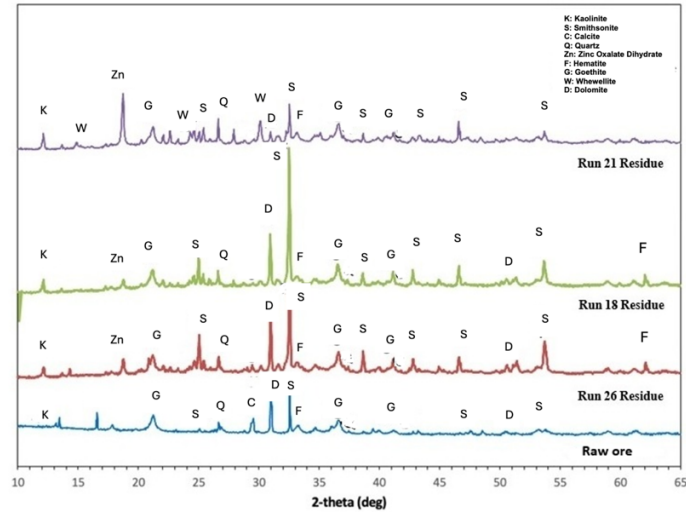


Fig. 1. XRD patterns of the raw ore and leaching residues from Run 21 (highest Zn recovery 67.98%), Run 18 (lowest Zn recovery 13.06%) and Run 26 (highest oxalic acid stock solution concentrations 0.25M and Zn recovery 35.27%). The patterns are displayed over $2\theta = 10\text{--}65^\circ$, whereas the XRD acquisition range was $2\theta = 10\text{--}90^\circ$

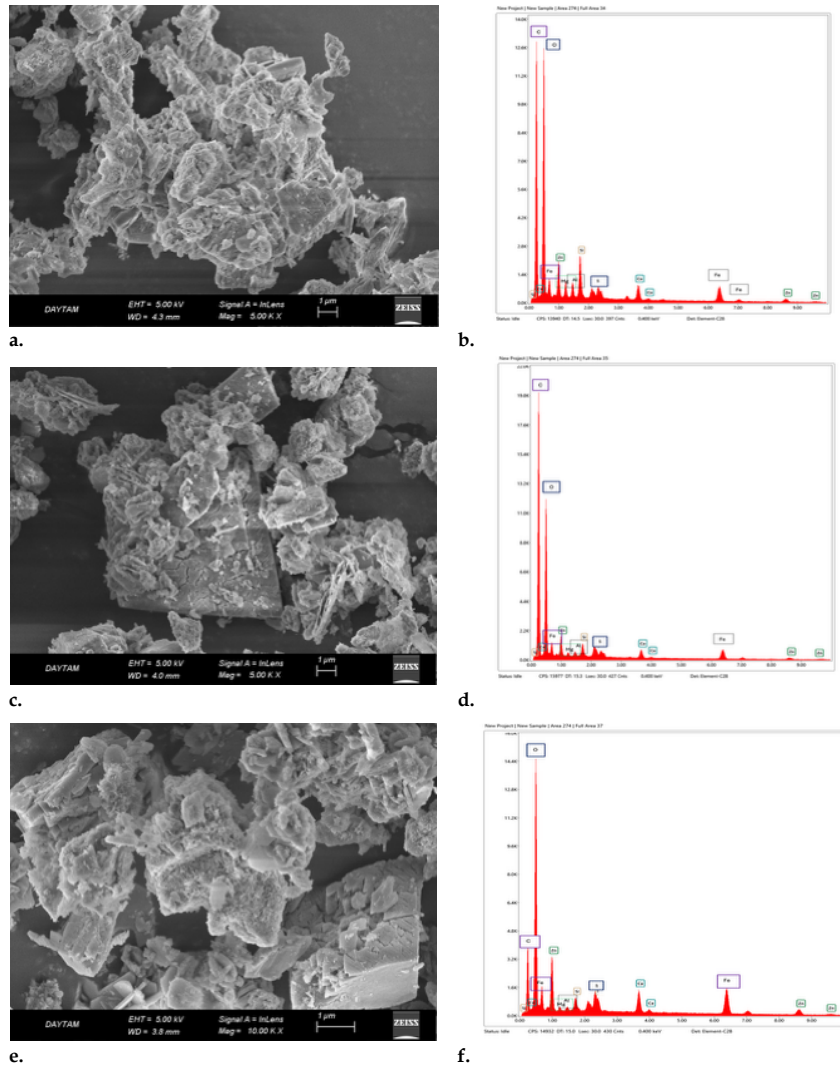


Fig. 2. SEM images and EDS spectra of leaching residues from (a, b) Run 18, with the lowest Zn recovery within the experimental design; (c, d) Run 21, with the highest Zn recovery within the experimental design; and (e, f) Run 26, conducted at the highest oxalic acid stock solution concentration

significant, with an F-value of 71.35 and $p < 0.0001$. The coefficient of determination ($R^2 = 0.9924$) and adjusted R^2 (0.9784) indicated that the model explained a large proportion of the variability in the experimental data. The predicted R^2 value of 0.8904 was in reasonable agreement with the adjusted R^2 . The Adeq Precision value of 39.4256, which was considerably higher than the recommended minimum value of 4, indicated an adequate signal-to-noise ratio. Furthermore, the lack of fit was not statistically significant relative to the pure error ($F = 1.32$, $p = 0.3875$), indicating no evidence of systematic model inadequacy. Overall, the quadratic model adequately described the experimental data within the experimental design region.

Table 3. Analysis of variance table for Zn recovery

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4268.56	20	213.43	71.35	< 0.0001	significant
A-Solid Ratio	107.10	1	107.10	35.81	< 0.0001	
B-Citric Acid stock solution concentration	241.17	1	241.17	80.63	< 0.0001	
C-Oxalic Acid stock solution concentration	777.03	1	777.03	259.78	< 0.0001	
D-Time	331.27	1	331.27	110.75	< 0.0001	
E-Temperature	334.06	1	334.06	111.68	< 0.0001	
AB	449.23	1	449.23	150.19	< 0.0001	
AC	24.50	1	24.50	8.19	0.0155	
AD	22.28	1	22.28	7.45	0.0196	
AE	688.80	1	688.80	230.28	< 0.0001	
BC	141.49	1	141.49	47.30	< 0.0001	
BD	0.4160	1	0.4160	0.1391	0.7163	
BE	74.65	1	74.65	24.96	0.0004	
CD	146.89	1	146.89	49.11	< 0.0001	
CE	361.95	1	361.95	121.01	< 0.0001	
DE	26.57	1	26.57	8.88	0.0125	
A ²	458.27	1	458.27	153.21	< 0.0001	
B ²	1.68	1	1.68	0.5619	0.4692	
C ²	4.96	1	4.96	1.66	0.2244	
D ²	0.0002	1	0.0002	0.0001	0.9931	
E ²	47.59	1	47.59	15.91	0.0021	
Residual	32.90	11	2.99			
Lack of Fit	20.20	6	3.37	1.32	0.3875	not significant
Pure Error	12.70	5	2.54			
Cor Total	4301.46	31				

Based on the p-values ($p < 0.05$) of the parameters, the main factors of solid ratio (A), citric acid stock solution concentration (B), oxalic acid stock solution concentration (C), leaching time (D), and temperature (E) were found to significantly affect Zn recovery. Among the interaction terms, AB, AC, AD, AE, BC, BE, CD, CE, and DE were statistically significant. Temperature's interaction with other variable parameters indicates that it plays a critical role in the process. Only citric acid stock solution concentration - leaching time was not found to be statistically significant ($p=0.7163$). In the quadratic terms, A² and E² were significant, while B², C², and D² were not. This suggests that the nonlinear response is driven by solid ratio and temperature. In the CCD-based evaluation of zinc recovery, a quadratic model was used to determine the contribution of the main factors, interaction terms, and second-order effects on the experimental response. The statistical summary of the models is presented in Table 4. The fundamental relationship between the response and the input factors is given in Equation

(6). In equation (6), the independent variables are expressed using coded values instead of their actual experimental values.

$$\text{Zn (\%)} = +45.59 + 2.11A + 3.17B - 5.69C + 3.94D + 3.73E + 5.30AB - 1.24AC + 1.18AD + 6.56AE - 2.97BC + 0.1613BD - 2.16BE - 3.03CD - 4.76CE - 1.29DE - 3.94A^2 + 0.2387B^2 + 0.4099C^2 + 0.0034D^2 - 1.27E^2 \quad (6)$$

To predict Zn recovery, the model was applied under the conditions $A = 2.5$, $B = 1.25$, $C = 0.05$, $D = 90$, and $E = 60$. Under these conditions, the predicted average Zn recovery was 32.86%, which does not exceed the highest experimentally observed recovery of 67.98%. Since the three factors (A , B , and C) are at axial levels, this prediction involves high uncertainty. This specific combination was not included in the experimental design. Furthermore, the predicted Zn recovery rate of 32.86% has not been experimentally verified. Therefore, it should not be considered a reliable prediction or an optimization result.

Numerical optimization of the fitted quadratic model was performed within the selected optimization region to maximize Zn recovery. To achieve maximum recovery, the following factors were constrained to the following ranges: 5–10% (w/v) solid-to-liquid ratio, 0.5–1.0 M citric acid stock solution concentration, 0.10–0.20 M oxalic acid stock solution concentration, 30–90 min leaching duration, and 40–60°C temperature. Within the region defined by the limits of the five parameters, the optimal condition was determined to be a solid content of 10% (w/v), a citric acid stock solution concentration of 1.0 M, an oxalic acid stock solution concentration of 0.10 M, a duration of 90 minutes, and a temperature of 60°C, yielding a predicted Zn recovery of 81.42%. The confidence interval for the predicted mean was determined to be 77.85–84.99%. To validate the predicted recovery value, three leaching experiments were conducted under the conditions specified by the model, yielding Zn recoveries of 78.40%, 80.01%, and 77.90%. The mean recovery was calculated as $78.77 \pm 1.10\%$ ($n = 3$). The difference between the predicted value and the experimental mean was 2.65 percentage points, corresponding to a relative prediction error of 3.25%.

Furthermore, the experimental mean of 78.77% fell within the prediction interval of approximately 77.2–85.6% for the mean of three independent validation experiments ($n = 3$).

Table 4. Fit summary of the regression models for Zn recovery

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	57062.87	1	57062.87			
Linear vs Mean	1817.62	5	363.52	3.81	0.0102	
2FI vs Linear	1936.78	10	193.68	5.66	0.0012	
Quadratic vs 2FI	514.16	5	102.83	34.38	< 0.0001	Suggested
Cubic vs Quadratic	20.20	6	3.37	1.32	0.3875	Aliased
Residual	12.70	5	2.54			
Total	61364.33	32	1917.64			
Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	
Linear	9.77	0.4226	0.3115	0.0264	4188.00	
2FI	5.85	0.8728	0.7536	0.7188	1209.59	
Quadratic	1.73	0.9924	0.9784	0.8904	471.38	Suggested
Cubic	1.59	0.9970	0.9817			Aliased

The diagnostic plots generated from the developed model demonstrate that it is statistically valid and adequate. The random distribution of residuals relative to the predicted values indicates the absence of systematic error and that the variance is constant (Fig.3a). The linear distribution of residuals in the normal probability plot indicates that the error terms follow a normal distribution (Fig.3b). The strong agreement between the estimated and experimental Zn (%) values demonstrates that the model provides highly accurate predictions (Fig.3c). The random distribution of residual points indicates that the assumption of independence among the data holds (Fig. 3d). Overall, the diagnostic plots and the non-significant lack of fit ($p = 0.3875$) indicate that the developed quadratic model adequately represents the experimental data within the investigated factor ranges.

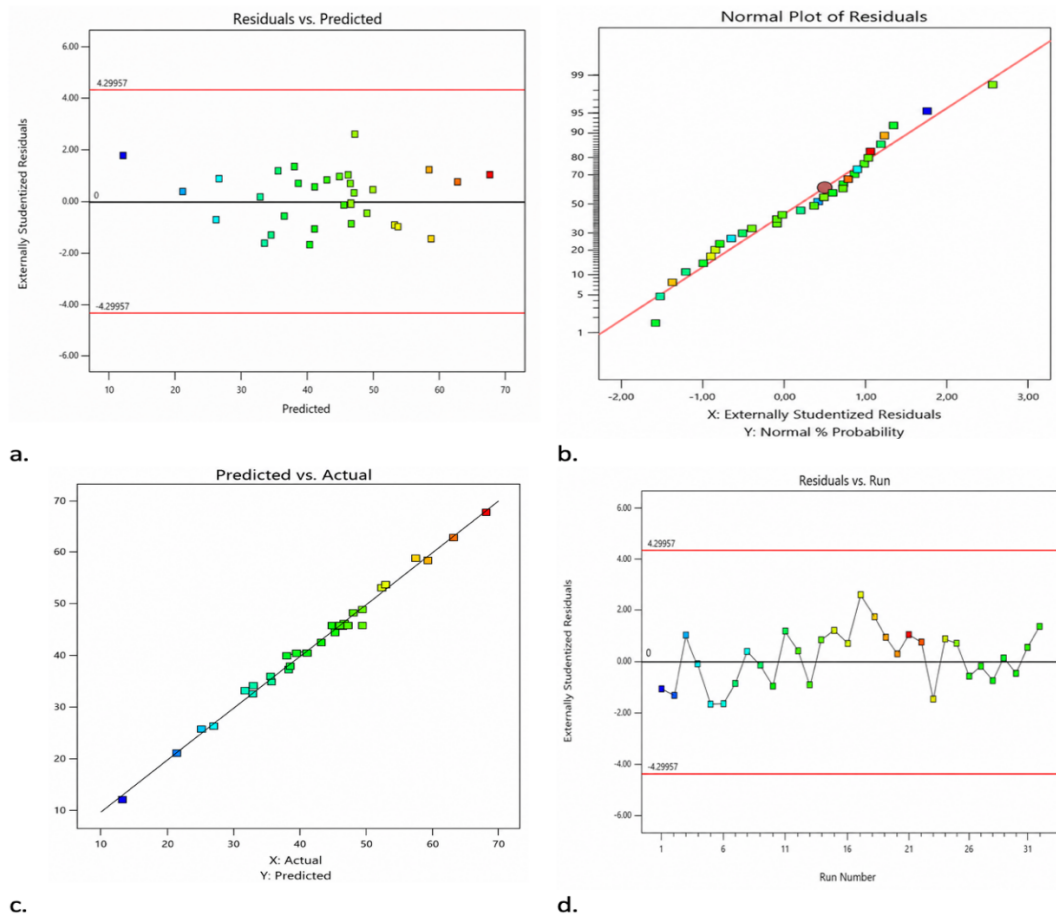


Fig. 3. Diagnostic plots for Zn recovery: (a) Externally studentized residuals vs. predicted values (b) normal probability plot of Externally studentized residuals (c) predicted values vs. actual values, (d) Externally studentized residuals vs. run number

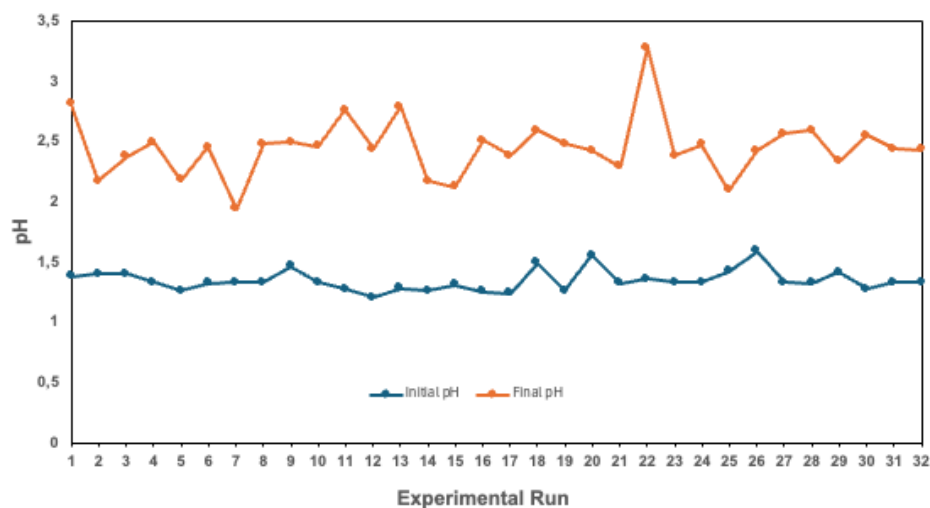


Fig. 4. Initial and Final pH values of the mixed acid leaching solutions for the experimental runs

The initial pH values for the citric acid-oxalic acid leaching process were in the range of 1.2–1.6. Measurements taken after leaching, as shown in Figure 4, indicate a general increase in pH, demonstrating that acid consumption occurs during the interaction between the organic acid solution and the ore. The presence of carbonate-bearing phases—such as smithsonite and calcite, identified via XRD analysis and a Loss on Ignition (LOI) value of 14.25%—suggests that the dissolution of these

carbonate phases consumes H^+ ions, thereby contributing to the observed rise in solution pH during leaching. However, since the LOI value is not solely attributable to carbonate decomposition, it should not be interpreted as a quantitative measure of carbonate content. Changes in pH may also influence complexation within the citrate and oxalate solutions.

3.2. Effect of process parameters on Zn leaching

Based on the F-values of the linear terms, the apparent order of influence of the independent variables on Zn recovery was oxalic acid concentration > temperature > leaching time > citric acid concentration > solids ratio. However, several statistically significant interaction terms were identified, some of which exhibited F-values higher than those of the corresponding main effects. Therefore, this ranking represents only the relative magnitude of the linear effects and should not be interpreted independently of the interactions among the process variables.

3.2.1. Effect of solid ratio (A)

The solid ratio had a statistically significant effect on Zn recovery ($F = 35.81$, $p < 0.0001$). Under center-level conditions, Zn recovery increased from 24.87% at 2.5% solids to an average value of approximately 46.07% at 7.5% solids. However, when the solid ratio was further increased to 12.5%, Zn recovery decreased to 32.76% under the same center-level conditions. This non-monotonic trend is consistent with the significant quadratic effect of A^2 ($F = 153.21$, $p < 0.0001$), confirming that Zn recovery did not vary linearly with solid ratio. The decrease observed at 12.5% solids may be attributed to insufficient acid capacity relative to the increased ore mass, possible acid depletion, and reduced mass-transfer efficiency at higher pulp density (Movahhedi et al., 2023). Moreover, the significant interactions of solid ratio with citric acid stock solution concentration, oxalic acid stock solution concentration, time, and temperature indicate that the effect of pulp density strongly depends on the combined experimental conditions. Although the highest experimental Zn recovery was obtained at a solid ratio of 10%, this result should be interpreted as the combined outcome of the selected factor levels rather than as the isolated effect of solid ratio alone (Fig. 5).

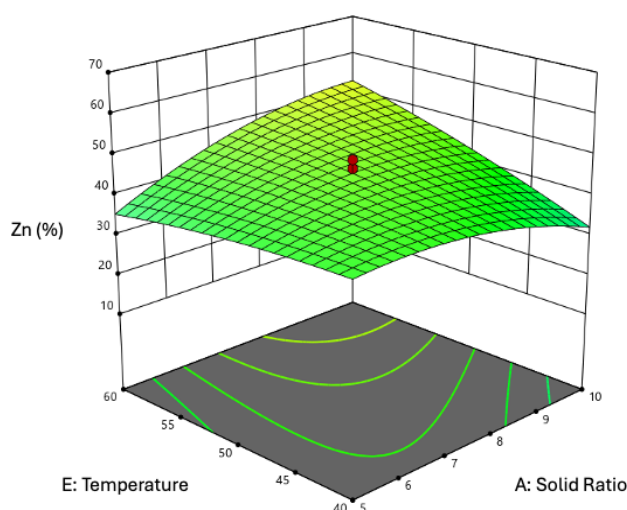


Fig. 5. Three-dimensional response surface plot showing the effect of solid ratio and temperature on Zn recovery

3.2.2. Effect of citric acid stock solution concentration (B)

Citric acid stock solution concentration had a statistically significant positive effect on Zn recovery ($F = 80.63$, $p < 0.0001$). Under otherwise center-level conditions, the lowest tested citric acid stock solution concentration of 0.25 M resulted in a Zn recovery of 39.12% (Run 1: $A = 7.5\%$, $C = 0.15$ M, $D = 60$ min, $E = 50^\circ\text{C}$). At the center level of citric acid stock solution concentration (0.75 M), the replicated center points produced an average Zn recovery of approximately 46.07%. When the citric acid stock solution concentration was increased to 1.25 M, Zn recovery reached 51.95% (Run 13). This shows that the

tendency of citrate ions to form complexes with dissolved zinc is supported by increasing citric acid stock solution concentration (Li et al., 2015). Furthermore, the statistically significant interaction between citric acid stock solution concentration and temperature (BE; $F = 24.96$; $p = 0.0004$) indicates that the interaction of temperature with citric acid stock solution concentration significantly alters Zn recovery (Fig. 6).

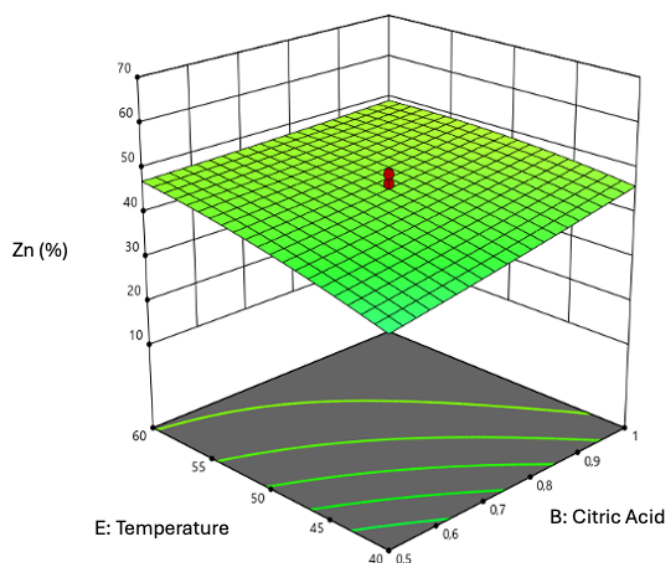


Fig. 6. Three-dimensional response surface plot showing the effect of citric acid stock solution concentration and temperature on Zn recovery

3.2.3. Effect of oxalic acid stock solution concentration (C)

Zn recovery reached 57.17% when the oxalic acid stock solution concentration was 0.05 M. At the replicated center points, where the oxalic acid stock solution concentration was 0.15 M, an average Zn recovery of approximately 46.07% was obtained. Increasing the oxalic acid stock solution concentration to 0.25 M reduced Zn recovery to 35.27%. According to the results, increasing the concentration of the oxalic acid stock solution even within the low concentration range selected to prevent the formation of metal oxalate species adversely affected Zn recovery. This indicates that, in addition to the tendency of organic acids to form complexes, the dissolution and transfer of Zn into the liquid are also controlled by competitive processes. Among the linear terms, oxalic acid concentration exhibited the largest effect in magnitude, and its negative model coefficient indicated that increasing the oxalic acid concentration reduced Zn recovery within the investigated range ($F = 259.78$, $p < 0.0001$). At relatively low concentrations, oxalate ions may promote Zn dissolution through complex formation with Zn^{2+} . The formation of sparingly soluble species, such as metal oxalates, at high concentrations and surface passivation may contribute to decreased Zn recovery (Sayilgan et al., 2010). In the event of zinc oxalate precipitation, dissolved Zn^{2+} ions may be removed from the leach solution, causing the zinc to be retained in the solid residue. This situation can lead to a reduction in zinc recovery. The adverse effect of increasing oxalic acid concentration cannot be attributed solely to zinc oxalate precipitation, as other mechanisms, including possible surface passivation, may also contribute. The sample used in the experiments contained 39.89% Fe_2O_3 . Citric and oxalic acids can interact with dissolved Fe species; the dissolution of Fe alongside Zn during leaching, followed by the formation of citrate and oxalate complexes, can affect Zn dissolution through competition. Furthermore, because the Fe concentrations in the leach solution were not determined in this study, the extent of Fe co-dissolution cannot be quantitatively assessed. Therefore, although potential competitive interactions involving Fe may also contribute to the observed leaching behaviour, their contribution cannot be confirmed from the present data. The interaction between oxalic acid concentration and temperature was statistically significant (CE , $F = 121.01$, $p < 0.0001$), demonstrating that the effect of oxalic acid concentration on Zn recovery depended strongly on temperature. As shown in Fig. 7, the magnitude and direction of the temperature effect varied according to the oxalic acid concentration.

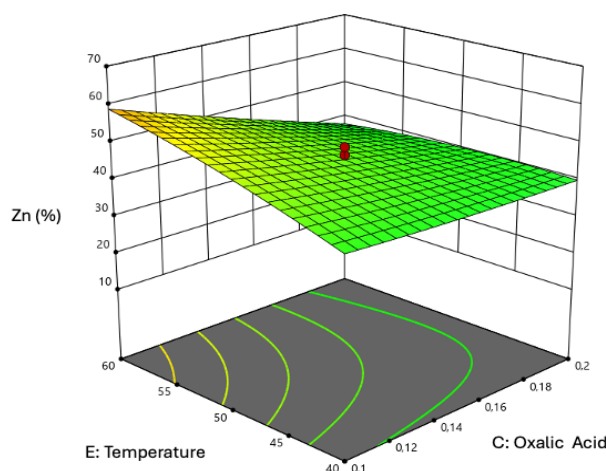


Fig. 7. Three-dimensional response surface plot showing the effect of oxalic acid stock solution concentration and temperature on Zn recovery

3.2.4. Effect of leaching time (D)

In zinc recovery, leaching time, a process parameter, was found to be statistically significant ($F = 110.75$; $p < 0.0001$). In experiments conducted at central levels ($A = 7.5\%$, $B = 0.75\text{ M}$, $C = 0.15\text{ M}$, and $E = 50\text{ }^{\circ}\text{C}$), the Zn recovery efficiency increased from 37.68% in 15 minutes to approximately 46.07% on average in 60 minutes and 52.59% in 120 minutes. This is thought to be due to increased contact between the acid solution and the ore surface as leaching time increases, which enhances the dissolution of zinc-containing phases (Hussaini et al., 2021). The second-order term of leaching time (D^2 : $F \approx 0.0001$; $p = 0.9931$) was not statistically significant. This indicates that the effect of leaching time is linear within the experimental range. The statistically significant interaction between leaching time and temperature (DE ; $F = 8.88$; $p = 0.0125$) indicates that temperature affects Zn recovery over leaching time. This can be explained by the acceleration of dissolution kinetics at higher temperatures. Although Zn recovery increased with leaching time under the center-level conditions, the highest experimental Zn recovery was obtained at 30 min under a different combination of factor levels. This confirms that the effect of leaching time should be interpreted together with the significant interactions among the process variables (Fig. 8). In Run 18, conducted at a 10% solid-to-liquid ratio, 0.5 M citric acid, 0.1 M oxalic acid, 30 min, and $40\text{ }^{\circ}\text{C}$, a comparatively low Zn recovery of 13.06% was obtained. For Run 18, the experiment was not repeated after verifying the Zn recovery calculations. Compared with Run 22, which employed the same solid ratio and acid concentrations but higher leaching time and temperature (90 min and $60\text{ }^{\circ}\text{C}$), the Zn recovery increased to 63.01%. However, because both leaching time and temperature were changed simultaneously, the difference between these two runs does not allow the individual contribution of either factor to be isolated. Both time (D) and temperature (E) were statistically significant, while their significant interaction ($D \times E$, $p = 0.0125$) indicates that their effects on Zn recovery depend on their combined levels. Therefore, the low recovery observed in Run 18 may be associated with the combined effect of the lower leaching time and temperature, although the individual contribution of each factor cannot be distinguished from this comparison.

3.2.5. Effect of temperature (E)

Temperature was found to have a statistically significant effect on Zn recovery ($F = 111.68$, $p < 0.0001$). Under center-level conditions, where $A = 7.5\%$, $B = 0.75\text{ M}$, $C = 0.15\text{ M}$, and $D = 60\text{ min}$, Zn recovery increased from 31.48% at $30\text{ }^{\circ}\text{C}$ to an average value of approximately 46.07% at $50\text{ }^{\circ}\text{C}$ and further to 47.52% at $70\text{ }^{\circ}\text{C}$. This increase indicates that higher temperature enhanced the reaction rate at the acid-mineral interface and promoted the dissolution of zinc-bearing phases (Hursit et al., 2009; Deng et al., 2015). The second-order term of temperature is statistically significant (E^2 : $F = 15.91$; $p = 0.0021$). This indicates that the limited increase in the experiments conducted at $50\text{ }^{\circ}\text{C}$ and $70\text{ }^{\circ}\text{C}$ shows a distinct curvature due to the effect of temperature.

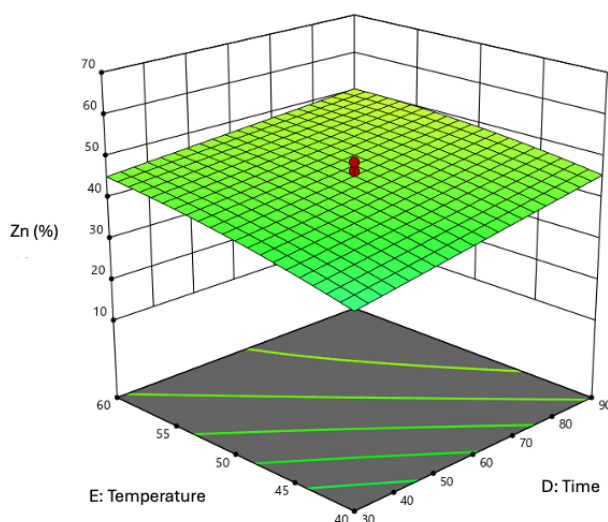


Fig. 8. Three-dimensional response surface plot showing the effect of leaching time and temperature on Zn recovery

The significant interactions between temperature and solid ratio (AE: $F = 230.28$; $p < 0.0001$), citric acid stock solution concentration (BE: $F = 24.96$; $p = 0.0004$), oxalic acid stock solution concentration (CE: $F = 121.01$; $p < 0.0001$), and leaching time (DE: $F = 8.88$; $p = 0.0125$) indicate that temperature affects Zn recovery depending on the process parameters. The highest experimental Zn recovery was obtained at 60°C; however, this result reflects the combined effects of temperature, acid concentrations, solid ratio, and leaching time rather than the isolated effect of temperature. This suggests that, although increasing temperature may enhance dissolution kinetics, its positive effect may be limited by possible secondary precipitation or surface passivation (Sayılğan et al., 2010; Li et al., 2024).

3.3. Comparison with previous studies and novelty

In this study, while the highest Zn recovery rate among the RSM-modified CCD 32 design trials was 67.98%, the rate calculated from three independent validation experiments conducted under the optimization conditions predicted by the model was 78.77%. This value is lower than the approximately 82% Zn recovery reported by Irannajad et al. (2013) using citric acid, the 83.5% dissolution yield obtained by Chen et al. (2024) in ammonium citrate medium, the 98.85% dissolution yield obtained by Şahin et al. (2025) using lactic acid, and the 97.70% yield obtained by Xin et al. (2025) in hybrid acid leaching medium. The differences observed in Zn recovery as a result of the experimental study may be attributed to variations in ore mineralogy, zinc-bearing phases, operating conditions, and experimental design. Therefore, rather than achieving the highest Zn recovery, the significance of the present study lies in revealing the behaviour of the mixed citric-oxalic acid system and quantitatively determining the individual and interaction effects of operating parameters.

Despite the complex-forming ability of organic acids, one of the key findings of this study is that increasing the oxalic acid concentration did not improve Zn recovery. According to the findings, oxalic acid had the highest linear effect in the negative direction, while citric acid showed a positive effect. In conclusion, the combined use of organic acids does not necessarily improve metal dissolution, and when designing mixed leaching experiments, it is necessary to quantitatively determine the interaction effects of the acids with individual and operational parameters. Furthermore, the experimental study revealed that oxalic acid concentration showed statistically significant interactions with solid content, citric acid concentration, leaching time, and temperature. This finding suggests that the negative effect of oxalic acid concentration on Zn recovery depends on the other operating parameters.

4. Conclusions

This study investigated the leaching of zinc from a complex zinc ore in a mixed citric-oxalic acid medium using a response surface methodology based on a modified central composite design and evaluated the

effects of operating parameters. High coefficients of determination ($R^2 = 0.9924$ and adjusted $R^2 = 0.9784$), along with non-significant lack of fit ($p = 0.3875$) and statistically significant results ($F = 71.35$, $p < 0.0001$) for the developed second-order model, demonstrated that the model adequately represented the experimental data across the examined factor ranges. Based on the F values of the linear terms, the apparent order of the influence of the independent variables on Zn recovery was determined as oxalic acid stock solution concentration > temperature > leaching time > citric acid stock solution concentration > solid ratio. This ranking should not be viewed as an ordering based on the overall importance of the variables; rather, it represents the relative magnitude of the linear main effects, given that statistically significant interactions were identified within the range of the experimental design examined. However, although oxalic acid concentration showed the largest linear effect in terms of magnitude, its effect was found to be negative within the examined range. The formation of sparingly soluble Zn-containing species at high oxalic acid concentrations may contribute to the observed decrease in Zn recovery.

Although the XRD patterns of the leach residues are interpreted as zinc oxalate dihydrate ($\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), their resemblance to the diffraction pattern of iron(II) oxalate dihydrate (humboldtine) prevents definitive phase identification based on the available data. SEM-EDS analyses confirmed the presence of Zn in the examined residue regions but could not clearly distinguish between undissolved primary Zn-bearing minerals and secondary Zn-bearing precipitates. Therefore, zinc oxalate precipitation and surface passivation may contribute to the observed decrease in Zn recovery, although their individual contributions have not been conclusively established.

The statistically significant interaction between solid ratio and temperature indicates that Zn recovery is governed by the combined effects of the variables rather than their individual effects. The highest experimental Zn recovery was achieved in Experiment 21 out of 32 experiments, at 67.98%, with a solid ratio of 10% (w/v), a stock solution concentration of 1.0 M citric acid, a stock solution concentration of 0.10 M oxalic acid, a leaching time of 30 minutes, and a temperature of 60°C. This result also reflects the combined effect of the selected operating conditions within the design area under investigation.

The optimal conditions predicted within the selected optimization region were determined to be a 10% (w/v) solid-to-liquid ratio, a 1.0 M citric acid stock solution concentration, a 0.10 M oxalic acid stock solution concentration, a duration of 90 minutes, and a temperature of 60°C, resulting in a predicted Zn recovery rate of 81.42%. Experiments conducted under these conditions yielded an average recovery of $78.77\% \pm 1.10\%$ ($n = 3$). This result corresponds to a relative prediction error of 3.25%, thereby supporting the predicted performance of the selected model.

In the investigated mixed acid system, increasing the oxalic acid concentration did not increase zinc recovery, showing a statistically significant negative effect. In zinc recovery using a mixed leaching system, it was observed that increasing the citric acid concentration had a positive effect, while increasing the oxalic acid concentration showed the opposite trend. This study investigated the opposing effects of acid concentration and the individual and interactive effects of operating parameters in the mixed leaching process using citric and oxalic acids. Furthermore, the absence of control experiments using only oxalic or citric acid limits the direct assessment of the individual contribution of each acid compared to the mixed system. Further studies including comparative single-acid experiments, detailed residue characterization, solution speciation, and process-scale evaluations are needed to assess the practical and environmental potential of the experimental design. The RSM-CCD approach provides an effective framework for modelling and statistically evaluating this multi-parameter organic acid leaching system.

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