



Optimization and Kinetic Study of Manganese Leaching from Pyrolusite Ore in Hydrochloric Acid Solutions with Oxalic Acid

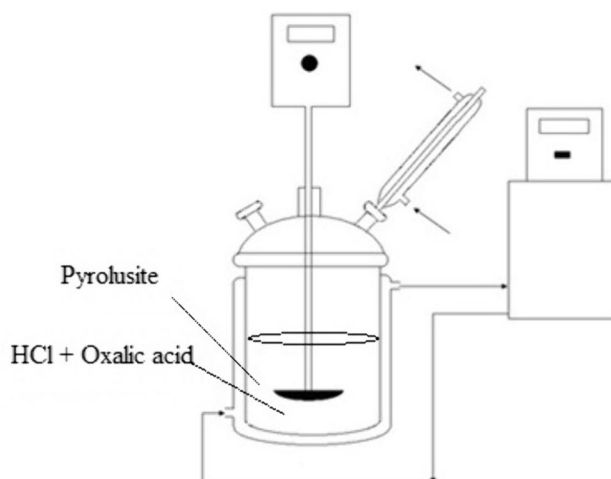
Mehmet Kayra Karacahan¹

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Abstract

The leaching behavior of pyrolusite minerals was examined in hydrochloric acid solutions, including oxalic acid, to evaluate the influence of various experimental conditions. The optimum parameters for the leaching process were found in the first stage, and the process's kinetics were assessed in the second. The concentrations of oxalic acid, hydrochloric acid, and temperature were chosen as independent variables in the optimization experiments, with the central composite design used to analyze the experimental data. The optimum concentrations for oxalic acid, hydrochloric acid, and temperature were determined to be 0.75 mol/L, 1.2 mol/L, and 60 °C, respectively. The leaching rate was determined to be 97.4% for 120 min of response time in optimum situations. The kinetic assessment experiments studied the effects of solid/liquid ratio, particle size, stirring speed, and temperature on the manganese leaching rate from pyrolusite. In the studies, the leaching rate was shown to rise with increasing temperature and stirring speed, as well as with decreasing particle size and solid/liquid ratio. The kinetic analysis revealed that the leaching kinetics matched the mixed kinetic model, and a mathematical model for the leaching process was developed. This process's activation energy was determined to be 29.05 kJ/mol.

Graphical Abstract



Keywords Pyrolusite · Manganese · Leaching · Oxalic acid · Central composite design

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✉ Mehmet Kayra Karacahan
mtanaydin@munzur.edu.tr

¹ Department of Chemistry and Chemical Processes, Tunceli Vocational School, Munzur University, Tunceli, Turkey

Introduction

Due to its various valences and remarkable physical and chemical properties, manganese is one of the precious metals used in many industrial areas, including chemistry,

micronutrients, catalysts, water treatment, fertilizer, medicine, textile, match/fireworks, glass, battery, electronics, plastic, alloy, and steel production [1–3]. Around 90–95 percent of the manganese produced globally is utilized to manufacture steel. Steel gains machinability, strength, and hardness from this potent reducing, desulfurizing, and dephosphorizing chemical [4, 5]. Manganese minerals can be divided into oxides, carbonates, silicates, sulfides, halides, and groups according to their chemical composition and structure [1, 6, 7].

To produce manganese alloys, ores with over 30% manganese and a manganese/iron ratio above 5 are essential [5]. Key manganese minerals include pyrolusite, manganite, hausmannite, rhodochrosite, and rhodonite. [8]. While rhodochrosite is highly valued, manganese oxide ores, especially pyrolusite, are widely used due to their abundance. Ongoing efforts focus on developing technologies for low-grade ore exploitation. Recovery involves reducing insoluble Mn(IV) to soluble Mn(II) since MnO₂ is stable in natural alkali or acid dissolution.

Various reducing agents in the acidic media were utilized to recover manganese from various sources, as given in Table 1. Oxalic acid was shown to be the most effective acid for dissolving most minerals due to the lesser danger of contamination of the treated materials following calcination. Compared to other organic acids, it also exhibits a high complexing ability and strong reducing power [8–10].

Manganese has a wide range of oxidation states and can be found in several oxides, including MnO, Mn₂O₃, Mn₃O₄, Mn₅O₈, and MnO₂, serving technological purposes in catalysis, superconductors, ion exchange, and more [21–23]. MnO₂ is a suitable catalyst for air purification, a reversible cathode for lithium batteries, and a way to selectively extract carbon monoxide from H₂-rich gas in fuel cells. Similarly, bixbyite (Mn₂O₃), which is utilized to make manganese-zinc ferrites for transformer cores, eliminates carbon monoxide

and nitrogen oxide from waste gases [24]. Nanoscale MnO, Mn₂O₃, and Mn₃O₄ formations, such as nanoscale manganese oxides, nanospheres, nanorods, nanoclusters, nanowires, nanosized platelets, ellipsoids, cubes, and rhombohedra, are typically synthesized by researchers using manganese oxalate compound [22, 24, 25]. Thus, the leaching of pyrolusite with oxalic acid-hydrochloric acid appears to be an essential prerequisite for producing manganese oxalate, a chemical whose economic value is vital for producing many valuable compounds.

Existing manganese studies primarily focus on leaching kinetics with reducing agents, exploring variables within specific ranges. Kinetic studies involve altering one experimental parameter while keeping others constant to analyze their impact on pyrolusite mineral leaching. However, this approach may not reveal parameter interactions. Process factors and values influence leaching effectiveness and progression. Understanding these interactions helps identify optimal conditions for the process. Statistical experimental design maximizes variable values to optimize the leaching procedure, allowing simultaneous alteration of experimental parameters. This approach yields valuable insights while minimizing the number of trials, making experimental design a powerful tool for observing variable interactions [26–28].

Response Surface Methodology (RSM) is a statistical and mathematical approach used to optimize engineering problems by conducting experiments and developing models to analyze the impact of variables. Its primary goal is to optimize response surfaces affected by various process factors. Industries, including pharmaceutical and food, have widely adopted RSM to enhance product quality, profitability, and process stability [26, 29, 30].

This study explores optimal conditions for leaching pyrolusite ore with hydrochloric acid and oxalic acid as a reducing agent, using a central composite design to investigate variables

Table 1 Recovery of manganese from various sources with different reducing agents in acidic medium

Minerals	Mn	Medium	Presence reductant material	References
Cryptomelane, chalcophanite, pyrolusite, and crednerite	11% MnO	HCl	H ₂ O ₂	[11]
MnO ₂	%20 Mn as MnO ₂	H ₂ SO ₄	Glucose	[12]
Mn mineral	26.43% MnO	H ₂ SO ₄	Oxalic acid	[8]
Pyrolusite, cryptomelane, hetaerolite and jacobsite	46.11% MnO	HNO ₃	Molasses	[13]
Pyrolusite	27.3% MnO	H ₂ SO ₄	Pretreated sawdust	[14]
Pyrolusite, psilomelane and manganomelane	56.31 MnO ₂	H ₂ SO ₄	K ₂ C ₂ O ₄	[3]
Cryptomelane, psilomelane, pyrolusite	51.43% MnO ₂	H ₂ SO ₄	SO ₂	[15]
MnO ₂ , MnO, Mn(OH) ₂ , Mn ₃ O ₄	45.62% Mn	H ₂ SO ₄	Waste tea	[16]
MnO ₂	38.2% Mn	H ₂ SO ₄	Sawdust	[17]
Pyrolusite	27.37%	H ₂ SO ₄	Hydrazine sulphate	[18]
Pyrolusite, braunite, cryptomelane	25.85% Mn	H ₂ SO ₄	Ascorbic acid	[19]
Pyrolusite	25.1% Mn	H ₂ SO ₄	Lignin	[20]

such as HCl concentration, oxalic acid concentration, and temperature. The results, including kinetics under optimal conditions and a recovery procedure for $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, are reported. Manganese is crucial for industries like steel production and can benefit economically from optimized extraction processes. Efficient leaching contributes to sustainable resource use and waste reduction, promoting positive environmental impacts. The study's findings are essential for industries aiming to enhance manganese extraction efficiency, potentially lowering costs and increasing competitiveness. Insights into activation energy variation with temperature offer energy-saving opportunities. Overall, this study advances chemical engineering, promoting economic benefits, environmental sustainability, and industrial efficiency. The findings have potential applications across various industries.

Method and Materials

Pyrolusite ore from Konya, Türkiye, was provided as a sample for this investigation. The pyrolusite sample was crushed, ground, and then sieved using conventional test sieves to produce various particle size (PS) fractions.

Trial Procedure

Leaching trials were carried out in a 1 L cylindrical reactor equipped with a mechanical stirrer, a temperature control unit, and a chiller to prevent solution loss through evaporation. 250 mL of hydrochloric acid solution was placed in the glass. After adding a certain amount of oxalic acid, it was brought to the reactor's operating temperature. A specific mass of ore was then added to the solution, and the stirring speed (SS) was adjusted. During the leaching, the solution was sampled at certain times and filtered. The amount of manganese in the leachate was determined using Flame AAS. The fraction of filtered manganese (X_{Mn}) was computed as Eq. (1). Each round of analysis was conducted twice, and the conversion fraction was calculated using the arithmetic mean of the findings.

$$X_{\text{Mn}} = \frac{n_1}{n_2} \quad (1)$$

where n_1 is the mass of manganese in the solution, and n_2 is the mass of manganese in the ore sample.

Trial Design

RSM is a set of mathematical and statistical tools that may be utilized to design trials, predict, and analyze variable effects, and optimize engineering issues. This approach tries to maximize the response surfaces impacted by numerous process factors through rigorous experimental design. A test is a set of trials in which the inputted variables are changed to determine the source of the change in the output response [31–33].

RSM was used in experiments using a central composite design (CCD) to analyze the performance of the manganese leaching and find the best operating conditions. This technique aids in the analysis of the interaction impact between various factors, as well as the optimization of the efficient factors with a small number of tests. The CCD was performed to maximize manganese output by leaching pyrolusite ore with hydrochloric and oxalic acid solutions. The experimental design took three elements into account: oxalic acid concentration (C), hydrochloric acid concentration (D), and temperature (E), as shown in Table 2.

Utilizing Stat-Ease Inc.'s design expert program (Version 10.0.0, MN, USA) and CCD-based RSM, leaching trials were performed.

RSM is utilized to develop a realistic model between three independent parameters: oxalic acid concentration, hydrochloric acid concentration, and temperature, coded as C , D , and E . The CCD layout consists of six axial points, eight factorial points, and six repeats at the center points comprising a sequence of 20 tests at five distinct levels ($-1, +1, 0, -\alpha, +\alpha$) [34]:

$$N = 2^n + (2 \times n) + n_e = 20 \quad (2)$$

N denotes the total number of trials, n denotes the number of design elements, and n_e denotes the number of duplicate experiments. The following is the general form of the polynomial equation of the second degree utilized to determine the response variable:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^n \sum_{j>1}^n \beta_{ij} X_i X_j \quad (3)$$

where Y was the anticipated outcome, n was the overall number of tests, β_0 , β_i , β_{ii} , and β_{ij} were the constant, linear, quadratic, and interaction coefficients, and X_i and X_j were coded

Table 2 Factors and levels for CCD

Factor	Notation	Range of level				
		$-\alpha$	-1	0	$+1$	$+\alpha$
Oxalic acid concentration, (mol/L)	A	0.0795	0.25	0.5	0.75	0.9205
Hydrochloric acid concentration, (mol/L)	B	0.395	0.6	0.9	1.2	1.404
Temperature, (°C)	C	33.18	40	50	60	66.82

variables that were independent. Both numerical and graphical representations were utilized, and an analysis of variance (ANOVA) was performed to determine the statistical significance of the regression coefficients [35, 36]. Before determining the impact of the trial factors on the leaching rate of manganese (Y) from pyrolusite, the optimal values of the factors were established utilizing CCD.

RSM was performed to obtain a realistic model between the examined factors and the trial response, i.e., the yield of leached manganese.

Results and Discussion

As a result of the analysis of the ore sample, the content of the mineral and its ignition loss compositions at 800 °C are given in Table 3. RIGAKU miniflex 600 X-ray diffractometer was utilized as XRD (X-ray diffraction) patterns, and the mineralogical makeup of the pyrolusite ore was determined. The ore sample's X-ray diffraction pattern is seen in Fig. 1. According to this graph, the ore sample's principal constituent was pyrolusite (MnO_2).

Results of Trial Design

One of the primaries aim of RSM is to determine the optimal settings of control parameters that result in the maximum response. As a result, a plausible fitting model that accurately describes the average response must be employed to calculate the optimum value. The type of the fitted model influences the optimization strategies used in RSM [31, 33, 37]. This study focused on two work phases and manganese leaching recoveries to evaluate the leaching behavior of manganese from pyrolusite ore. The key factors impacting the leaching process are assessed and optimized utilizing RSM in the first phase. The kinetics modeling is then studied in the second step.

Trial Design and Analysis

A total of 20 trial studies were performed, the values of which are given in Table 4.

Statistical Analysis and Modeling

Linear, two-parameter interaction, cubic, and various quadratic models were adapted to experimental data and statistically analyzed using a 95% confidence level, as shown in Table 5.

As can be observed, compared to other models, the quadratic model has higher R^2 and adjusted R^2 values and a lower

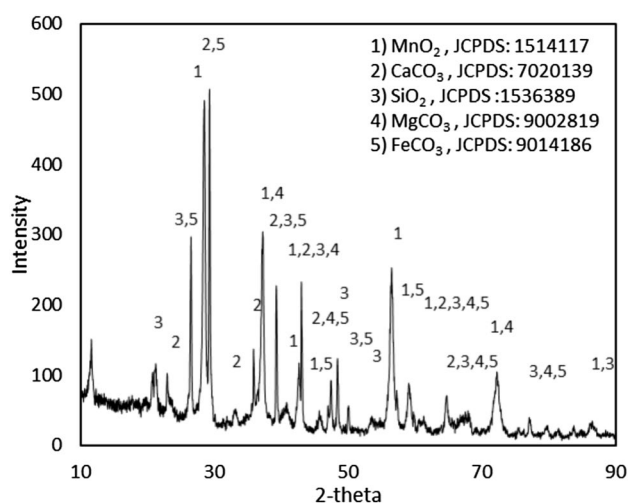


Fig. 1 XRD pattern for sample of ore utilized in this study

p -value for estimating the dissolution rate. After eliminating pointless terms (p -value > 0.05), a quadratic polynomial model was created following Eq. (3) and fitted to the experimental data, which can be expressed as Eq. (4).

Table 4 also includes the ANOVA outcomes for the created model.

$$Y = 85.59 + 2.5 \times C + 4.32 \times D + 4.56 \times e - 1.13 \times CD - 0.6 \times CE - 1.43 \times DE + 0.0366 \times C^2 - 0.2286 \times D^2 - 1.22 \times E^2 \quad (4)$$

Here, Y is the recovery of manganese (%), and C , D , and E represent oxalic acid concentration (mol/L), hydrochloric acid concentration (mol/L), and temperature (°C), respectively. F-tests were used to assess the statistical model, and ANOVA was used to identify each significant model term, as described in Table 6.

The F values of 32.59 indicate that the model is statistically significant. There is only a 0.01% chance that such a high model F value will occur due to noise. "Prob>F" values indicate that the model's terms are statistically significant. Table 6 shows that the order of significant terms is as follows $E > D > C > E^2 > DE > CD$. The "Lack of Fit F value" of 2.12 indicates that the Lack of Fit is insignificant compared to the pure error. A significant Lack of Fit F -value owing to noise has a 21.49% chance of occurring. The model's R^2 was 0.967. Therefore, the predicted R^2 is in good agreement with the adjusted R^2 . Adeq. Precision was discovered to be 21.2128, indicating that a signal-to-noise ratio greater than 4 is desirable [35].

Table 3 Chemical analysis of pyrolusite ore utilized in the study

Component	MnO ₂	CaO	Fe ₂ O ₃	SiO ₂	MgO	Al ₂ O ₃	Igniton loss
Value, %	57.66	10.00	8.04	7.08	0.44	0.93	15.85

Table 4 shows the experimental data from CCD studies as well as the anticipated manganese levels

Run	C:Oxalic acid Concentration (mol/L)	D:Hydrochloric acid Concentration (mol/L)	E:Temperature	YMn (%)
1	0.5	0.9	50	85.4
2	0.5	0.9	50	83.2
3	0.5	0.9	50	86.7
4	0.5	0.9	66.8179	91.1
5	0.75	1.2	60	92.2
6	0.920448	0.9	50	90.8
7	0.25	1.2	60	89
8	0.5	0.395462	50	78.1
9	0.5	1.40454	50	93.7
10	0.75	1.2	40	85.8
11	0.5	0.9	50	86
12	0.5	0.9	50	85.9
13	0.25	0.6	40	68.5
14	0.25	1.2	40	83.4
15	0.5	0.9	33.1821	75.1
16	0.25	0.6	60	83
17	0.75	0.6	40	78.6
18	0.0795518	0.9	50	82.5
19	0.5	0.9	50	86
20	0.75	0.6	60	87.5

Table 5 Statistical analysis of models for predicting the leaching recovery of manganese

ANOVA of models						
Source	Sum of Squares	Degree of freedom(DF)	Mean Square	F-value	p-value	
Mean vs Total	143,200	1	143,400			Suggested
Linear vs Mean	624.92	3	208.31	44.87	< 0.0001	Aliased
2FI vs Linear	29.25	3	9.75	2.81	0.0807	
Quadratic vs 2FI	21.98	3	7.33	3.18	0.0719	
Cubic vs Quadratic	6.45	4	1.61	0.5834	0.6867	
Residual	16.60	6	2.77			
Total	143,900	20	7196.35			
Statistical analysis summary of models						
Source	Std. Dev	R ²	Adjusted R ²	Predicted R ²	PRESS	Suggested
Linear	2.15	0.8938	0.8738	0.8159	128.73	Aliased
2FI	1.86	0.9356	0.9059	0.7577	169.39	
Quadratic	1.52	0.9670	0.9374	0.8038	137.17	
Cubic	1.66	0.9763	0.9248	– 1.9164	2039.14	
PRESS predicted residual error sum of square						

Figure 2 shows the three-dimensional response surface plots and contour plots which were constructed to show the effects of pyrolusite leaching using HCl acid and oxalic acid solutions and temperature variables on manganese recovery. It indicated a significant relationship between independent variables and their optimum response. The effects of HCl concentration and oxalic acid concentration were studied as they were found to affect the response significantly. As can

be seen from Fig. 2a, the manganese recovery increases with an increase in HCl concentration and oxalic acid concentration. The highest recovery of manganese value was obtained when both the variables were at the maximum point within the range studied. Figure 3b shows the effects of temperature and oxalic acid concentration on the recovery of manganese yield. It can be seen from Fig. 2b and c that the recovery of manganese yield increases with increasing temperature.

Table 6 ANOVA of second order model developed to predict the leaching recovery of manganese

Source	Sum of Squares	DF	Mean Square	F-value	p-value Prob>F	
Model	676.15	9	75.13	32.59	<0.0001	significant
A	85.44	1	85.44	37.07	0.0001	
B	255.20	1	255.20	110.72	<0.0001	
C	284.28	1	284.28	123.33	<0.0001	
AB	10.13	1	10.13	4.39	0.0625	
AC	2.88	1	2.88	1.25	0.2898	
BC	16.25	1	16.25	7.05	0.0241	
A ²	0.0193	1	0.0193	0.0084	0.9289	
B ²	0.7529	1	0.7529	0.3266	0.5803	
C ²	21.40	1	21.40	9.28	0.0123	
Residual	23.05	10	2.31			
Lack of Fit	15.66	5	3.13	2.12	0.2149	Not significant
Pure Error	7.39	5	1.8			
Cor Total	699.20	19				
Std. Dev	1.52		R ²	0.967		
Mean	84.63		Adjusted R ²	0.9374		
C.V.%	1.79		Predicted R ²	0.8038		
Adeq precision	21.2128					

It can be seen from Fig. 2 that the HCl acid concentration, oxalic acid concentration, and temperature on the dissolution of manganese from the pyrolusite mineral are effective parameters.

Optimization

Following the desirability approach, the numerical optimization technique established an optimum setting for maximum manganese leaching. The process-dependent (response) variables were optimized for oxalic acid, hydrochloric acid, and temperature, keeping the target of maximum manganese leaching. As a result of the optimization, oxalic acid 0.75 mol/L, hydrochloric acid 1.2 mol/L, and temperature 60 °C were determined. In these experimental studies, the stirring speed was kept constant at 400 rpm, the solid-to-liquid (SL) ratio was 14/250 g/mL, particle size was 137 µm and the time was 120 min.

Results of Leaching Experiments

As a result of these tests, it was determined that the trial and statistical analysis results had a logical connection. Following the optimization trials, second-step trials were carried out to find the leaching rate of pyrolusite in oxalic and hydrochloric acid solutions. These group trials investigated the effects of SL, SS, and PS on leaching rate. Manganese is found in the ore matrix as the pyrolusite mineral. The optimum conditions for leaching pyrolusite ore using oxalic acid and hydrochloric acid solutions were determined as 60 °C,

oxalic acid concentration 0.75 mol/L, and hydrochloric acid concentration 1.2 mol/L. The pyrolusite dissolution rate was calculated by SL ratio, PS, and SS as a time function while examining a parameter's effect in the trials.

Effect of Particle Size

To study the influence of PS on the leaching rate of pyrolusite ore, trials were performed on ore fractions with an average PS of 137, 115, 89.5, 69.5 and 63 µm, while the values of oxalic acid concentration, hydrochloric acid concentration, SL ratio, temperature, and SS were adjusted to 0.75 mol/L, 1.2 mol/L, 14/250 g/mL, 60 °C or 400 rpm. The results presented in Fig. 3 show that the dissolution rate decreases with increasing PS. Because the contact surface between the solid and the reactants increases as the PS reduces, the leaching rate typically rises as the PS reduces. After 120 min of extraction time at a PS of 137 µm, 89.5% of the manganese in the ore was dissolved, while by 45 min at a PS of 63 µm, 97% of the manganese had already leached out. These findings demonstrate that the average PS of the ore considerably influences pyrolusite leaching in oxalic acid and hydrochloric acid solutions.

Effect of Solid/Liquid Ratio

For SL ratios of 10/250, 12/250, 14/250, 16/250, and 18/250 g/mL, the impact of the SL ratio on the leaching of the pyrolusite mineral was investigated. The oxalic and hydrochloric acid concentrations, temperature, SS, and PS

were maintained at 0.75 mol/L, 1.2 mol/L, 60 °C, 400 rpm, and 115 µm, respectively, throughout these trials. Figure 4 demonstrates how the dissolving rates increase as the SL ratio decreases. A reduction in the leaching rate is anticipated because a rise in the SL ratio causes an increase in the solid per unit amount of liquid reagent. In 120 min of leaching time, 84.4% of the manganese in the ore was dissolved at an SL ratio of 18/250 g/mL, whereas 98.1% was dissolved at 10/250 g/mL in 60 min.

Effect of Stirring Speed

The SS influenced the 200, 300, 400, 500, and 600 r/min leaching rates. Oxalic acid and hydrochloric acid concentrations, temperature, the SL ratio, and PS were all held constant throughout the trials at 0.75 mol/L, 1.2 mol/L, 60 °C, 14/250 g/mL, and 115 µm, respectively. Figure 5 shows that the leaching rates increase as the SS increases. 69.5% of the manganese in the ore was removed after 120 min. of leaching at an SS of 200 rpm, whereas 96.1% was leached only after 60 min at an SS of 600 rpm. The leaching process depends on the agitation of the reactant content because it makes it easier for the leaching reagent to diffuse to the solid particle's outer surface and reduces the thickness of the diffusion layer that forms around the particle. As a result, increasing the SS typically enhanced the rate at which the metal species were leached from the ore. Also, when the SS increases, the solid particles are suspended in the solution, showing an even distribution throughout the reaction mixture. The effectiveness of leaching, therefore, rises due to improved interaction between the solid particles and the leach reagent.

Effect of Temperature

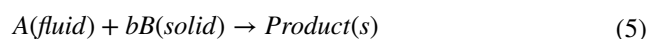
The studies were carried out at 20, 30, 40, 50, 60, and 70 °C while the concentrations of oxalic acid and hydrochloric acid, the SL ratio, the SS, and the PS were held constant at 0.75 mol/L, 1.2 mol/L, 14/250 g/mL, 400 rpm, and 115 µm, respectively. The data in Fig. 6 show that the leaching rate rises as the temperature increases. The temperature has a considerable impact on the manganese's ability to dissolve. It was discovered that 97.7% of manganese at 70 °C was dissolved in under 90 min, but 72.9% at 20 °C took 120 min to dissolve. Understanding how reaction temperature affects dissolve rate is significant because the activation energy derived from the Arrhenius equation may provide insight into the process's rate-controlling step.

Leaching Kinetics

Leaching processes' chemical reactions and mass transport properties can impact the total reaction rate. If the

overall rate of the chemical reaction is regulated, the liquid reactant's diffusion rate toward the solid–liquid interface and over the solid reactant becomes rapid. If the diffusion of the liquid reactant is slow, the chemical reaction step becomes rapid, and the mass transfer of the liquid reactant controls the overall rate. The mixed kinetic model (MKM) can manage the reaction rate if both diffusion and chemical reaction play a role in the general rate of the leaching process [38, 39]. The impacts of experimental factors such as the SS, SL ratio, and temperature, PS, on the leaching rate must be revealed to establish the rate-controlling stage in the leaching process. The kinetic assessment of a leaching process may have two important implications. Kinetic evaluation can assist in understanding how different factors impact the leaching rate. The mathematical model that will be developed because of this assessment will explain how the trial variables impact the rate of the leaching process. Thus, by regulating the values of the studied factors, the leaching operation may be performed at a specific rate. The rate-controlling step in the process can provide insight into the mechanism of the leaching reaction. Second, kinetic data regarding leaching efficiency and building industrial leaching reactors are crucial. Considering these factors, a kinetic study of the present leaching process was carried out. As is well known, the shrinking core model is the most comprehensive model used in the literature to disclose the rate expression of a leaching reaction [40].

According to this concept, the leaching reaction occurs on the spherical solid particle's outer surface, and the reaction surface diminishes toward the solid's center as the reaction progresses. The rate of the leaching reaction can be regulated via a surface chemical reaction, diffusion through a fluid film, or diffusion through the ash or product layer, according to the model [40, 41]. The chemical reaction between a fluid and a solid can be seen in Eq. (5).



When b is the stoichiometric coefficient, A and B are the fluid reactants and the solid being leached, respectively. The differential mass balance in the unstable state for component A on the spherical particle enclosed by a volume of fluid is as follows [42] Eq. (6) may be used to represent a steady-state differential mass balance for component A on a spherical particle enclosed by a volume of fluid [41].

$$\frac{D_e}{r^2} \frac{\partial y}{\partial r} \left(r^2 \frac{\partial C_A}{\partial r} \right) = 0 \quad (6)$$

Under specific boundary conditions, the analytical solution of Eq. (6) offers the most commonly utilized equations in the literature [40]. Equations illustrate the integral versions of these Eqs. (7–9).

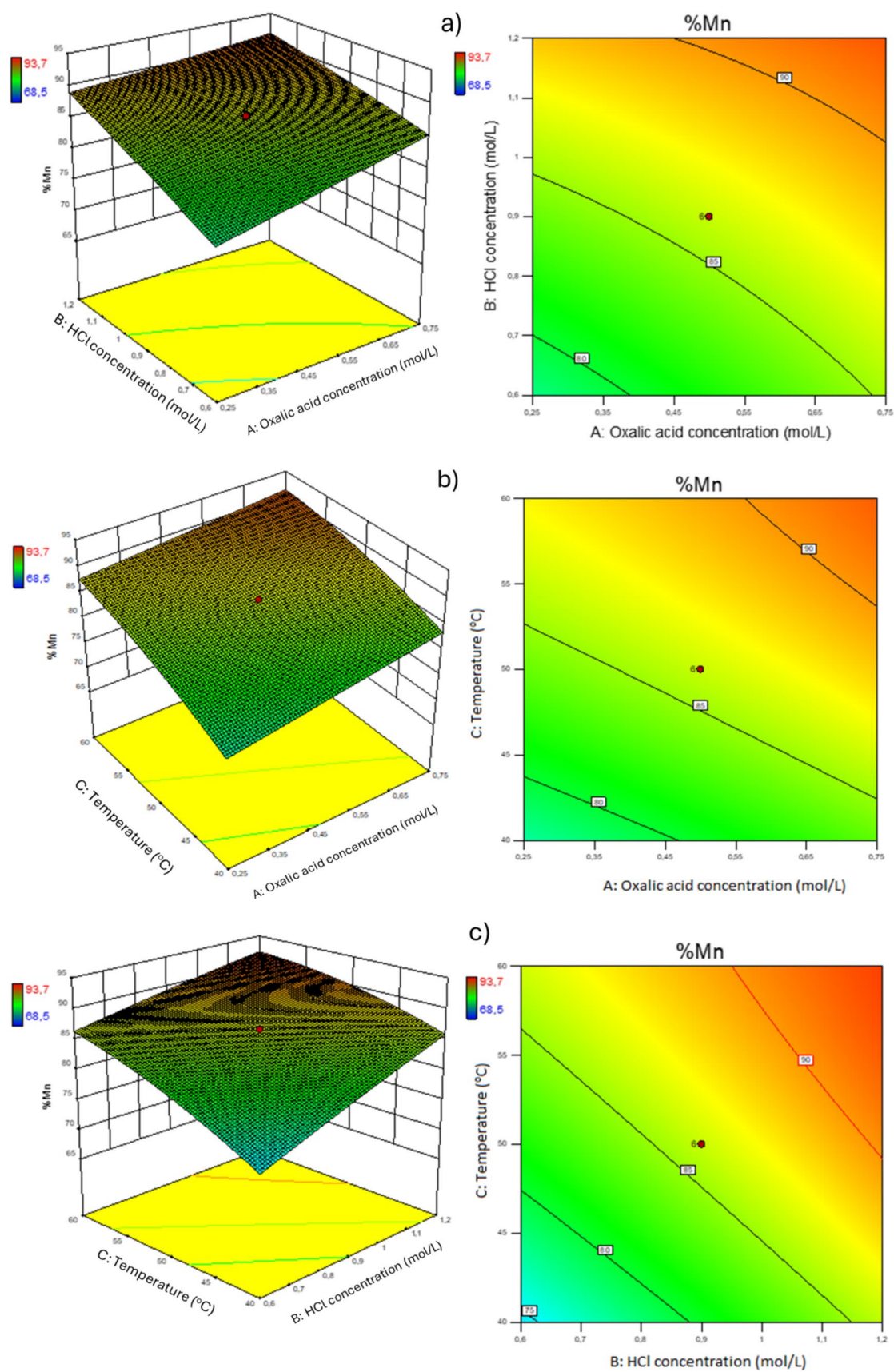


Fig. 2 RSM plots (left) and corresponding contour plots (right) showing the effects of interaction of **a** HCL concentration and oxalic acid concentration; **b** temperature and oxalic acid concentration; **c** temperature and HCL concentration on the manganese conversion fraction

$$x = k_f t \text{ (i)} \quad (7)$$

$$1 - (1 - x)^{\frac{1}{3}} = k_s t \text{ (ii)} \quad (8)$$

$$1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = k_p t \text{ (iii)} \quad (9)$$

In these equations, k_s , k_f , and k_p are the apparent rate constants for the surface chemical reaction (SCR) (ii), diffusion through the fluid film (DFF) (i), and diffusion through the product layer (DPL) (iii), respectively, and x is the fractional conversion, and t is the time.

In solid–liquid reaction systems, the pseudo-steady-state approach is often used for estimation. However, inaccuracies may arise from this assumption, especially when the concentration of liquid reactant is low. As a result, the pseudo-steady-state assumption must be utilized carefully for liquid–solid systems [41]. The experimental results obtained were evaluated using Eqs. (7–9) to identify the kinetic factors and rate-controlling step for the leaching of manganese from pyrolusite ore in hydrochloric acid solutions containing oxalic acid. These models are compatible with the kinetics of many leaching processes in literature. When the obtained trial data were investigated utilizing the models in Eqs. (7–9), it was found that these models could not clarify the manganese leaching from pyrolusite ore. The fractional conversion data obtained from the trials were evaluated using Eqs. (7–9) to compute the kinetic parameters and rate-controlling step for the leaching of manganese from pyrolusite ore. If the leaching response fits one of the kinetic models in Eqs. (7–9), then the graphs presented for the left sides of Eqs. (7–9) vs. time for each experimental parameter should have straight lines passing through the origin.

The slopes of the straight lines created when the graphs for Eqs. (7–9) were made indicate the apparent rate constant. Parabolic curves were seen when the change in the left side of Eq. (7) vs. time was plotted for the data from the experiment. As a result, this leaching process does not have a rate-controlling step due to the diffusion model through the fluid film. Straight lines with low correlation coefficients were seen when graphical representations of the left side of Eq. (8) vs. the reaction time were produced for all parameters using the conversion values obtained from the trials. As a result, the SCR does not serve as a rate-controlling step in this leaching process. The changes in the values of the left side of Eq. (9) vs. reaction time were then graphed using the experimental data. Straight lines with strong correlation

coefficients were discovered when these graphs were produced. As a result, the rate-controlling step may be diffused using the DPL. The leaching rate should be temperature-independent if DPL can control the rate of the leaching reaction. It can be observed from Fig. 5 that the reaction rate is affected by changes in the reaction temperature. As a result, the DPL model is insufficient to describe the rate-determining stage of this leaching process. Based on the experimental results and the assertions above, it can be concluded that these models cannot explain pyrolusite leaching. As previously stated, if chemical reaction and diffusion events influence the leaching rate, the reaction rate can be determined using an MKM. When the results shown in Figs. 3, 4, 5, and 6 are examined, the SL ratio, SS, average PS, and temperature affect the manganese leaching rate. This data suggests that an MKM may control the manganese leaching rate. As a result, the MKMs were examined to identify the rate-controlling phase in the present leaching process. Many MKMs have been presented in the literature [38, 40]. After experimenting with numerous MKMs, it was concluded that the model in Eq. (10) was based on the test results.

$$[1 - (1 - x)^{\frac{1}{3}}]^2 = k_m t \quad (10)$$

The SL ratio, temperature, SS, PS, and graphs were constructed utilizing the fractional conversion values obtained for each reaction period throughout the tests. Figures 7, 8, 9, and 10 show these graphs. These graphs show that straight lines with strong correlation coefficients are achieved for each factor. The apparent rate constants for the relevant parameter are given by the slopes of the straight lines in Figs. 7, 8, 9, and 10. Table 7 shows the MKM's apparent rate constant values and correlation coefficients.

The rate constant's dependency on the experimental values must be determined to precisely describe the mathematical model given in Eq. (10). For this purpose, a semi-empirical model indicating the rate constant's dependency on the experimental values can be stated as Eq. (11).

$$k_m = k_o SS^c SL^d PS^e \exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

where S , L , P , E_a , R , and T stand for the reaction temperature, activation energy, molar gas constant, SS, SL ratio, and PS. The response rate's dependency on the relevant parameters is shown by the constants c , d , and e , while the frequency factor is represented by k_o . Equations 10 and 11, when combined, may be expressed as follows:

$$[1 - (1 - X_{Mn})^{\frac{1}{3}}]^2 = k_o SS^c SL^d PS^e \exp\left(-\frac{E_a}{RT}\right) \cdot t \quad (12)$$

To determine the relevance of the constants e , d , and c , graphs of the logarithm of k_m versus the logarithm of

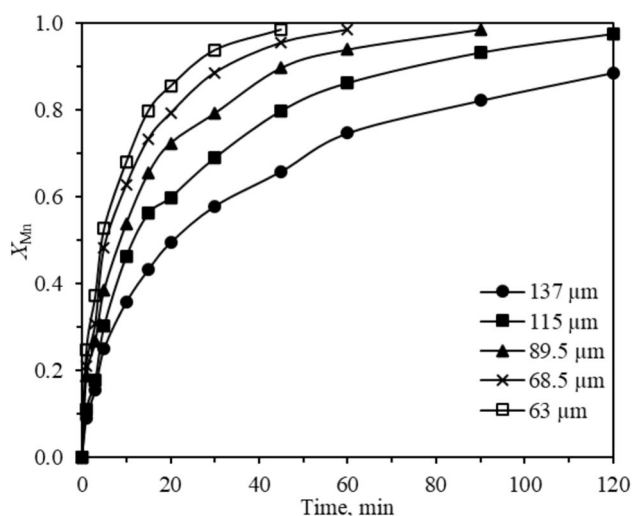


Fig. 3 Effect of average PS on the leaching rate of pyrolusite

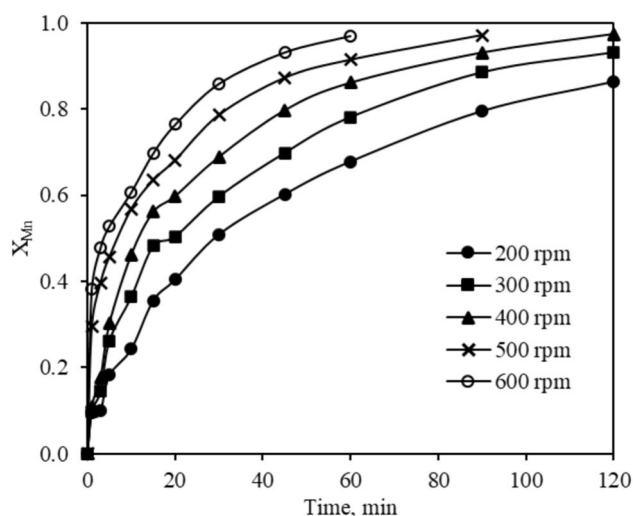


Fig. 5 Effect of SS on the leaching rate of pyrolusite

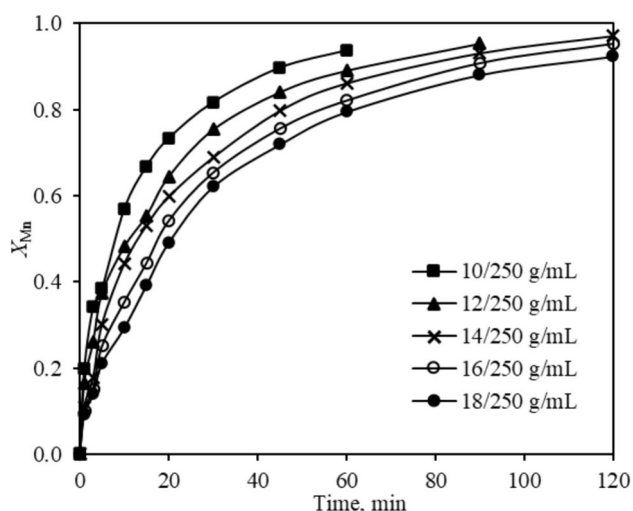


Fig. 4 Effect of SL ratio on the leaching rate of pyrolusite

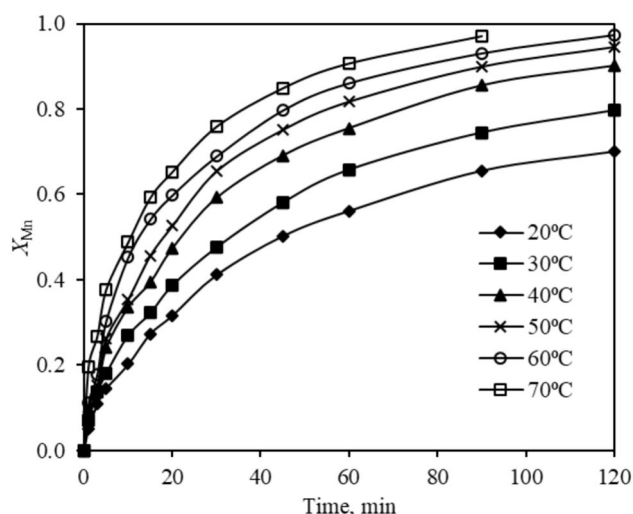


Fig. 6 Effect of reaction temperature on the leaching of pyrolusite

the relevant factor values must be shown. The slopes of the straight lines generated on the plots can be utilized to compute the constants' values; for the SL ratio, SS, and PS, the constants e , d , and c were estimated to be -2 , -1.2 , and 1.29 , respectively. The Arrhenius equation was utilized to compute the activation energy of this leaching process. Figure 11 depicts an Arrhenius plot to determine the activation energy of this leaching process. The activation energy was calculated to be 29.05 kJ/mol and the pre-exponential factor to be 145.8 s^{-1} , respectively. The mass transfer and the chemical reaction properties generally influence the overall rate of non-catalytic solid–liquid reactions. The diffusion of the liquid reactant from the solid reactant rapidly when the chemical reaction controls the overall rate. The mass transfer of the liquid reactant controls the overall rate in situations

where the diffusion of the liquid reactant occurs slowly and the chemical reaction step proceeds rapidly. The mixed kinetic model can control the reaction rate if both diffusion events and chemical kinetics impact the overall process rate. Particle size, stirring speed, acid concentration, and reaction temperature all have a significant impact on the rate at which manganese leaches from pyrolusite ore. The overall rate of non-catalytic solid–liquid reactions generally depends on both the chemical reaction and the mass transfer properties. Consequently, it is possible that the mixed kinetic model can control the rate of this process based on these findings. To identify the rate-controlling step of this leaching process, mixed kinetic models were employed using experimental data. Numerous leaching reactions have been studied using these kinetic models in the literature. According to

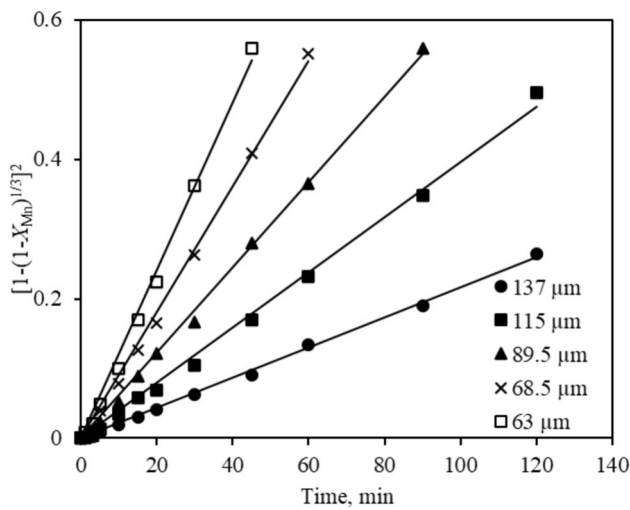


Fig. 7 Plot of $[1-(1-X_{Mn})^{1/3}]^2$ vs. time for different PSs

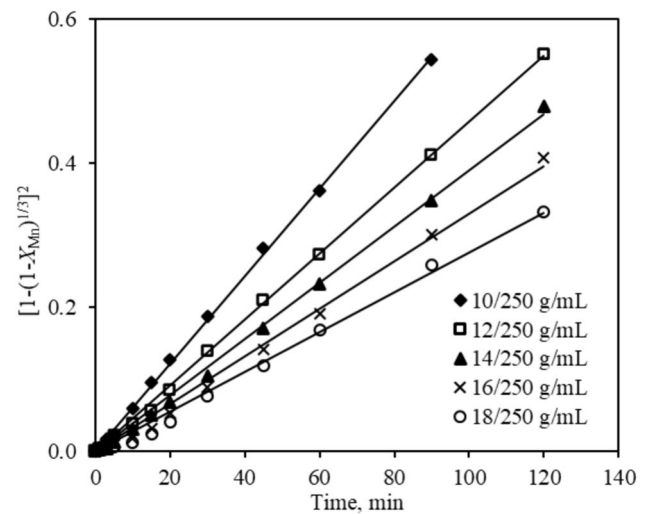


Fig. 9 Plot of $[1-(1-X_{Mn})^{1/3}]^2$ vs. time for different SL ratios

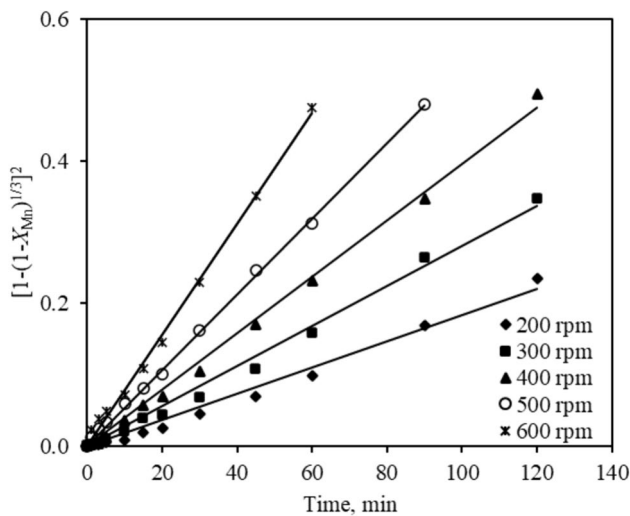


Fig. 8 Plot of $[1-(1-X_{Mn})^{1/3}]^2$ vs. time for different SSs

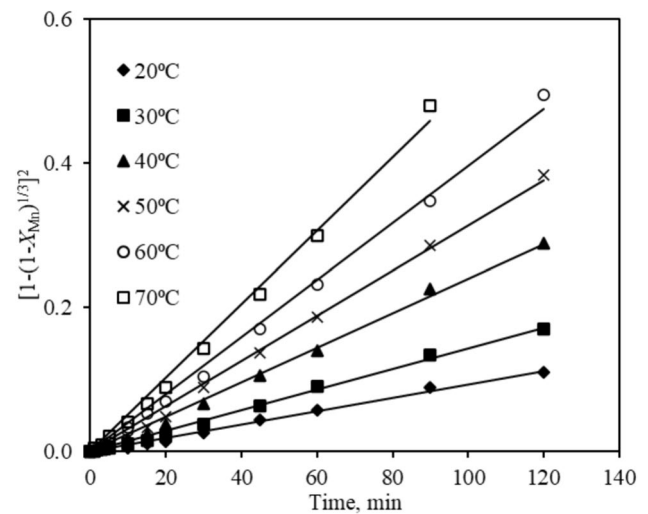


Fig. 10 Plot of $[1-(1-X_{Mn})^{1/3}]^2$ vs. time for different temperatures

the activation energy value, the mixed kinetic control model was followed in the dissolution of pyrolusite minerals in the solutions containing both oxalic acid and hydrochloric acid. When a process is chemically controlled, the activation energy is typically larger than 40 kJ/mol, whereas it is typically less than 40 kJ/mol in a diffusion-controlled process [43]. Figure 12 is a graphic indicating agreement between theoretical and experimental conversion values. This graph shows that there is enough agreement between the theoretical as well as the experimental findings. It is possible to estimate the rate control step of the reaction using the activation energy of a leaching process. The mass transfer properties are observed to have an impact on the reaction rate, given that the activation energy is less than 40 kJ/mol. As a result, the experimental parameters that characterize the kinetics

of pyrolusite leaching in oxalic acid and hydrochloric acid solutions may be represented as a mathematical formula as follows:

$$[1 - (1 - X_{Mn})^{1/3}]^2 = k_o S^{1.2} L^{-1.02} P^{-2.01} \exp\left(\frac{3494}{RT}\right) t \quad (13)$$

The pH was adjusted to 3–3.5 by adding ammonia to the filtered solution obtained after pyrolusite leaching. The solution was stirred at room temperature for about 1 h. The solution was filtered, and the resulting cake was dried in an oven at 80 °C for 3 h. The FTIR spectroscopic result of the obtained manganese oxalate precipitate is shown in Fig. 13. The XRD, SEM images, and EDX results of manganese oxalate, as well as the picture of manganese oxalate

Table 7 The apparent size constants for the kinetic models and correlation coefficients

Parameter	Surface chemical reaction $1-(1-x)^{1/3}$	Diffusion through the product layer $1-3(1-x)^{2/3}+2(1-x)$	Mixed kinetic model $[1-(1-x)^{1/3}]^2$
	$k_l [\text{min}^{-1}] R^2$	$k_r [\text{min}^{-1}] R^2$	$k_d [\text{min}^{-1}] R^2$
Solid/liquid ratio [g/mL]			
10/250	0.0121 0.9269	0.0119 0.9886	0.0061 0.9996
12/250	0.0087 0.9265	0.0086 0.9894	0.0046 0.9995
14/250	0.0069 0.9349	0.0070 0.9912	0.0039 0.9985
16/250	0.0063 0.9469	0.0062 0.9952	0.0033 0.9962
18/250	0.0058 0.9481	0.0055 0.9932	0.0028 0.9953
Stirring speed [rpm]			
200	0.0047 0.9580	0.0040 0.9982	0.0018 0.9903
300	0.0058 0.9436	0.0055 0.9976	0.0028 0.9947
400	0.0069 0.9336	0.0071 0.9916	0.0039 0.9978
500	0.0094 0.9019	0.0096 0.9808	0.0053 0.9992
600	0.0137 0.9116	0.0140 0.9855	0.0078 0.9982
Particle size [μm]			
137	0.0052 0.9316	0.0046 0.9958	0.0022 0.9989
115	0.0068 0.9613	0.0071 0.9916	0.0040 0.9978
89.5	0.0090 0.9638	0.0105 0.9840	0.0061 0.9989
68.5	0.0128 0.9702	0.0153 0.9888	0.0090 0.9985
63	0.0168 0.9661	0.0204 0.9899	0.0120 0.9971
Temperature [$^{\circ}\text{C}$]			
20	0.0034 0.9374	0.0023 0.9954	0.0029 0.9962
30	0.0042 0.9380	0.0033 0.9959	0.0014 0.9969
40	0.0054 0.9410	0.0049 0.9957	0.0024 0.9970
50	0.0062 0.9417	0.0060 0.9940	0.0031 0.9975
60	0.0069 0.9360	0.0071 0.9923	0.0040 0.9976
70	0.0091 0.9350	0.0092 0.9937	0.0051 0.9971

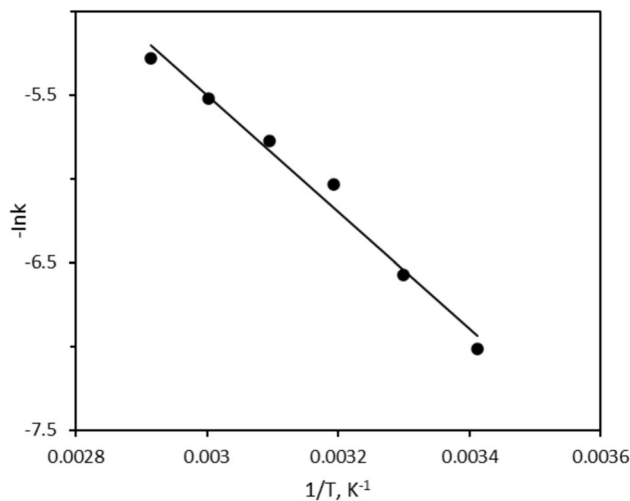


Fig. 11 Arrhenius plot for the leaching process

precipitated from the leaching solution are given in the supplementary data file. XRD pattern, SEM images and EDX results, and obtained by precipitation of manganese oxalate are given in Figs. S1, S2, and S3, respectively. The formation of $[\text{Mn}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ is confirmed by IR absorption.

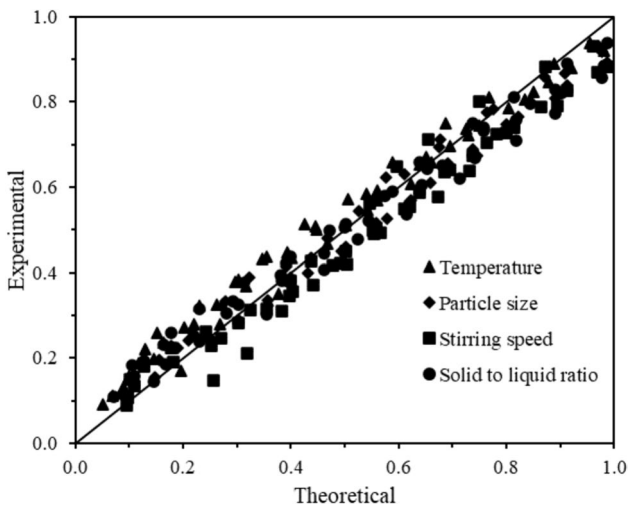


Fig. 12 All parameters agree with the experimental and theoretical conversion values

The modes of $\nu_{\text{s}(\text{C}-\text{O})+\delta(\text{OC}=\text{O})}$ are ascribed to the firm absorption peaks at 1363 and 1310 cm^{-1} . The asymmetrical vibrations of the carbonyl group caused an absorption peak at 1615 cm^{-1} , which is attributed to the occurrence

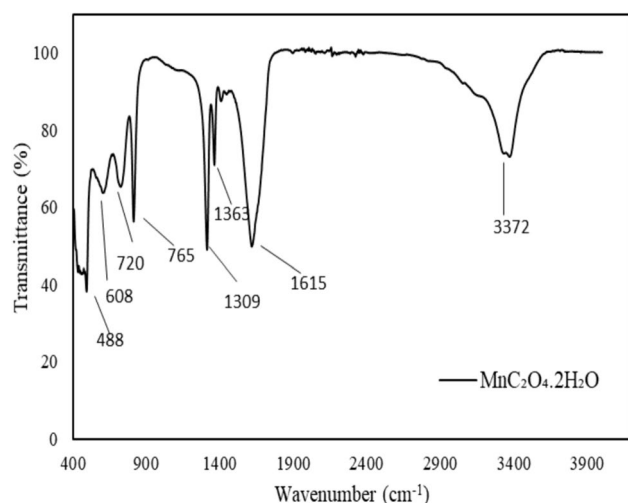


Fig. 13 FTIR spectra of obtained manganese oxalate

of the $[\text{Mn}(\text{C}_2\text{O}_4)2\text{H}_2\text{O}]$ compound [44]. 488 and 608 cm^{-1} can be metal–O stretching vibrations $\text{C}=\text{C}-\text{O}$ and $\text{O}-\text{C}-\text{O}$ bending vibrations are connected with the bands at 728 and 765 cm^{-1} , respectively. The hydration fingerprint in the collected powder is the wide band at 3372 cm^{-1} . These findings are consistent with prior publications on $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the literature [45–47]. The XRD graph of the waste obtained after leaching and the schematic flow chart representing the overall process are given in the supplementary data file. The waste sample obtained after the leaching process is given in Fig. S4. A schematic flow chart representing the overall process is given in Fig. S5.

While the optimized conditions achieve the highest manganese dissolution percentage (97.4%), it is crucial to ensure a consistent supply of oxalic acid at the optimized concentration. On an industrial scale, the supply, storage, and transportation of large quantities of oxalic acid need to be managed safely. The cost-effectiveness of using this concentration on a larger scale should be evaluated. Bulk purchasing can reduce costs but overhead must be considered. It is important to maintain the same SL ratio to achieve similar dissolution efficiency. This ratio needs to be carefully managed in larger reactors; this may require more precise control systems to ensure proper mixing.

Large-scale reactors can be designed to achieve the desired SL ratio while maintaining reaction efficiency. This may require special mixing equipment to ensure adequate suspension of solid particles. Similar to oxalic acid, maintaining a consistent concentration of hydrochloric acid is crucial for large-scale processing. This necessitates robust safety protocols to manage the inherent risks associated with corrosive chemicals.

Industrial-scale reactors may require special equipment to achieve and maintain the desired SL ratio, reaction temperature ($60\text{ }^\circ\text{C}$), and hydrochloric acid concentration (1.2 mol/L) throughout the mixture. Efficient heating systems and robust safety protocols are crucial for handling large volumes of corrosive chemicals. Achieving uniform mixing at 400 rpm in larger reactors might necessitate powerful, custom-designed mixing equipment. Operating at this speed for extended periods can lead to wear and tear, so equipment materials and maintenance schedules require careful consideration. Maintaining a consistent particle size ($115\text{ }\mu\text{m}$) across large batches is critical for consistent dissolution efficiency. Implementing fine grinding or sieving techniques may be necessary, along with strict quality control measures. The 120-min reaction time established in this study should be maintained on a larger scale to ensure complete manganese dissolution. However, extended reaction times in larger systems can impact production output. Strategies to optimize batch processing or implement continuous flow systems may be required. Conducting pilot plant studies provides valuable data on process behavior under scaled-up conditions, allowing for early identification and mitigation of potential challenges. Additionally, using Computational Fluid Dynamics (CFD) simulations can help predict how mixing, heating, and reaction kinetics will behave on larger scales, informing reactor design and operating conditions. A gradual scaling-up approach allows for adjustments and improvements at each stage, minimizing the risk of large-scale failures. Implementing advanced control systems for real-time monitoring and adjustment of process parameters helps maintain optimal conditions and consistent product quality. A comprehensive economic analysis is essential to ensure the financial viability of large-scale production. This analysis should consider raw material costs, energy consumption, equipment costs, and labor. This study has the potential to significantly impact the manganese extraction industry by reducing production costs, leading to economic benefits for both industries and consumers. Additionally, by promoting a more efficient leaching process, this research contributes to the sustainable use of natural resources and reduced waste generation, thereby fostering environmental benefits. The optimized process offers higher efficiency and lower costs, potentially enhancing the competitiveness of various industries. Understanding the activation energy (29.05 kJ/mol) provides insights into how temperature influences the leaching process, potentially leading to energy-saving opportunities. Overall, this research contributes to advancements in chemical engineering, enabling the design of more efficient and environmentally friendly processes. These advancements can be applied to other industries as well. The findings of this study have the potential to positively impact the extraction

of manganese and related chemical processes, leading to economic benefits, promoting environmental sustainability, increasing industrial efficiency, and contributing to advancements in chemical engineering with broader societal implications.

Conclusion

- (1) The dissolving kinetics of pyrolusite ore in oxalic acid and hydrochloric acid solutions were investigated. The objectives were to optimize and simulate the influential factors of the pyrolusite ore leaching process, and to define the rate control step of the leaching kinetics.
- (2) The CCD was utilized for statistical modeling and leaching process optimization. Therefore, a quadratic mathematical equation was developed and offered to describe the link between the effective operating parameters and the Mn leaching rate, with R^2 being evaluated as 0.967.
- (3) It was found that the order of essential terms related to the dissolution of manganese is temperature > oxalic acid concentration > hydrochloric acid concentration > square of temperature > interaction between hydrochloric acid concentration and temperature > oxalic acid concentration and hydrochloric acid concentration interaction.
- (4) ANOVA was utilized to assess the interaction and individual effects of the factors. It was determined that oxalic acid concentration, hydrochloric acid concentration, temperature, hydrochloric acid concentration temperature of the interaction, and the square of the temperature were the most interactive effects on the dissolution of manganese.
- (5) Optimized values with the highest percent dissolution of manganese (97.4%) were obtained: oxalic acid 0.75 mol/L, SL ratio 14/250 g/mL, hydrochloric acid concentration 1.2 mol/L, temperature 60 °C, SS 400 rpm, time is 120 min and particle, and the particle size was kept constant at 115 µm.
- (6) Manganese leaching rate increases with increasing SS, temperature, decreasing PS, and SL ratio. At temperatures ranging from 20 °C to 70 °C, the leaching rate is governed by an MKM.
- (7) This system's activation energy was determined to be 29.05 kJ/mol. In this leaching system, a mathematical model was built that included the trial parameters describing the reaction kinetics. This study shows that building mathematical models for process simulation organization statistics can aid in estimating and comprehending trial parameters.
- (8) The RSM leaching technique is a simple and successful method of recovering high manganese from pyrolusite

ore. Recovering manganese ions in a leach solution as metallic or manganese compounds is possible by utilizing solvent extraction and electrolysis procedures.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s40831-024-00869-4>.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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