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Acid Leaching of Manganese Oxide with Hydrochloric Acid and Willow Bark Using Design Expert Method

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ABSTRACT

Manganese is widely used in various industries, including metal alloys, batteries, pigments, glass, ceramics, and the production of cast iron and stainless steel. Leaching is an essential process in mineral processing, which, according to the Pourbaix diagram, should be carried out under acidic and reducing conditions. Different types of reducing agents have been employed for manganese ore leaching, classified into three main categories: chemical reductants, plant-based reductants, and microorganisms. In this study, a manganese concentrate (MnO: 39.76%) was obtained from the Cheragah Amir Tabriz deposit using a shaking table Device. The X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses of the concentrate showed that the MnO, CaO, and SiO2 contents were 38.9%, 28.9%, and 4.77%, respectively. The major mineral phases identified in the concentrate were pyrolusite, calcite, and silica. Willow bark was used as a natural reducing agent, and hydrochloric acid was applied as a leaching agent. The effects of key process parameters, including hydrochloric acid concentration, reducing agent dosage, leaching time, and temperature, were systematically investigated. Under the optimal conditions—0.5 M hydrochloric acid concentration, 5 g willow bark, 4 hours of leaching time, and a temperature of 75°C—the manganese dissolution efficiency reached 97.06%.

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1. Introduction

Manganese and its compounds are essential in numerous industries, including metallurgy, chemical manufacturing, battery production, and electronics. However, as demand for manganese-based products rises and high-grade manganese ores become scarcer, the processing of low- and medium-grade ores has become increasingly critical [1]. In 2025, manganese is the fifth most consumed metal after iron, aluminum, copper, and zinc [2]. This growing disparity is projected to escalate manganese prices in the future. The depletion of high-quality manganese deposits, driven by rising consumption, has contributed to higher costs for the metal, raw ore, and manganese alloys [3]. Additionally, the intricate mineral composition of low-grade ores poses technical and economic challenges for their efficient extraction and processing. Manganese ores are classified into three grades based on manganese content: high-grade (or metallurgical-grade) ores containing 44–48% manganese, medium-grade ores with 35–44% manganese, and low-grade ores containing less than 35% manganese [4-5].

The extraction of manganese from manganese oxide ore deposits is carried out through pyrometallurgy, hydrometallurgy, and biohydrometallurgy [6]. The conventional thermal treatment method involves roasting manganese oxide minerals with carbon at approximately 700–900°C [7]. Hydrometallurgy offers advantages over pyrometallurgical and biohydrometallurgical processes and has attracted researchers' attention over the years due to its high efficiency and low energy consumption. Since manganese recovery from manganese ore requires the reduction of manganese oxide, the type of reducing agent used in hydrometallurgical processes has become a key factor in the development of such extraction methods. A major advantage of the leaching method is direct reduction, where the reduction and leaching stages occur in a single step. A wide range of reducing agents has been employed for manganese recovery from various types of manganese ores and secondary sources [8-9].

The leaching efficiency of manganese oxide ores depends on several factors, among which the choice of reducing agent plays a pivotal role [10] To achieve cost-effective and high-recovery manganese extraction, researchers have utilized various reducing agents, broadly categorized into three groups: chemical reducing agents [11-12], microorganisms [4; 9; 13-16] and plant-based reducing agents [10, 12, 17-18] among the plant-based reducing agents used for dissolving manganese oxide ores are sawdust [19], sugarcane molasses [9], corn stalks [20], tea waste [21], orange peel [22], and others [11, 13].

In another study, reductive leaching of pyrolusite in a sulfuric acid medium was conducted using orange peel as a reducing agent. A manganese recovery of 98.1% was obtained under optimal conditions of 90°C, 4h, 0.1 M sulfuric acid concentration, and a weight ratio of orange peel to manganese ore of 1.5 [22]. In one study, banana peel was used as a reducing agent in the reductive leaching process of low-grade manganese ore. Under optimal conditions—15% sulfuric acid concentration, 4 g of banana peel, 5 g of ore, a leaching time of 2 hours, and a temperature of 120°C—the highest manganese recovery was achieved [23].

Relatively few studies have been conducted on the leaching of manganese ore using plant-based reducing agents. In the present study, the effective parameters of leaching manganese oxide ore using willow bark were investigated, which has not been addressed in previous research. Willow bark was selected as the reducing agent due to the presence of natural reducing compounds such as proanthocyanidins and antioxidants. Some reports related to wastewater and water treatment have examined the properties of willow bark, which contains reducing compounds [24-25]. These compounds can help reduce manganese oxides and facilitate the reductive leaching process. Hydrochloric acid was used as the leaching agent, and willow bark was employed for the first time as a reducing agent in the reductive leaching of manganese concentrate.

2. Materials and methods

2.1. Sample Preparation

In the leaching experiments, a pyrolusite concentrate was used. After determining the optimal crushing and shaking table conditions, a concentrate with a grade of 38.9% MnO and d80: 180 µm was obtained. The chemical analysis of the concentrate, performed using X-ray fluorescence (XRF), is presented in Table 1. The major impurities in the manganese concentrate were CaO (28.9%) and SiO_2 (4.77%). The mineralogical analysis results (Fig. 1) revealed that the primary minerals in the concentrate were pyrolusite, calcite, and silica. The SEM analysis results in Fig. 2 confirm the presence of minerals constituting the studied ore. The distribution of manganese (Mn), silicon (Si), sulfur (S), and calcium (Ca) elements is shown in Fig. 2.

Table 1. Chemical analysis of the concentrate by XRF.

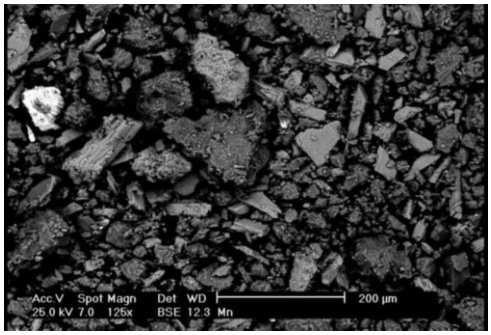
Chemical composition	**MnO**	**CaO**	**SiO_2**	**BaO**
Content(%)	38.9	28.9	4.77	1.16
Chemical composition	**Fe_2O_3**	**SO_3**	**MgO**	**P_2O_5**
Content(%)	0.57	0.48	0.35	0.24

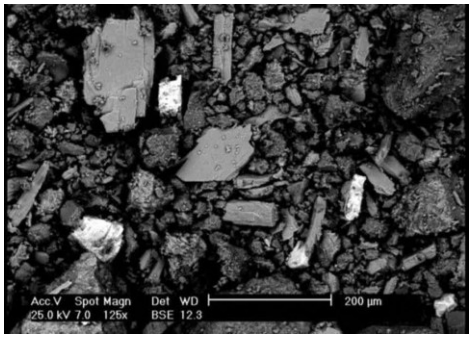
2.2. Materials and Equipment

The chemical composition of the concentrate was characterized using X-ray fluorescence spectroscopy (XRF) with a PHILIPS X'UNIQUE II spectrometer. For mineral phase identification, X-ray diffraction (XRD) analysis was conducted using a PHILIPS Expert Pro diffractometer. Scanning electron microscopy (SEM) studies were carried out, conducted using an XL 30 microscope (Philips). Atomic Absorption Spectroscopy (AAS) was used to determine the dissolution recovery of manganese, employing flame atomic absorption spectroscopy for measuring the concentration of manganese ions (model: AA240FS). For the leaching experiments with willow bark as a reducing agent, a magnetic hot plate stirrer (model: HSD 330, MTOPS) was utilized. Other equipment used throughout the study included thermometers, pH meters, sieves, and related laboratory apparatus. Laboratory-grade sulfuric acid (97–99%) and triple-distilled water were used for the experiments. Willow bark was prepared and ground. It was then dried at room temperature for 24 hours, passed through a 1 mm screen, and used in various quantities for different experiments.

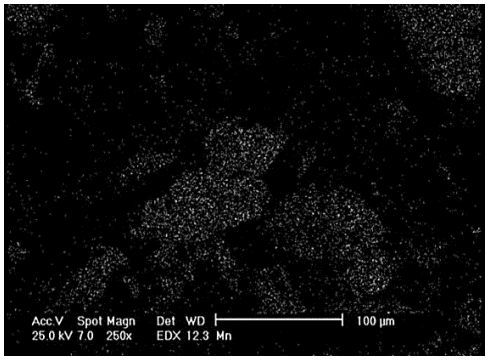
2.3. Method

The leaching experiments were performed using willow bark as a reducing agent to investigate the effects of key parameters, including reaction time, temperature, Hydrochloric acid concentration, and Amount of willow bark. The experimental procedure began with the preparation of a leaching solution by adding Hydrochloric acid to triply distilled water, which was then diluted to a final volume of 250 mL. This solution was transferred to a beaker and heated to the predetermined experimental temperature. Once the target temperature was achieved, 5 g of upgraded manganese concentrate was introduced into the solution. The stirring speed was kept constant at 450 rpm in all experiments. Following a 2-minute equilibration period, the willow bark reducing agent was added to initiate the leaching process, allowing for systematic evaluation of the various parameters under investigation.

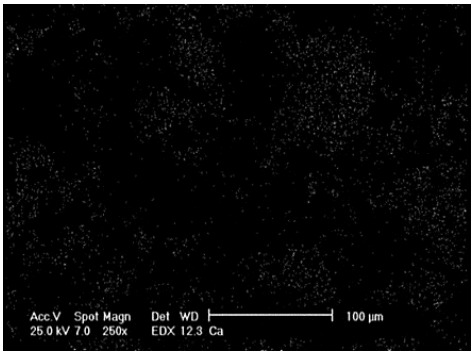




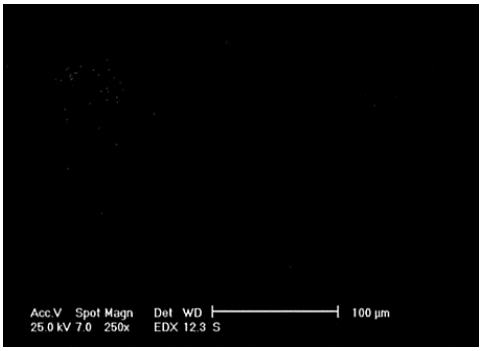
(a) SEM images of the concentrate were obtained



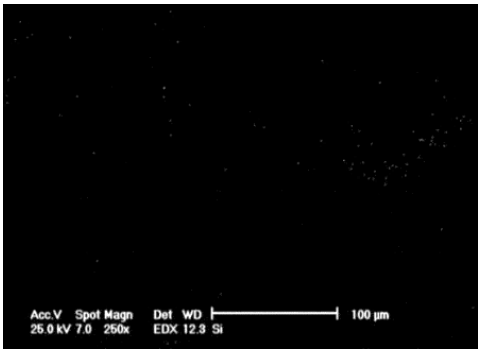
(b) Manganese distribution



(c) Calcium distribution



(d) Sulfur distribution



(e) Silicon distribution

Fig. 1. Results of SEM studies.

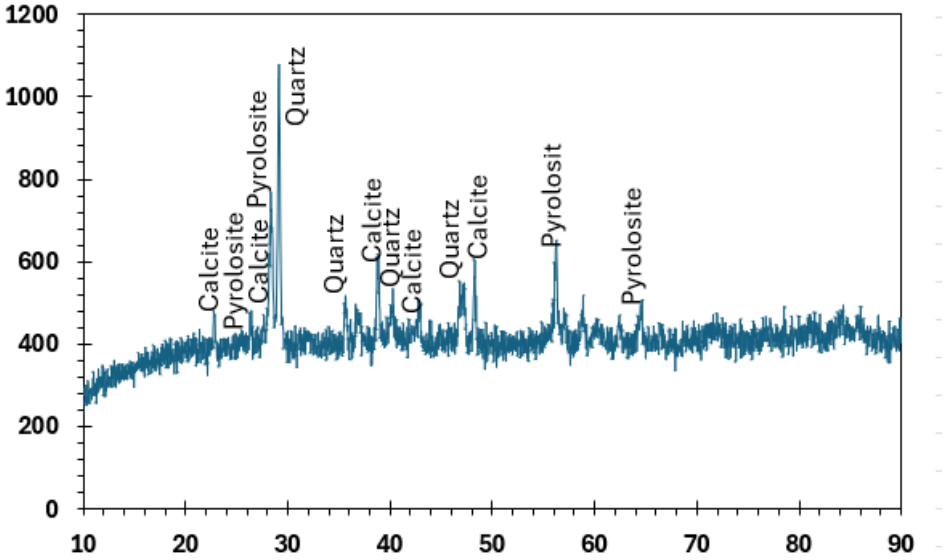


Fig. 2. Mineralogical analysis results by XRD.

3. Result

3.1. Experimental design

Based on previous studies on acidic and reductive leaching of manganese ore using reducing agents such as banana peel, tea waste, corn residues, tree leaves, and others, the important parameters and their ranges have been identified. It is worth noting that several preliminary tests were conducted before designing the main experiments to evaluate the feasibility of the process. Therefore, the effective parameters and their ranges were selected based on these preliminary tests and prior studies. The experimental design was carried out using the Taguchi method, and 16 series of experiments were conducted with different combinations of acid (x_1), reducing agent (x_2), temperature (x_3), and time (x_4). The independent variables and their coded/ actual levels are listed in Table 2.

Table 2. Levels of independent variables in the Taguchi design.

Parameter	Symbol	Taguchi levels			
		Level1	Level2	Level3	Level4
Acid concentration (M)	x_1	0.5	1	1.5	2
Reducing agent (g)	x_2	1.25	2.5	5	10
Temperature (°C)	x_3	30	45	60	75
Time (min)	x_4	30	60	120	240

3.2. Effect of parameters

Table 3 presents the coded/actual values of the parameters and the experimental results. Assuming all variables are measurable, the response can be expressed by Equation (1):

$$y = f(x_1.x_2.x_3.x_4) \quad (1)$$

where y is the output response and x_i represents the input variables. The data from the experiments were entered into Minitab software, and the final regression model for manganese recovery was derived as Equation (2):

$$Y = 42{,}37 + 8{,}23x_1 + 12{,}45x_2 + 5{,}67x_3 + 18{,}32x_4 - 3{,}12x_1x_2 - 2{,}45x_1x_3 - 1{,}78x_1x_4 - 1{,}23x_2x_3 + 0{,}89x_2x_4 + 2{,}34x_3x_4 - 4{,}56{x_1}^2 - 3{,}78{x_2}^2 - 2{,}34{x_3}^2 - 1{,}89{x_4}^2 \quad (2)$$

The regression analysis revealed reaction time as the most influential parameter with a coefficient of 18.32, followed by the reducing agent quantity (coefficient: 12.45), highlighting its crucial role in the leaching process. Optimal conditions achieving maximum recovery (97.06%) were obtained with low acid concentration (0.5 M), moderate reducing agent dosage (5 g), high temperature (75°C), and extended duration (240 minutes). Experiment number 16 was conducted in triplicate to ensure the reliability and reproducibility of the results. All three tests yielded recovery values within a close range, specifically from 94.93% to 97.06%, demonstrating consistent performance and confirming the robustness of the experimental conditions for this particular trial.

The model demonstrated excellent agreement with experimental data, as evidenced by an R^2 value of 0.936 (Table 4), while the highly significant p-value (<0.0001) confirmed the statistical validity of the proposed model.

Table 3. Taguchi experimental design and parameter optimization results.

No	Acid (M)	Reducer (g)	Temp (°C)	Time (min)	Recovery (%)	SNRA1	MEAN1
1	0.5	1.25	30	30	10.68	20.5714	10.68
2	1	2.5	45	30	15.21	23.6426	15.21
3	1.5	5	60	30	18.26	25.2300	18.26
4	2	10	75	30	20.16	26.0898	20.16
5	1	5	30	60	22.21	26.9310	22.21
6	0.5	10	45	60	36.19	31.1718	36.19
7	2	1.25	60	60	28.04	28.9556	28.04
8	1.5	2.5	75	60	39.29	31.8856	39.29
9	1.5	10	30	120	46.23	33.2985	46.23
10	2	5	45	120	40.34	32.1147	40.34
11	0.5	2.5	60	120	32.16	30.1463	32.16
12	1	1.25	75	120	30.24	29.6116	30.24
13	2	2.5	30	240	46.52	33.3528	46.52
14	1.5	1.25	45	240	64.35	36.1710	64.35
15	1	10	60	240	90.54	39.1368	90.54
16	0.5	5	75	240	97.06	39.7408	97.06

Table 4. Parameters of the Taguchi experimental design.

R^2	R^2-adjusted	P-value
0.936	0.853	**0.0001**

Analysis of variance (ANOVA) reveals that reaction time emerges as the most statistically significant parameter affecting the response, with an F-value of 77.59 and an extremely significant p-value < 0.000003. While temperature (p-value = 0.043) and reducing agent quantity (p-value = 0.026) also demonstrate statistically significant effects, their influence is substantially weaker compared to reaction time (Table 5).

Table 5. ANOVA results of the regression model for metal recovery.

Source of Variation	Df	Sum of Squares	Mean Square	F-value	P-value
Regression	4	8437.52	2109.38	22.78529	0.000028
Acid concentration (M)	1	160.06	160.06	1.7291	0.2153
Reducing agent (g)	1	613.24	613.24	6.6243	0.0259
Temperature (°C)	1	481.38	481.38	5.1999	0.0435
Time (min)	1	7182.84	7182.84	77.5904	0.000003
Error	11	1018.31	92.57		
Total	15	9455.83			

Fig. 3 clearly shows that time has the greatest impact on the reductive leaching process. The reducing agent (willow bark) and temperature are other influential factors in the reductive leaching of manganese concentrate. Additionally, acid concentration has the least effect on the leaching process.

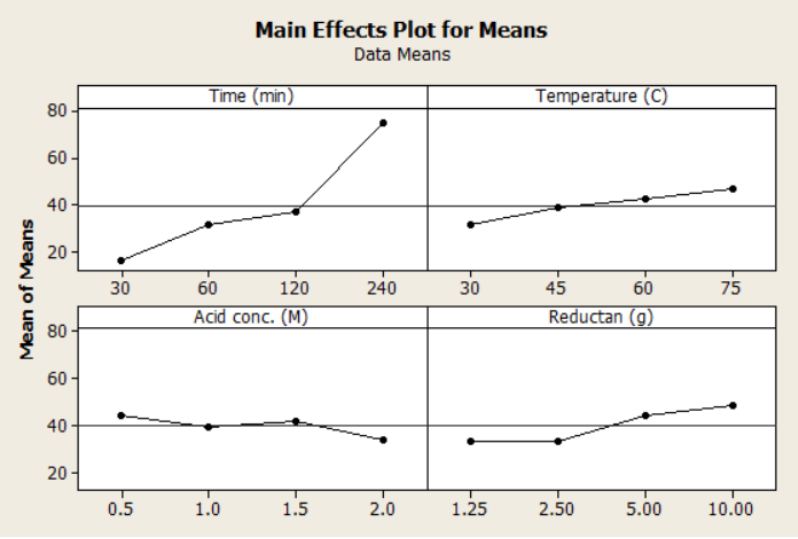


Fig. 3. Effect of factors on manganese recovery.

3.3. Interaction Effects of Parameters

3.3.1. Time-Temperature Effects

Fig. 4 shows that in the low temperature range (30-40°C) and short duration (less than 50 minutes), the system exhibits the lowest recovery efficiency (less than 20%). Increasing the reaction time to 50-100 minutes within the same temperature range improves the recovery to 20-40%. The optimal operational conditions are observed in the temperature range of 55-75°C and duration of 220-240 minutes, which deliver the highest recovery (>80%).

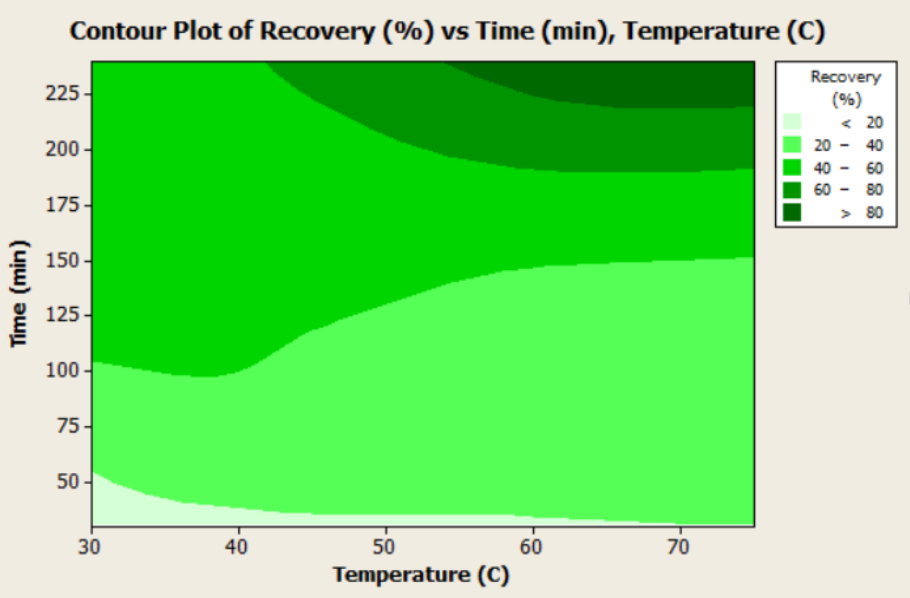


Fig. 4. Investigation of temperature and time effects on manganese recovery.

3.3.2. Interaction Effects of Acid and Time

As shown in Fig. 5, the synergistic relationship between acid concentration and leaching duration significantly influences manganese recovery efficiency. Results from examining different regions indicate that the highest recovery (>80%) is achieved in the acid concentration range of 0.5-1.25 M and reaction time of 220-240 minutes. This optimal range represents conditions where dissolution rate, system stability, and completion of main reactions are in a favorable balance. At low acid concentrations (0.5-1.25 M) and short reaction times (less than 50 minutes), recovery below 20% is observed, primarily due to kinetic limitations and incomplete dissolution reactions. When reaction time is increased to 35-145 minutes, the system achieves 20-40% recovery across a wide range of acid concentrations (0.5-1.75 M). At times above 190 to 220 minutes, recovery is in the range of 40 to 60 percent, and at times above 220 minutes, recovery is above 80 percent.

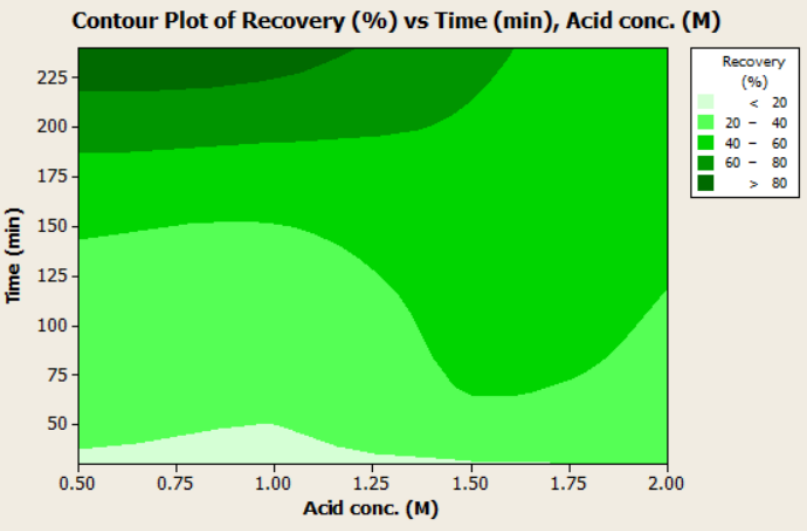


Fig. 5. Effects of acid concentration and time on manganese recovery.

3.3.3. Interaction effects of willow bark and time

Fig. 6 illustrates the interaction between reaction time and reducing agent quantity on manganese extraction efficiency. The results demonstrate that the highest recovery (>80%) is obtained within the range of 4-10 grams of reducing agent combined with a reaction time of 200-240 minutes. Under conditions of short duration (less than 50 minutes) and moderate reducing agent quantities (2-7 grams), recovery remains below 20%, primarily due to incomplete reduction reactions. When the reaction time is extended to 45-170 minutes, the system achieves recovery of 20-40% across a broad range of reducing agent quantities (1-10 grams). From an operational perspective, these findings indicate that the optimal reducing agent quantity falls within the range of 4-7 grams, with a minimum required reaction time of 200 minutes to achieve desirable recovery.

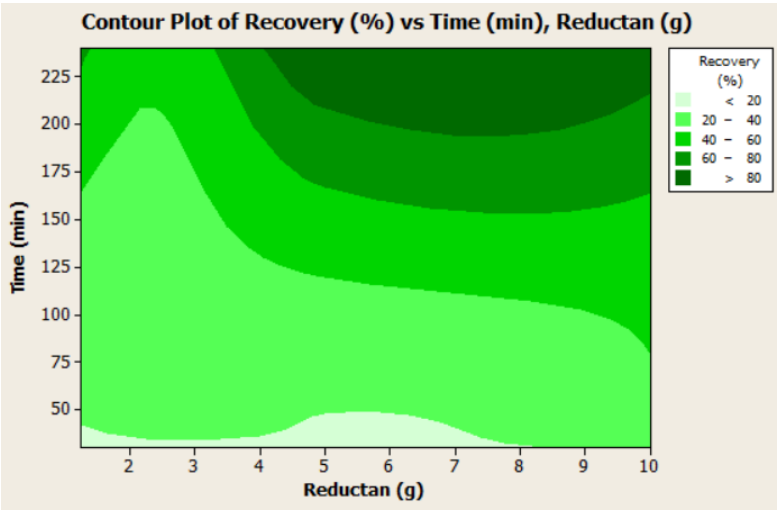


Fig. 6. Investigation of reducing agent concentration and time effects on manganese recovery.

3.3.4. Interaction effects of acid concentration and temperature

Fig. 7 illustrates the interdependent effects of acid concentration and temperature on manganese extraction recovery. The results indicate that the highest recovery (>80%) is achieved within the acid concentration range of 0.75-1 M combined with temperatures of 55-65°C. Under conditions of low acid concentration (0.5-1 M) and reduced temperatures (30-45°C), recovery remains below 20%, primarily due to insufficient activation energy to overcome the reaction's thermodynamic barrier. With gradually increasing the temperature to the range of 45-75°C, the recovery of manganese dissolution reaches 20-60% in a wide range of acid concentrations (0.5-2 M).

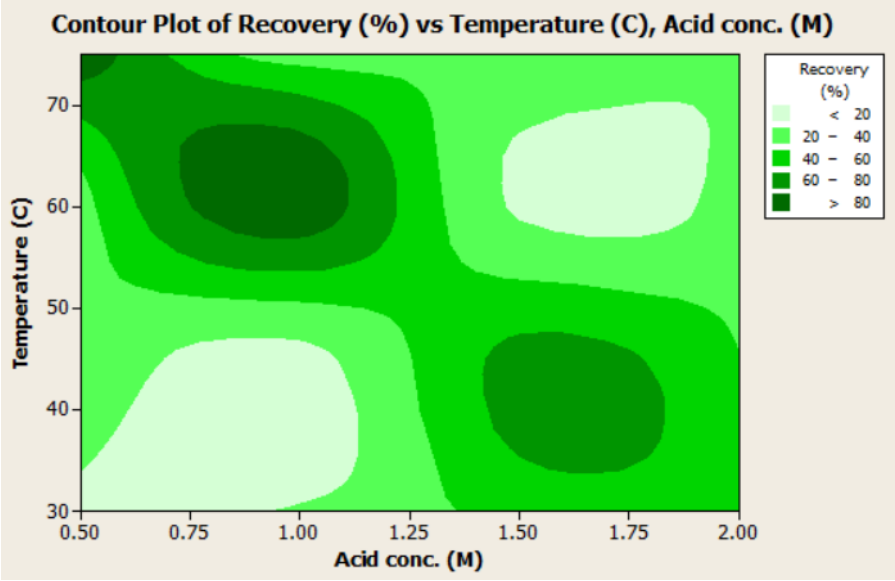


Fig. 7. Investigation of acid concentration and temperature effects on manganese recovery.

3.3.5. Interaction effects of willow bark and temperature

Fig. 8 shows the interaction effect of willow bark content and temperature on manganese recovery. The results from the study of different areas indicate that the highest recovery (>80%) is achieved in two specific ranges of reducing agent content of 4-8 g at 75 °C and 10 g at 60-65 °C. At low reducing agent content (2-5 g) and medium temperatures (40-65 °C), recovery is less than 40%, which is due to the limitation in the formation of active manganese complexes [12; 20; 22; 23] With a gradual increase in reducing agent content to the range of 5-10 g and temperature to 65-75 °C, the recovery increases to 60-80%. The results show that a temperature of 75°C with 4 to 8 grams of willow bark is the optimal leaching condition for manganese concentrate in terms of recovery.

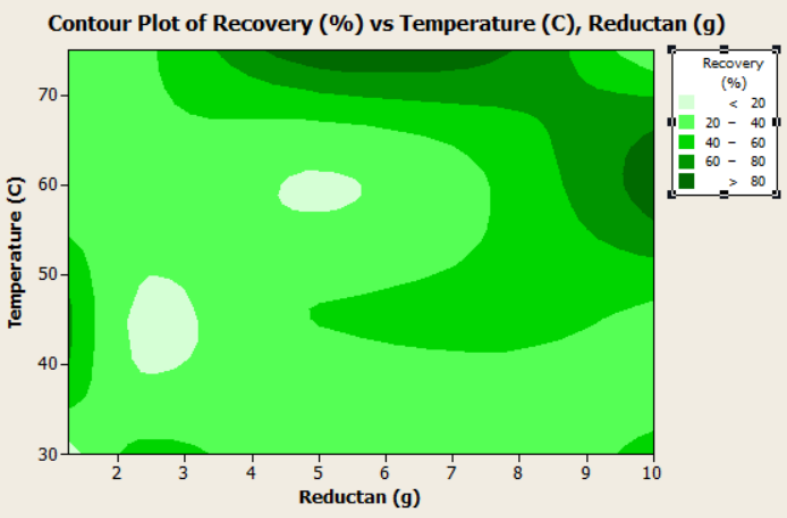


Fig. 8. Investigation of reducing agent quantity and temperature effects on manganese recovery.

3.3.6. Interaction effects of willow bark and acid concentration

Fig. 9 shows the interaction of reducing agent amount and acid concentration on manganese extraction recovery. The results from the different regions indicate that the highest recovery (>80%) is achieved in two distinct ranges: reducing agent amount of 4.5-5.8 g with very low acid concentration (0.5-0.6 M) and high reducing agent amount (5.9-10 g) with moderate acid concentration (0.75-1 M). In the low ranges of both parameters (1-6 g reducing agent and 0.5-1.25 M acid), recovery is less than 20%. With a gradual increase in acid concentration to the range of 0.75-2 M and reducing agent amount to 1-10 g, recovery increases to 20-40%.

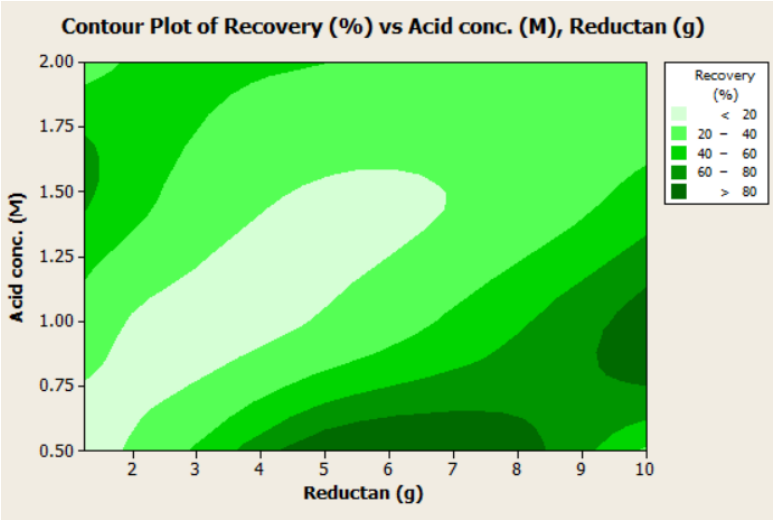


Fig. 9. Investigation of reducing agent quantity and acid concentration effects on manganese recovery.

4. Discussion

Compared to previous studies that employed plant-based reductants such as orange peel and banana peel, the present study introduces willow bark as a novel and effective reducing agent for the reductive leaching of manganese concentrate. While previous methods reported manganese recovery rates of 98.1% (using orange peel) and high yields with banana peel under more severe conditions (e.g., 120°C, high acid concentration), the current study achieved a comparable recovery rate of 97.06% under milder conditions (75°C and 0.5 M HCl). This demonstrates the potential of willow bark not only in terms of effectiveness but also in terms of lower energy and chemical consumption.

From an environmental perspective, the use of naturally abundant and biodegradable materials such as willow bark may reduce the environmental footprint of the leaching process compared to conventional synthetic reducing agents. Regarding scalability, willow bark is a renewable biomass resource available in many regions, suggesting that this method can be scaled up for industrial applications with further optimization and supply chain considerations.

The use of willow bark as a plant-based reductant is a more environmentally sustainable approach compared to synthetic chemical reductants and can help reduce the consumption of chemicals and the generation of hazardous waste. However, the use of hydrochloric acid still poses challenges regarding safety and environmental pollution, which must be controlled through appropriate treatment and management systems.

5. Conclusion

The use of low-grade manganese resources is very important, considering the exhaustion of high-grade manganese mines and the existence of low-grade manganese mines in the country. In the present study, a concentrate with a grade of approximately 40% MnO was prepared from a feed with a grade of 13% MnO using gravity methods. The results of XRF, XRD, and SEM studies show that pyrolusite, calcite, quartz, and barite are the main minerals constituting the concentrate. In the present study, hydrochloric acid was used as a dissolving agent, and willow bark was used as a reducing agent in the manganese ore leaching process. The parameters of time and hydrochloric acid concentration had the greatest and least effect on the reductive leaching process, respectively. Manganese dissolution of 97.06% was achieved under optimal leaching conditions at a half-molar concentration of hydrochloric acid, reaction time of 4 hours, reaction temperature of 75°C, and amount of 5 grams of willow bark. The use of new plant-based reductants instead of chemical reductants in the manganese ore leaching process, the investigation of associated elements with manganese during leaching, the examination of environmental issues related to the leaching of manganese ore using plant-based reductants, and a detailed study of the mechanisms involved in the process could be proposed as future research directions.

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Ethical Considerations

The authors avoided data fabrication, falsification, and plagiarism, and any form of misconduct.

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Conflict of Interest

The authors declare no conflict of interest.

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