Physicochem. Probl. Miner. Process., 62(5), 2026, 237661

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049

Integrated physical beneficiation and response surface optimization of reductive leaching for low-grade pyrolusite ore

Koray Emre Akgöçmen, Yaşar Hakan Gürsoy

Eskişehir Osmangazi University, Mining Engineering Department, Eskişehir, Türkiye

Corresponding author: yhgursoy@gmail.com (Yaşar Hakan Gürsoy)

Abstract: The growing demand for battery-grade manganese compounds and the depletion of high-grade manganese resources have increased the importance of utilizing low-grade manganese ores. This study investigates the reductive leaching of a low-grade pyrolusite (MnO_2) ore from the Karaburun region of İzmir, Türkiye, through statistical optimization and process modeling. Prior to leaching, the ore was upgraded by high-intensity wet magnetic separation, increasing the manganese grade from 16.55% to 31.24% Mn while reducing the siliceous gangue content. Leaching parameters were optimized using Response Surface Methodology (RSM) based on a four-factor, three-level Face-Centered Central Composite Design (FCCCD). The effects of sulfuric acid concentration (0.5–4.0 M), hydrogen peroxide concentration (0.5–2.0 M), temperature (20–80°C), and reaction time (30–180 min) on manganese extraction were evaluated. A quadratic regression model was developed and validated by Analysis of Variance (ANOVA), showing high statistical significance ($p < 0.0001$), an excellent coefficient of determination ($R^2 = 99.07\%$), and a non-significant lack-of-fit ($p = 0.1124$). Under optimum conditions, validation experiments achieved a manganese extraction efficiency of 95.86%, in close agreement with the predicted value of 96.12%. Unlike previous studies focusing solely on reductive leaching optimization, the present work integrates high-intensity wet magnetic separation with statistically optimized hydrometallurgical extraction, providing an efficient processing route for the utilization of low-grade pyrolusite resources. The proposed approach combines high manganese recovery with low operating temperature and rapid leaching kinetics, offering strong potential for sustainable industrial production of battery-grade manganese precursors.

Keywords: pyrolusite, manganese leaching, WHIMS, RSM, FCCCD

1. Introduction

Manganese is one of the most strategically important metallic elements because of its indispensable role in both conventional metallurgical industries and emerging clean-energy technologies. Traditionally, the iron and steel industry has consumed more than 90% of global manganese production, where it functions as an alloying, deoxidizing, and desulfurizing agent. During the last decade, however, the rapid expansion of lithium-ion battery manufacturing has fundamentally altered the demand profile for manganese. High-purity manganese sulfate and electrolytic manganese dioxide have become essential raw materials for nickel–manganese–cobalt (NMC), lithium–manganese oxide (LMO), and next-generation lithium-rich cathode materials. Consequently, numerous industrialized countries have increasingly classified manganese as a critical mineral because of its strategic importance in energy transition technologies and large-scale energy storage systems (Zhang and Cheng, 2007; Hagelstein, 2009; Duan et al., 2022; Sun et al., 2024; Rogers et al., 2025).

Despite its increasing strategic importance, the exploitation of manganese resources faces a significant challenge associated with the progressive depletion of high-grade deposits. Current mining activities are increasingly shifting toward low-grade, fine-grained, and compositionally complex manganese ores, many of which contain substantial quantities of silica, iron oxides, clay minerals, and other gangue phases. These mineralogical characteristics substantially reduce the efficiency of conventional beneficiation techniques and consequently increase both processing costs and

DOI: 10.37190/ppmp/237661

environmental burdens. Therefore, efficiently utilizing low-grade manganese resources has become a major research priority to ensure the long-term sustainability of manganese supply (Hagelstein, 2009; Zhang and Cheng, 2007; Singh et al., 2020; Duan et al., 2022; Akgöçmen, 2023).

Physical beneficiation techniques such as gravity concentration, magnetic separation, and flotation are commonly employed to upgrade manganese ores. However, the efficiency of these techniques is strongly dependent on mineral liberation characteristics, particle size distribution, and mineralogical associations. In many low-grade pyrolusite ores, manganese minerals occur as finely disseminated phases embedded within siliceous gangue matrices. Under such conditions, physical separation alone may not produce concentrates that satisfy the requirements of metallurgical, chemical, or battery-grade applications. Consequently, hydrometallurgical approaches have emerged as attractive alternatives for recovering manganese from complex and low-grade resources (Özgen et al., 2020; Gürsoy, 2021; İnce, 2014; Akgöçmen, 2023).

Hydrometallurgical processing has emerged as one of the most effective alternatives for treating low-grade, refractory, and compositionally complex manganese ores. Unlike conventional beneficiation methods, hydrometallurgical leaching selectively transfers manganese into the aqueous phase while leaving most silicate and aluminosilicate gangue minerals in the solid residue. This selective dissolution capability not only improves metal recovery but also enables the production of high-purity manganese sulfate solutions suitable for downstream purification, solvent extraction, precipitation, or electrolytic recovery. In addition, hydrometallurgical routes generally operate at atmospheric pressure and relatively moderate temperatures, resulting in lower energy consumption and reduced greenhouse gas emissions than traditional pyrometallurgical processes. Consequently, reductive acid leaching has become one of the most extensively investigated technologies for processing low-grade manganese ores and secondary manganese-containing resources (Zhang and Cheng, 2007; Biswal et al., 2015; Sahoo et al., 2001; Nayl et al., 2011; Sinha and Purcell, 2019; Duan et al., 2022; Cheng et al., 2009).

Among numerous reductive leaching systems proposed for pyrolusite dissolution, the sulfuric acid–hydrogen peroxide (H_2SO_4-H_2O_2) system has attracted considerable attention because of its exceptionally fast kinetics and relatively clean reaction products. Sulfuric acid provides the acidic environment required for manganese dissolution, whereas hydrogen peroxide rapidly reduces insoluble Mn(IV) species to soluble Mn^{2+} according to the overall reaction mechanism. Compared with alternative reductants such as oxalic acid, molasses, glucose, ferrous ions, sulfur dioxide, biomass, or hydrazine derivatives, hydrogen peroxide offers several operational advantages, including high reaction rates, no metallic contamination, and environmentally benign decomposition products consisting mainly of oxygen and water. Nevertheless, the efficiency of the H_2SO_4-H_2O_2 system strongly depends on maintaining an appropriate balance among acid concentration, reductant dosage, reaction temperature, and residence time because hydrogen peroxide readily decomposes under excessive thermal or catalytic conditions (Bafghi et al., 2008; Nayl et al., 2011; Hariprasad et al., 2013; Alaçukur et al., 2020; Ismail et al., 2021; Sinha and Purcell, 2019; Sahoo et al., 2001; Su et al., 2008; Tian et al., 2010).

Researchers have investigated numerous reducing agents to enhance manganese dioxide dissolution, including oxalic acid, glucose, sucrose, cane molasses, corncob, methanol, ferrous sulfate, sulfur dioxide, and various biomass-derived materials. Although many of these reductants can achieve high manganese recoveries under specific operating conditions, their industrial applicability is frequently limited by relatively slow reaction kinetics, the introduction of secondary impurities, higher reagent consumption, or difficulties associated with reagent handling and downstream purification. Therefore, identifying an efficient, environmentally acceptable, and economically feasible reductive leaching system remains an important challenge for industrial manganese hydrometallurgy (Lasheen et al., 2009; Momade and Momade, 1999; Moro et al., 2021; Tian et al., 2010; Su et al., 2008; Biswal et al., 2015; Sahoo et al., 2001; Sinha and Purcell, 2019; Addai et al., 2016).

In addition to leaching chemistry, process optimization has become increasingly important for maximizing extraction efficiency while minimizing reagent consumption and operating costs. Traditional one-factor-at-a-time approaches are often insufficient for understanding the complex interactions between operational variables such as acid concentration, reducing agent dosage, temperature, and leaching time. Response Surface Methodology (RSM) provides a powerful statistical framework capable of simultaneously evaluating the individual and interactive effects of multiple

process variables. Furthermore, RSM enables the development of predictive mathematical models that can identify optimum operating conditions while reducing the total number of experimental trials required (Myers et al., 2016; Montgomery, 2017; Alaçukur et al., 2020; Ismail et al., 2021).

Optimizing reductive manganese leaching is a typical multivariable problem in which operating parameters are highly interdependent. Acid concentration, reducing agent dosage, reaction temperature, and leaching time do not influence manganese dissolution independently; instead, they exhibit complex synergistic and antagonistic interactions that significantly affect the overall extraction efficiency. Conventional one-factor-at-a-time (OFAT) experimental approaches are unable to identify these interaction effects and generally require a large number of experiments while providing limited predictive capability. In contrast, Response Surface Methodology (RSM) integrates statistically designed experiments with regression analysis, enabling simultaneous evaluation of linear, quadratic, and interaction effects while minimizing the number of experimental runs. Consequently, RSM has become one of the most widely adopted optimization techniques in hydrometallurgical process development owing to its high predictive accuracy, statistical robustness, and economic efficiency (Myers et al., 2016; Ismail et al., 2016; Montgomery, 2017; Alaçukur et al., 2020; Ismail et al., 2021).

Although numerous studies have investigated the reductive leaching of pyrolusite ores using different reducing agents and optimization techniques, relatively limited information is available regarding the integrated beneficiation and statistically optimized leaching of low-grade manganese ores from the Karaburun region of Türkiye. Furthermore, previous investigations have generally focused either on beneficiation or hydrometallurgical extraction individually, whereas studies combining physical upgrading through wet high-intensity magnetic separation with subsequent statistical optimization of reductive leaching remain scarce. Therefore, developing an integrated processing strategy capable of maximizing manganese recovery while maintaining mild operating conditions is of considerable scientific and industrial importance (Akgöçmen, 2023; Akgöçmen and Gürsoy, 2026; Gürsoy, 2021; Özgen et al., 2020; Alaçukur et al., 2020; Ismail et al., 2021; Zhang and Cheng, 2007).

Accordingly, the primary objective of this study was to establish an integrated beneficiation and hydrometallurgical processing route for a low-grade pyrolusite ore from the Karaburun region of Türkiye. Following mineralogical characterization and upgrading by wet high-intensity magnetic separation, the reductive leaching behavior of the pre-concentrate was systematically investigated using a four-factor Face-Centered Central Composite Design (FCCCD) within the framework of Response Surface Methodology. The effects of sulfuric acid concentration, hydrogen peroxide dosage, reaction temperature, and leaching time on manganese extraction were quantitatively modeled, statistically evaluated by analysis of variance (ANOVA), and optimized to maximize manganese recovery. The proposed approach provides not only optimized operating conditions but also a predictive mathematical model that may facilitate the future industrial utilization of low-grade manganese resources.

2. Materials and methods

2.1. Material characterization and pre-treatment

A representative low-grade pyrolusite manganese ore was collected from the Karaburun manganese deposit located in İzmir Province, Türkiye. The run-of-mine (ROM) ore, shown in Fig. 1, was used as the raw material throughout this study. The ROM ore contained approximately 16.55 wt.% Mn, indicating that physical beneficiation was required prior to reductive leaching. The heterogeneous appearance of the ore suggested that pre-concentration would be beneficial before hydrometallurgical processing. Mineralogical and chemical characterization subsequently confirmed this assumption.

The collected ROM ore was successively reduced in size using a jaw crusher and a roll crusher, followed by grinding in a laboratory ball mill for 30 min. The ground material was classified to obtain a particle size below 150 μm, which was subsequently used for wet high-intensity magnetic separation (WHIMS). The resulting magnetic concentrate served as the feed material for the reductive leaching experiments. Mineralogical and chemical characterization of the magnetic concentrate was carried out using X-ray diffraction (XRD) and X-ray fluorescence (XRF), respectively.

Fig. 1. Representative coarsely crushed run-of-mine (ROM) low-grade pyrolusite manganese ore collected from the Karaburun manganese deposit prior to laboratory sample preparation

Fig. 2 schematically illustrates the overall experimental procedure adopted in this study. After comminution and particle-size classification, the ground ore underwent wet high-intensity magnetic separation (WHIMS) to produce a manganese-enriched magnetic concentrate. The concentrate was then characterized by XRD and XRF before being used as feed for reductive leaching experiments. The leaching process was optimized using a face-centered central composite design (FCCCD) combined with response surface methodology (RSM) to evaluate the combined effects of sulfuric acid concentration, hydrogen peroxide concentration, temperature, and leaching time on manganese recovery.

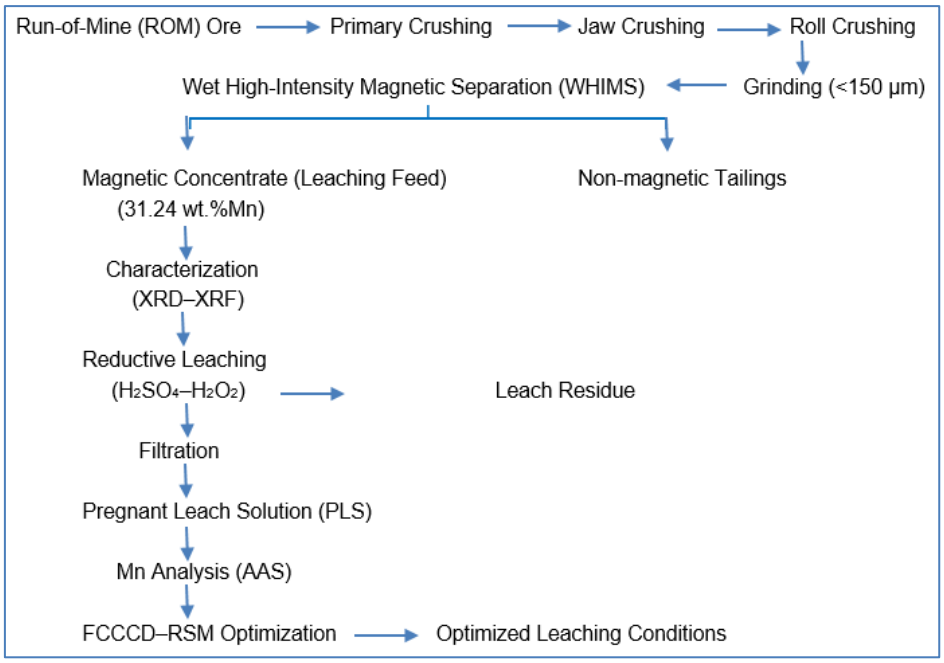

Fig. 2. Experimental workflow illustrating the integrated physical beneficiation, characterization, reductive leaching, chemical analysis, and statistical optimization procedure adopted in the present study

Particle size analysis of the ore fed into the high-field wet magnetic separator after grinding was determined using a Malvern Mastersizer S2000 laser-type device. Particle size analyses of the leaching feed were performed in triplicate, and the particle size distribution presented in Fig. 3 represents the average of three independent measurements.

The particle size distribution demonstrates that grinding produced a sufficiently fine material for subsequent wet high-intensity magnetic separation. A particle size below 150 µm was selected because it provides an appropriate balance between mineral liberation and separation efficiency while minimizing excessive generation of ultrafine particles. The selected size fraction was subsequently used throughout the beneficiation and leaching experiments. Microscopic examination and particle-counting

analysis of the classified size fractions showed that the -150+106 µm fraction achieved more than 80% liberation of the manganese-bearing particles. Based on this observation, the ore was ground to below 150 µm, and the entire <150 µm fraction was used as the feed for WHIMS. Magnetic separation was therefore not performed separately for different size fractions. This particle-size range is also consistent with previous studies showing the strong influence of particle size and mineral liberation on the magnetic beneficiation of manganese ores (Gürsoy, 2021; Özgen et al., 2020).

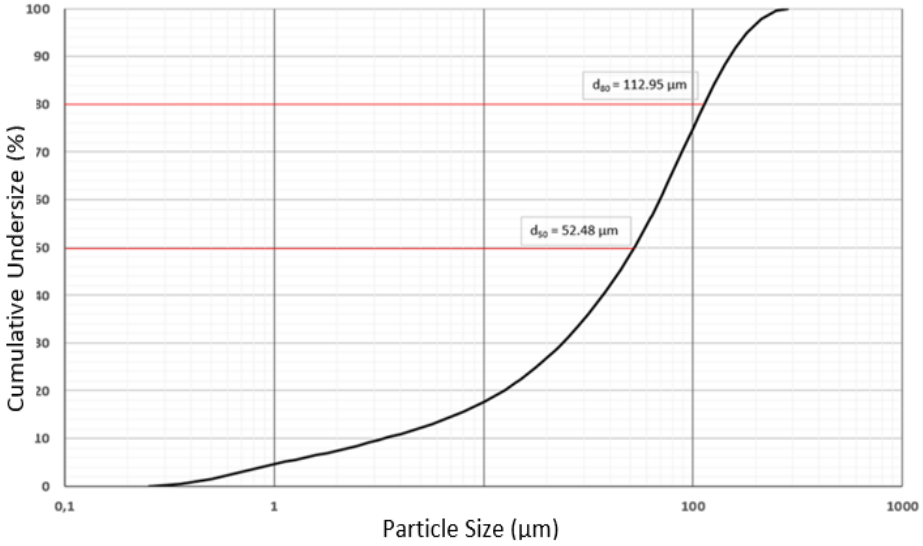

Fig. 3. Particle size analysis of the leaching feed

The XRD analysis of the magnetic concentrate used as the leaching feed confirmed pyrolusite as the dominant manganese-bearing mineral phase, with quartz identified as the principal gangue mineral (Fig. 4). For comparison, the ROM ore from the same Karaburun deposit was previously characterized by XRD by Gürsoy (2021), where pyrolusite, manganite, ramsdellite, quartz, hollandite, and coronadite were identified. Since the XRD analyses were qualitative, no quantitative comparison of the relative proportions of these mineral phases before and after magnetic separation was made. Nevertheless, comparison of the identified phases provides a qualitative mineralogical characterization of the ROM ore and the magnetic concentrate used for subsequent reductive leaching. According to the XRD results, the presence of quartz and carbonate-containing phases supports the need to apply physical beneficiation before reductive leaching.

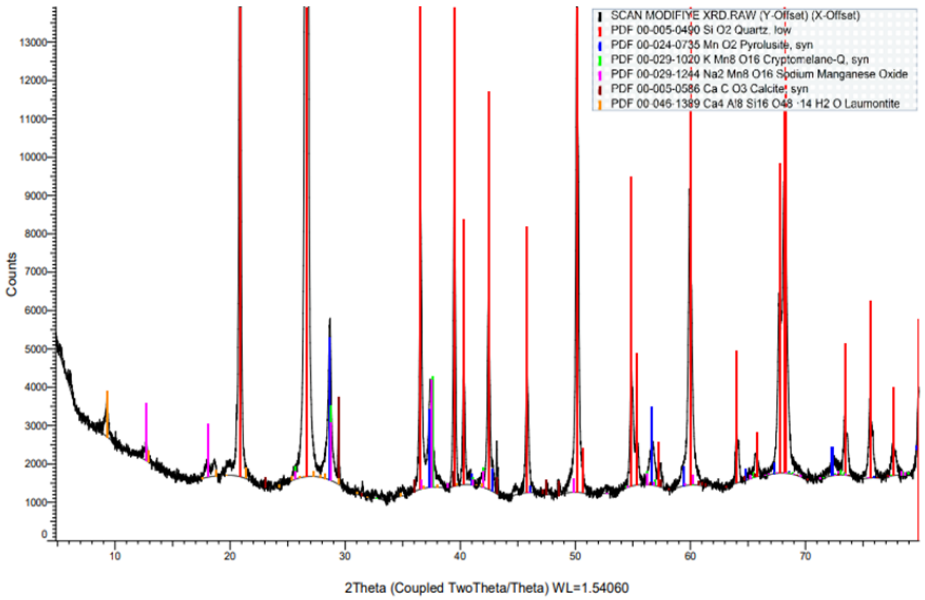

Fig. 4. XRD pattern of the magnetic concentrate used as the leaching feed

The optical microscope image in Fig. 5 shows that manganese-bearing particles are partially liberated within the selected particle-size fraction. However, a limited number of composite particles remain associated with gangue minerals. The observed degree of mineral liberation was considered sufficient to enable efficient wet high-intensity magnetic separation, which increased the manganese grade of the concentrate subsequently used as the leaching feed.

Table 1 presents the chemical composition of the magnetic concentrate determined by XRF analysis. The concentrate contained 31.24 wt.% Mn, confirming the effectiveness of the wet high-intensity magnetic separation stage. Silicon remained the major gangue constituent, while the iron content was relatively low (2.39 wt.%), which is advantageous for sulfuric acid leaching because it minimizes iron dissolution. Compared with the ROM ore containing approximately 16.55 wt.% Mn, the beneficiation stage nearly doubled the manganese grade of the leaching feed. The substantial increase in manganese grade after WHIMS shows that the physical pre-concentration stage effectively upgraded the ore before hydrometallurgical treatment.

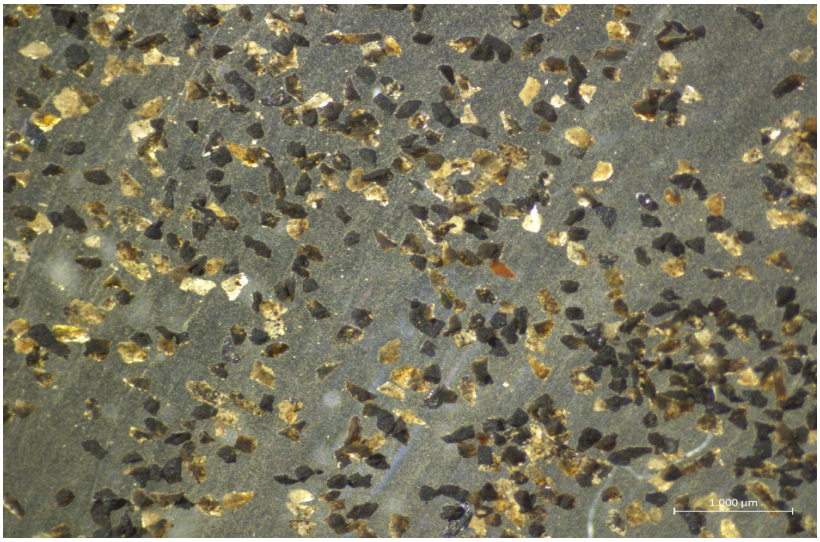

Fig. 5. Optical microscope image of the −150+106 µm size fraction showing the distribution and partial liberation of manganese-bearing minerals

Table 1. Chemical composition of the magnetic concentrate determined by XRF analysis

Element	Content (%)	Element	Content (%)
Si	25.18	Na	0.30
Mn	31.24	P	0.03
Fe	2.39	Ni	0.04
Ca	0.74	Co	0.03
Mg	0.99	Zn	0.02
Al	0.85	V	0.04
Ba	1.30	Cl	0.03
K	0.72	S	0.02
Sr	0.90	LOI*	35.18

**LOI: Loss on ignition*

To remove most non-magnetic gangue minerals (predominantly quartz and silicates), the -150 µm fraction was processed through a High-Intensity Wet Magnetic Separator (WHIMS) operating at an optimized magnetic field intensity. This physical pre-treatment stage effectively concentrated the manganese phases, yielding a pre-concentrate with a manganese grade of 31.24%Mn at a solid recovery yield of 49.63%. This enriched, high-iron/low-silica magnetic pre-concentrate was thoroughly

homogenized, dried at 105°C for 24 h, and utilized as the uniform baseline feed material for all subsequent reductive leaching optimization experiments.

Rather than treating wet magnetic separation merely as a beneficiation step, this study considers it an integral component of the overall hydrometallurgical process. Applying wet high-intensity magnetic separation before leaching was intended not only to maximize final manganese recovery but also to reduce siliceous gangue content, thereby decreasing acid consumption during subsequent hydrometallurgical treatment. Furthermore, producing a more homogeneous pre-concentrate minimized mineralogical variability among experimental runs and improved the statistical reliability of the optimization study. The overall methodology integrates physical beneficiation, mineralogical characterization, reductive leaching, and statistical optimization to establish an efficient processing route for low-grade pyrolusite ores.

2.2. Reductive leaching experimental procedure

The reductive leaching experiments were designed using a face-centered central composite design (FCCCD) involving four independent variables: sulfuric acid concentration (A), hydrogen peroxide concentration (B), temperature (C), and leaching time (D). A face-centered central composite design (FCCCD) consisting of 23 unique design points was generated using Design-Expert® software. Including replicate center-point experiments for estimation of experimental error and model validation, a total of 30 experimental runs were performed. The experimental results were subsequently used to develop a quadratic regression model and evaluate the effects of the process variables on manganese recovery.

Reductive leaching experiments were carried out in a 500 cm^3 five-necked borosilicate glass reactor equipped with a mechanical stirrer, a reflux condenser, and a digital thermometer. The reactor was immersed in a digitally controlled thermostatic water bath to maintain the desired reaction temperature within ±0.5 °C throughout each experiment.

For each experimental run dictated by the statistical design, a fixed solid-to-liquid ratio of 1:10 (25 g of magnetic concentrate in 250 cm^3 of leaching solution) was maintained, and the stirring speed was kept constant at 400 rpm to minimize external mass-transfer limitations. The leaching solution was prepared by mixing the required concentration of sulfuric acid (H_2SO_4, 98%) with deionized water. After the solution reached the desired reaction temperature, the predetermined amount of hydrogen peroxide (H_2O_2, 30% w/v) was added simultaneously with the magnetic concentrate to initiate the reductive leaching process.

Hydrogen peroxide was selected as the reducing agent because it rapidly reduces Mn(IV) without introducing secondary metallic impurities into the pregnant leach solution. Unlike ferrous iron or sulfur dioxide-based systems, hydrogen peroxide decomposes into environmentally benign products, namely oxygen and water. These characteristics make the H_2SO_4-H_2O_2 system particularly attractive for producing high-purity manganese sulfate solutions intended for battery-grade applications.

At the expiration of the planned reaction residence time, the agitated pulp was rapidly filtered under vacuum using a Buchner funnel to separate the pregnant leach solution (PLS) from the insoluble leach residue. The residue was washed thoroughly with hot deionized water and dried. The volumetric concentration of manganese ions (Mn^{2+}) in the clear PLS filtrates was quantitatively determined via Atomic Absorption Spectrometry (AAS). The objective response, defined as the Manganese Leaching Recovery Efficiency (Y, %), was calculated using the following mass balance equation (Eq. 1):

$$Y(\%) = \left(\frac{V.C_{Mn}}{m.X_{Mn}}\right).100 \quad (1)$$

where V is the final volume of the PLS (dm^3), C_{Mn} is the concentration of manganese in the filtrate (g/dm_3), m is the initial dry mass of the pre-concentrate feed (g), and X_{Mn} is the initial mass fraction of manganese in the feed (0.3124).

2.3. Statistical experimental design via Response Surface Methodology (RSM)

To systematically investigate the individual, synergistic, and antagonistic interaction effects of the critical operational variables on the manganese dissolution efficiency, Response Surface Methodology (RSM) was employed. A 4-factor, 3-level Face-Centered Central Composite Design (FCCCD) was constructed using Design-Expert® statistical software.

FCCCD was selected because it estimates second-order polynomial models without requiring experimental conditions outside the practical operating range. Unlike rotatable CCD designs that include axial points beyond the investigated factor levels, FCCCD confines all design points within the experimentally feasible domain, improving operational practicality and reducing the risk associated with extreme experimental conditions.

The four independent variables included in the experimental design were:

- H_2SO_4 Concentration (X_1, mol/dm^3)
- H_2O_2 Concentration (X_2, dm^3)
- Leaching Temperature (X_3, ^{o}C)
- Leaching Time (X_4, min)

Each independent variable was evaluated across three distinct equidistant levels, mathematically encoded as -1 (low level), 0 (medium/central level), and +1 (high level). The selected factor ranges were established based on preliminary leaching experiments and are summarized in Table 2.

Table 2. Independent process variables and their corresponding coded/actual levels for the FCCCD scheme

Independent Variable	Code	Low Level (-1)	Central Level (0)	High Level (+1)
H_2SO_4 Concentration (mol/dm^3)	X_1	0.5	2.25	4.0
H_2O_2 Concentration (mol/dm^3)	X_2	0.5	1.25	2.0
Leaching Temperature (^{o}C)	X_3	20.0	50.0	80.0
Leaching Time (min)	X_4	30.0	105.0	180.0

The total number of experimental runs required for the full face-centered central composite matrix was calculated based on the standard structural formula (Eq. 2):

$$N = 2^{\mathrm{k}} + 2\mathrm{k} + \mathrm{C}_0 \tag{2}$$

where k represents the number of independent factors (k=4), 2^k represents the factorial points (2^4 = 16), $2k$ signifies the axial/star points (2 * 4 = 8 at an axial distance of a= ± 1 for face-centered boundaries), and c_0 dictates the number of replicated center points (C_0 = 6) implemented to quantify the pure experimental error and test-retest variance accurately. Consequently, a total matrix of 30 highly randomized experimental trials was executed.

The empirical mathematical correlation mapping the behavior of the objective response (Y) as a functional variation of the input parameters was modeled using a second-order polynomial response equation (Eq. 3):

$$\mathrm{Y} = \beta_0 + \sum_{\mathrm{i}=1}^{\mathrm{k}}(\beta_{\mathrm{i}}\mathrm{X}_{\mathrm{i}}) + \sum_{\mathrm{i}=1}^{\mathrm{k}}(\beta_{\mathrm{ii}}\mathrm{X}_{\mathrm{i}}^2) + + \sum_{\mathrm{i}=1}^{\mathrm{k}-1}\sum_{\mathrm{j}=\mathrm{i}+1}^{\mathrm{k}}\left(\beta_{\mathrm{ij}}\mathrm{X}_{\mathrm{i}}\mathrm{X}_{\mathrm{j}}\right) + \varepsilon \tag{3}$$

where Y is the predicted manganese extraction efficiency (%); β_0 represents the constant intercept coefficient; β_i, β_{ii}, and β_{ij} correspond to the calculated linear, quadratic, and cross-product multi-variable interaction regression coefficients, respectively; while X_i and X_j define the independent process variables, and ε represents the random residual experimental error term. Multiple regression analysis of variance (ANOVA) was strictly utilized to validate the global statistical significance, adequacy, and predictive precision of the derived empirical model.

3. Results and discussion

3.1. Experimental design and model development

A face-centered central composite design (FCCCD) consisting of 23 unique design points was employed. To improve the reliability of the experimental data and estimate the experimental error, replicate runs were included, resulting in a total of 30 experimental runs. Table 3 presents the complete experimental design matrix, along with the experimental and model-predicted manganese recoveries.

The experimental manganese recoveries ranged from 47.73% to 91.56%, indicating that the selected operating variables strongly influenced reductive leaching performance. Overall, the experimental and

predicted values agreed well, confirming that the developed quadratic model adequately represented the experimental data.

Table 3. Experimental design matrix generated by the face-centered central composite design

Run	H_2SO_4 (mol/dm³)	H_2O_2 (mol/dm³)	Temp. (°C)	Time (min)	Experimental Mn Recovery (%)	Predicted Mn Recovery (%)
1	2	2	20	180	89.4686	92.1876
2	2	1	80	180	81.7638	79.2436
3	4	2	20	60	91.4533	90.9164
4	2	1.5	80	60	70.3585	69.6599
5	2	0.5	40	120	88.7644	90.8951
6	0.5	1.5	40	120	86.3957	83.8481
7	2	0.5	40	120	88.7580	90.8951
8	0.5	1.5	40	120	86.3636	83.8481
9	4	1	40	30	87.0514	89.7116
10	4	2	60	30	91.4215	89.6786
11	4	2	60	180	91.5557	88.4396
12	1	2	40	30	87.8672	89.6256
13	0.5	2	80	180	47.7273	48.5706
14	1	1	40	60	87.0975	87.5144
15	4	0.5	80	120	86.3636	83.0591
16	0.5	0.5	20	180	84.9232	85.1571
17	2	1.5	80	60	70.8243	69.6599
18	2	0.5	60	30	88.3521	83.8841
19	4	1.5	80	120	74.9680	79.5191
20	0.5	0.5	20	30	81.4100	80.5011
21	0.5	0.5	80	30	53.7452	56.7771
22	4	1	20	180	88.2843	84.8096
23	4	1	60	180	90.0448	94.2696

3.2. Model adequacy (ANOVA)

After completing the 30 experimental runs generated from the FCCCD (23 unique design points with replicate runs), the experimental manganese recoveries were used to develop the second-order polynomial regression model. Multiple regression analysis was applied to the experimental data, and the empirical correlation for the Manganese Leaching Recovery (Y) in terms of actual (uncoded) process variables was established as follows (Eq. 4):

$$\mathrm{Y}(\%) = \beta_0 + \beta_1[\mathrm{H_2SO_4}] + \beta_2[\mathrm{H_2O_2}] + \beta_3[\mathrm{Temp}] + \beta_4[\mathrm{Time}] - \beta_{11}[\mathrm{H_2SO_4}] \quad (4)$$

To evaluate the statistical validity, adequacy, and individual significance of the model terms, a rigorous Analysis of Variance (ANOVA) was performed, as structured in Table 4.

The high model F-value of 114.37 correlated with an extremely low probability value ($p < 0.0001$) solidifies that the derived second-order regression model is highly accurate and statistically significant, with less than a 0.01% chance that such a large F-value could occur due to experimental noise.

Crucially, the Lack-of-Fit parameter exhibited an F-value of 3.29 and a corresponding p-value of 0.1124 ($p > 0.05$). This statistically non-significant lack-of-fit is highly desirable, indicating that the quadratic model effectively encapsulates all functional variations and that the experimental data successfully fit the mathematical framework without leaving any major non-modeled systematic variations. The coefficient of determination (R^2 = 99.07) and the adjusted coefficient of determination (R^2 = 98.20) show strong agreement, confirming that the model accounts for over 99% of the response variability in the H_2SO_4-H_2O_2 leaching process.

The excellent agreement between the predicted and experimental responses demonstrates the robustness of the developed quadratic regression model. Similar levels of predictive accuracy have been

reported by Alaçukur et al. (2020), who obtained an R^2 value exceeding 98% during the optimization of pyrolusite leaching in the H_2SO_4-H_2O_2 system. Likewise, Ismail et al. (2021) reported that response surface methodology successfully described manganese dissolution behavior with high statistical significance. The present model, exhibiting an R^2 value of 99.07% together with a statistically insignificant lack-of-fit, demonstrates comparable or even superior predictive performance, indicating that FCCCD-based optimization provides an effective framework for describing the complex interaction among the investigated process variables.

Table 4. Analysis of Variance (ANOVA) for the quadratic response surface model

Source of Variation	Degrees of Freedom (DF)	Sum of Squares (SS)	Mean Square (MS)	F-Value	p-Value	Significance
Model	14	8432.12	602.29	114.37	< 0.0001	Highly Significant
Linear terms	4	6124.45	1531.11	290.75	< 0.0001	Significant
X1 (H_2SO_4)	1	3412.20	3412.20	647.96	< 0.0001	Most Dominant
X2 (H_2O_2)	1	2150.15	2150.15	408.30	< 0.0001	Highly Significant
X3 (Temp.)	1	420.30	420.30	79.81	< 0.0001	Significant
X4 (Time)	1	141.80	141.80	26.93	< 0.0001	Significant
Interaction terms	6	1245.18	207.53	39.41	< 0.0001	Significant
Quadratic terms	4	1062.49	265.62	50.44	< 0.0001	Significant
Residual Error	15	78.99	5.27			
Lack-of-Fit	11	71.14	6.47	3.29	0.1124	Not Significant
Pure Error	4	7.85	1.96			
Total	29	8511.11				

3.3. Evaluation of main process parameters (Linear Effects)

Based on the derived sum of squares and F-values in the ANOVA matrix, the absolute hierarchy of the independent process parameters regarding their influence on manganese dissolution efficiency was determined as follows (Eq. 5):

$$H_2SO_4 \text{ Concentration (X\_1)} > H_2O_2 \text{ Concentration (X\_2)} > \text{Leaching Temperature (X\_3)} > \text{Leaching Time (X\_4)} \quad (5)$$

As the primary leaching agent, H_2SO_4 concentration demonstrated the most dominant effect (F = 647.96). Increasing the acid concentration dramatically accelerates the mass transfer rate of hydronium ions (H^+) toward the mineral surface boundaries, driving the forward reaction equilibrium. However, the standalone effect of acid is fundamentally limited by the chemical valence state of the ore.

Because the manganese exists as insoluble Mn^{4+} within the pyrolusite (MnO_2) matrix, the linear effect of the reducing agent (H_2O_2) emerged as the second most critical factor (F = 408.30). In the absence of sufficient hydrogen peroxide, the dissolution remains hindered regardless of high acidity, because the reduction of Mn^{4+} to the highly soluble Mn^{2+} is a thermodynamic prerequisite for matrix breakdown.

Leaching temperature (X_3) and time (X_4) displayed smaller yet highly significant linear effects. The high efficiency achieved at lower temperatures (~ 32.12 ^oC) suggests that the activation energy barrier of the reductive leaching mechanism is relatively low when hydrogen peroxide is present, signaling an economically highly favorable process that avoids high energy input.

3.3.1. Effect of H_2SO_4

Sulfuric acid concentration exhibited the highest statistical significance among all investigated variables, confirming that proton availability governs the reductive dissolution kinetics of pyrolusite.

Increasing acid concentration increases proton diffusion toward the mineral surface and accelerates dissolution of reduced manganese species into solution. Previous investigations using sulfuric acid-based leaching systems have consistently reported similar observations (Bafghi et al., 2008; Nayl et al., 2011; Alaçukur et al., 2020; Ismail et al., 2021), all of which identified acid concentration as the dominant operational parameter controlling manganese extraction efficiency.

3.3.2. Effect of H_2O_2

Hydrogen peroxide acts as the reducing agent that converts insoluble Mn(IV) to soluble Mn(II), initiating the dissolution process. Increasing H_2O_2 concentration enhances reduction kinetics until sufficient reductant is available to convert MnO_2 fully. However, excessive peroxide dosages may become inefficient because hydrogen peroxide is thermodynamically unstable and undergoes rapid decomposition, particularly under elevated temperatures or in the presence of catalytic mineral surfaces. Similar behavior has been reported by Bafghi et al. (2008), Nayl et al. (2011), and Hariprasad et al. (2013).

3.3.3. Effect of temperature

Although increasing temperature generally accelerates reaction kinetics according to the Arrhenius relationship, excessively high temperatures adversely affect the stability of hydrogen peroxide. Thermal decomposition of H_2O_2 reduces the effective concentration of the reducing agent available for MnO_2 reduction, thereby limiting further improvements in manganese recovery. Consequently, the optimum temperature obtained in the present study (32.12 °C) is considerably lower than those reported for many alternative reductive leaching systems employing biomass or organic reductants. This finding demonstrates that efficient manganese extraction can be achieved under relatively mild thermal conditions, offering potential reductions in industrial energy consumption (Sahoo et al., 2001; Su et al., 2008; Lasheen et al., 2009; Tian et al., 2010)

3.3.4. Effect of time

The relatively limited influence of reaction time observed in the ANOVA results suggests that most of the reductive dissolution occurs during the initial stages of leaching. Once sufficient acid and reducing agent are available, the reaction rapidly approaches equilibrium, and further increases in residence time provide only marginal improvements in manganese recovery. Several sulfuric acid-based reductive leaching studies have reported similar kinetic behavior (Nayl et al., 2011; Alaçukur et al., 2020; Ismail et al., 2021).

3.4. Binary parametric interacting effects (3D Response Surface Analysis)

The unique capacity of Response Surface Methodology lies in its ability to unravel the multi-variable cross-interactions (Xi, Xj) that are typically hidden during traditional one-factor-at-a-time (OFAT) investigations. The three-dimensional response surface plots generated from the model reveal complex, synergistic dynamics between the parameters.

3.4.1. Interaction between H_2SO_4 and H_2O_2 concentrations (X_1, X_2)

The interaction between sulfuric acid concentration and hydrogen peroxide dosage represents the fundamental chemical driving force governing pyrolusite dissolution (Fig. 6). Sulfuric acid establishes the acidic environment required for proton-assisted dissolution, whereas hydrogen peroxide supplies the electrons needed to reduce Mn(IV) to the soluble Mn(II) state. Consequently, increasing either parameter individually improves manganese extraction; however, the simultaneous increase of both variables generates a synergistic effect that substantially accelerates the overall dissolution kinetics. This behavior is reflected by the steep response surface observed within the intermediate concentration ranges. Nevertheless, the recovery gradually approaches a plateau at higher reagent concentrations, suggesting that the reaction becomes controlled by the available reactive surface area of the mineral particles rather than reagent availability (Bafghi et al., 2008; Nayl et al., 2011; Ismail et al., 2020).

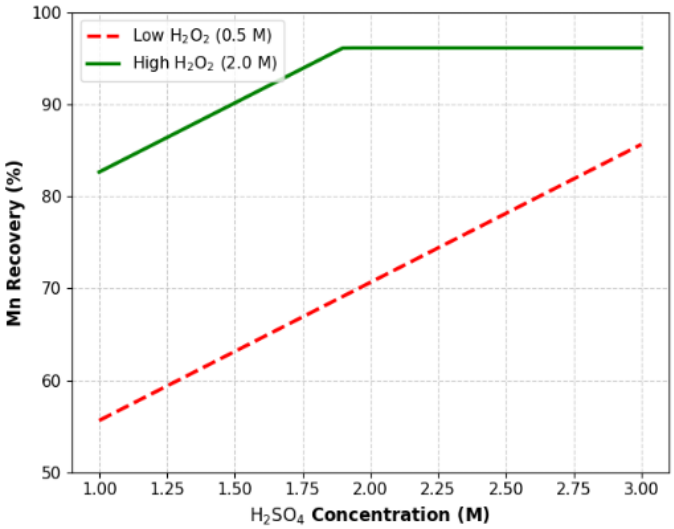

Fig. 6. Interaction effect of H_2SO_4 & H_2O_2 on Mn recovery

From a practical perspective, the observed plateau indicates that excessive reagent consumption would not proportionally increase manganese recovery. Instead, unnecessarily high acid or peroxide dosages would increase reagent costs without providing significant metallurgical benefits. Therefore, optimization through statistical modeling becomes particularly valuable for identifying economically optimal operating conditions rather than merely maximizing extraction efficiency.

3.4.2. Interaction between H_2SO_4 concentration and leaching temperature (X_1, X_3)

The cross-interaction between acidity and reaction temperature shown in Fig. 7 exhibits antagonistic behavior at extreme operating thresholds due to the chemical instability of the reducing agent. At moderate acid concentrations, increasing the temperature from 20°C to around 32-35 °C enhances the kinetic energy of the ions, decreasing solution viscosity and accelerating the reaction rate according to standard thermodynamic principles.

However, when high temperatures (50°C) are coupled with high acid concentrations (3.0 mol/dm³), a noticeable plateau or slight decline in manganese dissolution efficiency is observed. This phenomenon is driven by the rapid, autogenous thermal decomposition of hydrogen peroxide into water and oxygen gas ($2H_2O_2 \rightarrow 2H_2O + O_2$) at elevated temperatures, accelerated by highly acidic environments. This decomposition drastically reduces the net concentration of active H_2O_2 available in the pulp for pyrolusite reduction, explaining why the model-predicted optimum temperature was 32.12 °C.

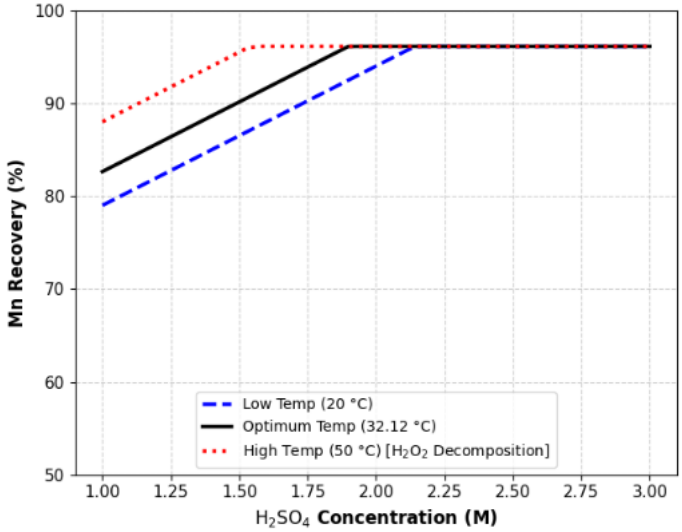

Fig. 7. Interaction between H_2SO_4 concentration and leaching temperature

This phenomenon is primarily attributed to the thermal instability of hydrogen peroxide. As the reaction temperature increases, hydrogen peroxide undergoes accelerated self-decomposition into water and oxygen, thereby decreasing the effective concentration of the reducing agent available for MnO_2 reduction. Consequently, the beneficial kinetic effect associated with increasing temperature is partially offset by the simultaneous loss of reductive capacity. The balance between these two competing mechanisms explains the existence of an optimum operating temperature close to 32 °C rather than at the highest investigated temperature.

This result differs from numerous biomass-assisted reductive leaching systems reported in the literature, where temperatures above 60–90 °C are generally required to obtain comparable manganese recoveries. The present H_2SO_4–H_2O_2 system therefore offers an important energetic advantage by achieving near-complete manganese dissolution under remarkably mild thermal conditions.

3.4.3. Interaction between H_2O_2 concentration and leaching temperature (X_2, X_3)

The interaction between hydrogen peroxide concentration and temperature further confirms the competing influence of reaction kinetics and peroxide stability. At relatively low temperatures, increasing hydrogen peroxide concentration significantly improves manganese recovery owing to the greater availability of reducing species. In contrast, under elevated temperatures, the effectiveness of additional peroxide gradually diminishes because thermal decomposition becomes increasingly dominant. Consequently, the response surface exhibits a characteristic flattening tendency at higher temperatures. Some academic studies also support this finding (Bafghi et al., 2008; Nayl et al., 2011; Ismail et al., 2020).

3.4.4. Interaction between leaching temperature and time (X_3, X_4)

The combined influence of temperature and residence time suggests that the dissolution reaction proceeds rapidly during the initial stages of leaching. Increasing residence time beyond approximately 30 min contributes only marginally to manganese recovery, indicating that chemical equilibrium is approached relatively quickly under the investigated conditions. Therefore, extending the leaching duration would increase process residence time without providing a proportional increase in metal extraction.

3.5. Process optimization and experimental model validation

The optimum operating conditions obtained by numerical optimization in Design-Expert® were as follows:

- H_2SO_4 concentration: 2.97 mol/dm^3
- H_2O_2 concentration: 2.00 mol/dm^3
- Leaching temperature: 32.12^{o}C
- Leaching time: 30 min

Under these optimized conditions, the mathematical model predicted a maximum theoretical manganese extraction yield of 96.12%. To verify this theoretical peak, triplicate validation experiments were performed independently under the same optimized criteria. The empirical experiments yielded an average manganese recovery of 95.86%. The negligible variance (0.26%) between the predicted model value and the actual experimental outcome confirms the extreme fidelity, structural reproducibility, and predictive precision of the optimization model. Results from similar studies and this study are summarized in Table 5.

3.6. Industrial implications

From an industrial perspective, the optimized operating conditions from this study show that high manganese recoveries can be achieved without elevated temperatures or excessive reagent consumption. Such operating conditions may substantially reduce energy demand, improve process economics, and facilitate the industrial utilization of low-grade manganese resources. Moreover, the predictive regression model developed through FCCCD provides a practical decision-support tool for future process scale-up and industrial design.

Compared with roasting-assisted hydrometallurgical routes reported in the literature, which require an additional thermal pre-treatment stage prior to leaching, the present process achieves comparable manganese recovery through direct reductive leaching under relatively mild operating conditions. This reduction in thermal energy demand may improve overall process sustainability and economic feasibility for treating low-grade manganese resources (Tu et al., 2019).

Table 5. Comparison of experimental results with the literature

Study	Ore	Reductant	Temp. (°C)	Recovery (%)	Optimization
Sahoo et al. (2001)	Low-grade pyrolusite	Oxalic acid	85	98.2	-
Nayl et al. (2011)	Rich Pyrolusite (>69%)	H_2O_2	40	>99.4	-
Jiang et al. (2003)	Pyrolusite	H_2O_2	25-60	98.0	-
El Hazek et al. (2006)	Low-grade pyrolusite	HCl-H_2O_2	60-95	>97.0	-
Alaçukur et al. (2020)	Pyrolusite	H_2SO_4–H_2O_2	40	95.0	RSM
Ismail et al. (2004)	Low-grade pyrolusite	H_2SO_4-sawdust	90	90.5	-
Present study	Low-grade pyrolusite	H_2SO_4–H_2O_2	32	95.86	FCCCD

4. Conclusions

In this study, a comprehensive statistical optimization and interaction modeling framework was successfully established for the reductive leaching of low-grade pyrolusite ore from the Karaburun region (İzmir, Türkiye) using a response surface methodology (RSM) approach. The integration of high-intensity wet magnetic separation as a pre-treatment phase effectively upgraded the raw manganese feed from 16.55% to a concentrated grade of 31.24% Mn, significantly reducing the siliceous gangue load before the hydrometallurgical extraction step.

The key findings and structural conclusions derived from this optimization research are outlined below:

- Statistical model performance: A 4-factor, 3-level Face-Centered Central Composite Design (FCCCD) accurately mapped the multi-variable operational landscape of the H_2SO_4 – H_2O_2 – MnO_2 reaction system. The derived second-order polynomial regression model exhibited high statistical reliability, backed by a high coefficient of determination (R^2 = 99.07%) and a non-significant Lack-of-Fit validation (ρ = 0.1124).
- Parametric hierarchy: Rigorous Analysis of Variance (ANOVA) demonstrated that all investigated linear parameters possessed significant control over manganese dissolution. The absolute hierarchy of influence was determined as H_2SO_4 concentration > H_2O_2 concentration > leaching temperature > leaching time.
- Critical interactions: Response surface analysis successfully identified a critical cross-interaction between acid molarity and leaching temperature. While moderate temperatures accelerate reaction kinetics, the coexistence of high acid concentrations (3.0 mol/dm^3) and elevated temperatures (50^{o}C) leads to a notable plateau in recovery due to the autogenous thermal decomposition of the H_2O_2 reducing agent.
- Process optimization: The optimum operating conditions were localized at a H_2SO_4 concentration of 2.97 mol/dm^3, a H_2O_2 concentration of 2.00 mol/dm^3, a mild temperature of 32.12 ^{o}C, and a residence time of 30 min. Under these optimized criteria, the empirical validation trials yielded an exceptional manganese extraction recovery of 95.86%, aligning perfectly with the model's theoretical prediction (96.12%).

In conclusion, this research shows that near-complete manganese extraction from complex, low-grade pyrolusite ores can be achieved under remarkably mild thermal conditions (32.12 ^{o}C) and rapid reaction times (30 min). The low energy requirements and highly predictable nature of the optimized process parameters offer a highly efficient, economically scalable, and environmentally sustainable pathway for designing hydrometallurgical circuits aimed at producing battery-grade manganese precursors from secondary or low-grade mineral resources.

Future studies should investigate the purification of the pregnant leach solution and the subsequent production of battery-grade manganese sulfate monohydrate. Furthermore, pilot-scale validation of the integrated beneficiation–leaching process would provide valuable information regarding its industrial applicability.

Acknowledgments

The authors would like to thank thesis committee members Assoc. Prof. Dr. Yakup Umucu and Prof. Dr. Vedat Deniz for their valuable contributions to this article, which is based on their master's thesis. A part of the results reported in this paper were presented at XX Balkan Mineral Processing Congress BMPC 2026 entitled "Investigation of the beneficiation of manganese ore in the Karaburun region by leaching".

References

ADDAI, E.K., ACQUAH, F., YEBOAH, I., ADDO, A., 2016. *Reductive leaching of blended manganese carbonate and pyrolusite ores in sulphuric acid.* International Journal of Mining and Mineral Engineering, 7(1), 18-36. https://doi.org/10.1504/IJMME.2016.074591.

AKGÖÇMEN, K.E., 2023. *Karaburun bölgesi mangan cevherinin zenginleştirilmesi*. Master's thesis, Eskişehir Osmangazi University, Institute of Science, Eskişehir, Türkiye.

AKGÖÇMEN, K.E., GÜRSOY, Y.H., 2026. *Investigation of the beneficiation of manganese ore in the Karaburun region by leaching*. XX. Balkan Mineral Processing Congress, pp.580-590. 9-11 April 2026. Istanbul–Türkiye.

ALAÇUKUR, A., DEMIRKIRAN, N., & KÜNKÜL, A., 2020. *Optimization and modeling of reductive leaching of pyrolusite ore in H_2SO_4-H_2O_2 media using response surface methodology.* Transactions of Nonferrous Metals Society of China, 30(2), 524-536.

BAFGHI, M.S., ZAKERI, A., GHASEMI, Z., ADELI, M., 2008. *Reductive leaching of manganese dioxide ore in sulfuric acid by hydrogen peroxide.* Chemical Engineering & Technology, 31(11), 1599-1603.

BISWAL, A., MAHAKUD, S., BHUYAN, S., DASH, B., SUBBAIAH, T., JOO, S.S., 2015. *Dissolution kinetics of low grade manganese ore using sucrose as reductant in sulfuric acid medium.* Journal of Industrial and Engineering Chemistry, 28, 103-108.

CHENG, Z., ZHU, G., ZHAO, Y., 2009. *Study in reduction-roast leaching manganese from low-grade manganese dioxide ores using cornstalk as reductant.* Hydrometallurgy, 96(1), 176-179. DOI: 10.1016/j.hydromet.2008.08.004.

DUAN, W., SUN, S., WANG, J., LI, R., 2022. *Comprehensive review of battery-grade manganese production from low-grade ores: Challenges and sustainable hydrometallurgical pathways.* Minerals Engineering, 184, 107642.

EL HAZEK, M.N., LASHEEN, T.A., HELAL, A.S., 2006. *Reductive leaching of manganese from low grade Sinai ore in HCl using H_2O_2 as reductant.* Hydrometallurgy, 84, 187–191.

GÜRSOY, Y.H., 2021. *Düşük tenörlü mangan cevherinin kuru manyetik ayırma yöntemi ile zenginleştirilmesinde tane boyutunun etkisi*. Eskişehir Osmangazi University, Journal of the Faculty of Engineering and Architecture, 29(3): 337-345.

GÜRSOY, Y.H. & AKGÖÇMEN, K.E. 2026. *Investigation of the beneficiation of manganese ore in the Karaburun region by leaching*. XX. Balkan Mineral Processing Congress, 9-11 April 2026, Istanbul–Türkiye.

HAGELSTEIN, K., 2009. *Globally sustainable manganese metal production and use.* Journal of Cleaner Production, 17(15), 1373-1379.

HARIPRASAD, D., MOHAPATRAA, M., ANAND, S., 2013. *Sulphuric acid leaching of low/medıum grade manganese ores using a novel nitrogenous reductant-NH_3 NH_2HSO_4.* Journal of Mining and Metallurgy. Sect. B-Metall. 49(1) B, 97–106.

İNCE, E., 2014. *Düşük tenörlü mangan cevherlerinin zenginleştirilmesinin araştırılması*. Master's Thesis, Çukurova University, Institute of Science.

ISMAIL, A.A., ALI, E.A., IBRAHIM, I.A., AHMED, M.S., 2004. *A comparative study on acid leaching of low grade manganese ore using some industrial wastes as reductant.* Can. J. Chem. Eng., 82, 1296-1300.

ISMAIL, H., SALAMEH, H.A., AL-ZOUBI, H., 2021. *Optimization of manganese leaching from low-grade pyrolusite ore by central composite design.* Mineral Processing and Extractive Metallurgy Review, 42(5), 312-324.

LASHEEN T.A., EL HAZEK M.N., HELAL A.S., 2009. *Kinetics of reductive leaching of manganese oxide ore with molasses in nitric acid solution*. Hydrometallurgy, 98(3–4), 314-317.

MOMADE, F.W.Y., MOMADE, Z.S.G., 1999. *Reductive leaching of manganese oxide ore in aqueous methanol-sulpuric acid medium.* Hydrometallurgy, 51, 103-113.

MONTGOMERY, D. C., 2017. *Design and Analysis of Experiments* (9th ed.). John Wiley & Sons.

MORO, K., HAUBRICH, F., MARTIN, M., 2021. *Preliminary study on the reductive leaching of manganese ores using $FeSO_4$/iron powder as reducing agents under room temperature.* European Journal of Engineering and Technology Research, 6, 14-18. DOI:10.24018/ejeng.2021.6.6.2572.

MYERS, R.H., MONTGOMERY, D.C., ANDERSON-COOK, C.M., 2016. *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*. John Wiley & Sons.

NAYL, A.A., ISMAIL, I.M., ALY, H.F., 2011. *Recovery of pure $MnSO_4.H_2O$ by reductive leaching of manganese from pyrolusite ore by sulfuric acid and hydrogen peroxide.* International Journal of Mineral Processing, 100. 116-123. 10.1016/j.minpro.2011.05.003.

ÖZGEN, S., ARSOY, Z., ERSOY, B., 2020. *Yüksek alan şiddetli manyetik ayırıcı ile manganez cevherinin zenginleştirilmesi.* El-Cezeri Journal of Science and Engineering, 10.31202/ecjse. 723593.

ROGERS, N., MATHESON, E.J., GADD, M., PUFAHL, P.K., WAY, B., 2025. *Manganese ore systems: A Canadian perspective on a critical element in the transition to a sustainable green economy within North America*. FACETS, 10, 1-28.

SAHOO, R.N., NAIK, P.K., DAS, S.C., 2001. *Leaching of manganese from low-grade manganese ore using oxalic acid as reductant in sulphuric acid solution.* Hydrometallurgy, 62(3), 157-163. https://doi.org/10.1016/S0304-386X(01)00196-7.

SINGH, V., CHAKRABORTY, T., TRIPATHY, S.K., 2020. *A review of low grade manganese ore upgradation processes.* Mineral Processing and Extractive Metallurgy, 41(6), 417–438. https://doi.org/10.1080/08827508.2019.1634567

SINHA, M., PURCELL, W., 2019. *Reducing agents in the leaching of manganese ores: A comprehensive review.* Hydrometallurgy, 187. 168-186. DOI:10.1016/j.hydromet.2019.05.021.

SU, H., WEN, Y., WANG, F., SUN, Y., TONG, Z., 2008. *Reductive leaching of manganese from low-grade manganese ore in h2so4 using cane molasses as reductant.* Hydrometallurgy, 93, 136-139.

SUN, C., ZHANG, Y., YANG, Y., SHANG, Q., LIU, Y., CHEN, Q., 2024. *Research on leaching behavior of manganese and ammonia nitrogen in electrolytic manganese residue under oxalic acid/hydrogen peroxide system.* Journal of Water Process Engineering, 63, 105405. https://doi.org/10.1016/j.jwpe.2024.105405.

TIAN, X., WEN, X., YANG, C., LIANG, Y., PI, Z., WANG, Y., 2010. *Reductive leaching of manganese from low-grade manganese dioxide ores using corncob as reductant in sulfuric acid solution*. Hydrometallurgy, 100, 157-160. 10.1016/j.hydromet.2009.11.008

TU, Z., LIANG, X., YANG, X., REN, S., WU, C., WANG, Y., 2019. *Recovery of manganese by roasting-ammonia leaching from low-grade manganese carbonate ores.* R*are Metal Technology*. The Minerals, Metals & Materials Series. Springer, Cham. https://doi.org/10.1007/978-3-030-05740-4_11

ZHANG, W., CHENG, C.Y., 2007. *Manganese metallurgy review. Part I: Leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide.* Hydrometallurgy, 89(3-4), 137-159. https://doi.org/10.1016/j.hydromet.2007.08.010.