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A Novel Two-Stage Method of Co-Leaching of Manganese–Silver Ore and Silver-Bearing Pyrite Based on Successive Chemical and Bio Treatments: Optimization and Mechanism Study

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Abstract: In this work, bio-hydrometallurgy technology was employed and a novel two-stage method based on successive chemical and bio treatments was proposed to collaboratively utilize manganese–silver ore and silver-bearing pyrite. In the optimization research of the chemical leaching stage, the sensitive factors for the Mn leaching efficiency were screened by Plackett–Burman design, and central compound design was performed to settle the optimized parameters. A mixed strain of bacteria containing *Sulfobacillus thermosulfidooxidans, At. caldus* and *Leptospirillum ferrooxidans* was applied in the bioleaching stage. A conventional cyanidation process carried out with the Mn leaching residuals suggested an efficient recovery of Ag. Applying a two-stage method with 284.94 kg/t silverbearing pyrite addition and 277.44 kg/t sulfuric acid consumption with a temperature at 77.73 °C and stirring speed at 287.76 rpm. Mineral behaviors were investigated with XRD and SEM/EDS analysis, and it was revealed that the oxidation of sulfur is the crux in reducing the usage of reagents, and the presence of leaching bacteria enhanced the oxidation efficiently. Through optimization and mechanism study, this paper provides an opportunity to co-leach the manganese–silver ore and silver-bearing pyrite process in a more economical and environmental way.

Keywords: manganese–silver ore; silver-bearing pyrite; bio-hydrometallurgy technology; co-leaching; optimization; sulfur element bio-oxidation

1. Introduction

As crucial resources of manganese and silver, manganese–silver ore and silver-bearing pyrite occupy an irreplaceable position in the manganese and silver industries [1–3]. With the increasing demands for manganese and silver, more attention has been focused on the novel processing method for the refractory raw materials. Manganese–silver ore [4] is a typical refractory raw material resource with pyrolusite (MnO₂) and psilomelane ((Ba,H₂O)₂Mn₅O₁₀), the most common manganese and silver-bearing minerals. However, due to the complicated mineral structures, low silver–manganese grades, complex occurrence states of silver, small granularity of valuable minerals and high contents of harmful impurities and gangue minerals, it is often faced with economic and environmental challenges when applying the traditional recovery technologies to manganese–silver ores [5–7].

In recent years, with the continuous decrease of ore grade and the increasing demand for the recovery of other associated valuable metals, the combined process of multiple metallurgical technologies has been employed much more commonly [8]. The major applied



Citation: Sun, J.; Shang, H.; Zhang, Q.; Liu, X.; Cai, L.; Wen, J.; Yang, H. A Novel Two-Stage Method of Co-Leaching of Manganese–Silver Ore and Silver-Bearing Pyrite Based on Successive Chemical and Bio Treatments: Optimization and Mechanism Study. *Metals* **2023**, *13*, 438. https://doi.org/10.3390/ met13020438

Academic Editors: Jean François Blais and Daniel Assumpcao Bertuol

Received: 12 December 2022 Revised: 1 February 2023 Accepted: 16 February 2023 Published: 20 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). metallurgical processes in the treatment of manganese–silver concentrate are pyrometallurgy and hydrometallurgy, determined according to the properties of raw materials and target products. Pyrometallurgy [9] was used to produce MnSO₄, with the mature technology of a reduction-roasting sulfuric acid leaching process. However, with the increase demand of environmental protection, hydrometallurgy is much more favored with advantages in relieving the pressure of carbon emission and air pollution [10]. The reduction leaching process is the most mature and widely used hydrometallurgy technology as many reducing reagents such as iron powder, pyrite, sulfur dioxide, sodium sulfite and other reducing substances could be applied in this process [11]. Among them, the "two-ores method" [12] using pyrite as the reducing reagent is the most economical technology. The major reactions in the "two-ores method" process are shown as Equations (1)–(5) [13].

$$15MnO_2 + 2FeS_2 + 14H_2SO_4 \rightarrow 15MnSO_4 + Fe_2(SO_4)_3 + 14H_2O$$
(1)

$$3MnO_2 + 2FeS_2 + 6H_2SO_4 \rightarrow 3MnSO_4 + Fe_2(SO_4)_3 + 6H_2O + 4S$$
 (2)

$$2Fe^{3+} + FeS_2 \rightarrow 3Fe^{2+} + 2S \tag{3}$$

$$2Fe^{2+} + MnO_2 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$$
(4)

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \tag{5}$$

However, despite a tremendous amount of research and application work that has been carried out [14–16], the "two-ores method" still faces the problems of environmental pollution, large reagent consumption and high energy consumption. Crucially, the low grade of manganese–silver ore is cutting down the economic benefits of the "two-ores method" operating process. Additionally, with the overexploitation of high-grade ore and the decline in the discovery of new deposits, the eco-friendly treatment process for low-grade manganese–silver ore is of increasing importance.

Since its advent, bio-hydrometallurgy technology [17] has played an indispensable role in the clean processing of complex low-grade mineral resources. In particular, the bioleaching of uranium, copper, gold, nickel and cobalt has achieved extraordinary ecological and economic benefits. Thus, with the advantages of low energy consumption, less waste residue and applicability for low-grade ore [18], bio-hydrometallurgy technology has attracted researchers to constantly make efforts to broaden its application. Despite the shortage of insufficient bioleaching reaction rates, bio-hydrometallurgy technology is still successfully applied in the large-scale metallurgical industry, especially in the preoxidation of gold-bearing pyrite [19]. The bio-oxidation technology [20] mostly applies Leptospirillum thermoperoxidans, Acidthiobacillus caldus, Sulfobacillus and other moderate thermophilic bacteria to oxidize pyrite containing gold and silver. The bio-oxidation operation temperature is about 40~50 °C, and the pulp pH is about 1.0~1.5. Under extreme conditions, the pH may be even lower than 1.0 caused by sulfuric acid generation in the bio-oxidation of pyrite [21]. The major biological reactions in the bioleaching process are shown in Equations (6) and (7). The bioleaching microorganisms could also accelerate the reaction rate of Equations (3) and (5), promoting the decomposition of pyrite.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \tag{6}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$
(7)

This research aims to improve the "two-ores method" and develop a novel method of two-stage co-leaching for the collaborative utilization of manganese–silver ore and silver-bearing pyrite. The bioleaching microorganisms were employed to accelerate the dissolution of pyrite, producing sulfuric acid to reduce the additional amount of sulfuric acid in the reduction process of manganese–silver ore. Response surface methodology (RSM) [22] with the Plackett–Burman design (PBD) [23] and central compound design (CCD) [24] were used to determine the sensitive factors and establish the optimum leaching parameters. ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer), XRD (X-ray Diffraction), SEM (Scanning Electron Microscope) and EDS (Energy Dispersive Spectroscopy) were used to reveal the mechanism for the decomposition and dissolution of manganese–silver ore and silver-bearing pyrite during co-leaching. Our work focuses on the optimization of leaching parameters and the bioleaching behaviors of both manganese–silver ore and silver-bearing pyrite, providing new technical ideas and theoretical foundations for the efficient and clean utilization of low-grade manganese–silver ores and silver-bearing pyrite.

2. Materials and Methods

2.1. Minerals and Bacteria

The original manganese–silver ore used in this study was collected from La Yesca, Nayarit, Mexico, provided by Silvercop Metals Inc. Other minerals were removed through magnetic and flotation separation. Multi-element analysis indicated that the manganese–silver concentrate contains 25.22% of Mn, 24.30% of Fe, 0.083% of S, 0.24% of Cu, 0.072% of C, 3.05% of Zn and 869.90 g/t of Ag. The flotation reagents were removed, and the manganese–silver concentrate samples were dried and ground evenly into different fineness.

The purified silver-bearing pyrite used in this study was provided by Silvercop Metals Inc. Multi-element analysis indicated that the manganese–silver concentrate contains 0.28% of Mn, 46.83% of Fe, 39.59% of S, 0.24% of Cu, 0.56% of Zn, 0.14 g/t of Au and 61.40 g/t of Ag. The flotation reagents were removed, and the silver-bearing pyrite samples were dried and ground to fine powder guaranteeing that the particle size was less than 0.074 mm.

The mixed strain of bacteria applied in this study was obtained from the National Engineering Research Center for Environment-friendly Metallurgy in Producing Premium Non-ferrous Metals in Beijing, China. The strain mainly contains *Sulfobacillus thermosulfidooxidans* (50.17%), *At. caldus* (33.71%) and *Leptospirillum ferrooxidans* (16.12%). The leaching bacteria were cultured in a modified culture medium, which contains 3 g (NH₄)₂SO₄, 0.50 g K₂HPO₄, 0.10 g KCl, 0.01 g Ca(NO₃)₂, 2 g FeSO₄·7H₂O, 0.1 g sulfur and 10 g pyrite per liter. The pH value was adjusted to 2.00 with 0.1 M H₂SO₄.

2.2. Chemical Leaching Experiments

The optimum chemical leaching parameters for manganese-silver concentrate and silver-bearing pyrite were determined by the single factor test method, Plackett-Burman experimental design and standard response surface methodology design based on central composite design. The amount of silver-bearing pyrite addition, the amount of sulfuric acid addition, temperature, the particle size of manganese-silver concentrate, pulp density, Fe(III) concentration, stirring speed and leaching time [25] were chosen as the impactor factors in the single factor text and the Plackett–Burman experiment. The factors and their levels used in the single factor test are shown in Table 1. The levels of factors used in the Plackett–Burman experiments are determined by the results of the single factor test. The factors and their levels used in the RSM study are determined by the results of the Plackett-Burman experiments. The chemical experiments were carried out in a 500 mL stirring tank with the temperature controlled by an Electro-Thermostatic Water Bath. A 200 mL solution with certain concentrations of manganese-silver concentrate, silver-bearing pyrite and sulfuric acid was added to the 500 mL stirring tank. Before experiments, the manganese– silver concentrate and silver-bearing pyrite samples were sprayed with 95% ethanol and exposed to ultraviolet light for 24 h to avoid the influence of native microorganisms in the ore samples. Other leaching parameters were set at the required point. Mn leaching efficiency was assigned as the response of this leaching system in the PBD and CCD studies. The amount of silver-bearing pyrite addition, the amount of sulfuric acid addition and pulp density were calculated according to Formulas (8)~(10).

$$X = C_1 / C_2 \tag{8}$$

$$Y = C_3 / C_2 \tag{9}$$

$$Z = 100 \times C_4 / (C_4 + C_5) \tag{10}$$

where X is the amount of silver-bearing pyrite addition (kg/t); Y is the amount of sulfuric acid addition (kg/t); Z is the pulp density (wt%); C₁ is the mass of silver-bearing pyrite (g); C₂ is the mass of manganese–silver concentrate (g); C₃ is the mass of added sulfuric acid (g); C₄ is the mass of ore (g); C₅ is the mass of solution (g).

Table 1. The factors and their levels used in the single factor test.

Factors	Level 1	Level 2	Level 3	Level 4	Level 5
Amount of silver-bearing pyrite addition (kg/t)	100	200	300	400	500
Amount of sulfuric acid addition (kg/t)	100	200	300	400	500
Temperature (°C)	30	45	60	75	90
Particle size of					
manganese-silver concentrate	40%	50%	60%	70%	80%
$(-74 \ \mu m \ content \ account)$					
Pulp density/wt%	10	15	20	25	30
Fe(III) concentration (g/L)	0	1	2	3	4
Stirring speed (rpm)	100	200	300	400	500
Leaching time (h)	1	2	3	4	5

2.3. Bioleaching Experiments

The selected chemical leaching residues used in the bioleaching tests were washed using sterilized ultra-pure deionized water and dried at room temperature before bioleaching. The bioleaching tests were carried out using a pH-stat batch stirred tank reacting system, as shown in Figure 1. An amount of 50 g of chemical leaching residues was put into a 400 mL boiling flask containing 200 mL ultrapure deionized water. The pH of the solution in the tank is monitored by a computer connected to a pH meter. The computer controlled one peristaltic pump. The pH of the leaching system was maintained at a set range of below 2.00 by adding 5% (vol/vol) H_2SO_4 . The stirring speed was set at 150 rpm and the temperature was maintained at 45 °C by an Electro-Thermostatic Water Bath. The leaching bacteria were subjected to centrifuge at the logarithmic growth stage to avoid the interference of introducing ions. Before innovation, the bacterial cell concentration of cultured bacterial fluid was determined by direct microscopic count using a Helber Bacteria Z30000 bacteria counting chamber (Thoma, UK). To maintain an initial bacteria density of 2×10^7 cells/mL, the supernatant fluid of a certain volume was centrifuged and washed into the bioleaching tank. The initial bacteria density was 2×10^7 cells/mL. Throughout the experiments, the evaporated water was compensated with sterilized ultra-pure water based on weight loss at one-day intervals. The bioleaching experiments were performed for 4 days. Samples of 5 mL were taken at one-day intervals for chemical analysis. Then, the residue samples were taken for XRD and SEM/EDS analysis.



Figure 1. pH-stat batch stirred tank reacting system.

2.4. Cyanidation Tests

The selected samples were filtered and washed several times with de-ionized water. The cyanide leaching experiment was carried out in an agitated reactor for 24 h with 20 kg/t sodium cyanide addition. Samples were leached at a pulp density of 40 wt% with pH value adjusted at 11 using calcium oxide.

2.5. Analysis Methods

The concentration of Mn and Ag in the leachate and residual was detected by ICP-OES (725-Agilent Technologies, Santa Clara, CA, USA) to calculate the leaching efficiency of manganese and silver, and samples were analyzed after total digestion. The pH values in the slurries were measured using an FE-20 pH meter (METTLER TOLEDO, Columbus, OH, USA). The Eh values in the slurries were measured using a Pt electrode with an Ag/AgCl reference electrode. Leached samples were characterized by X-ray diffraction (XRD). SEM/EDS JSM-6510 was used to observe the leached samples.

2.6. Chemicals

All chemicals were of analytical reagent grade from Beijing Chemical Reagents Corporation and used without further purification. Ultrapure deionized water was used throughout the experiment.

3. Results and Discussion

3.1. Single Factor Test

The effects of the parameters of the amount of silver-bearing pyrite addition, the amount of sulfuric acid addition, the temperature, the particle size of manganese–silver concentrate, pulp density, Fe(III) concentration, stirring speed and leaching time on the leaching efficiency of manganese was investigated via single factor test with other experimental conditions set at the best or second best point. The changes in Mn leaching efficiency are shown in Figure 2.



Figure 2. Changes in Mn leaching efficiency with amount of silver-bearing pyrite addition (**a**), amount of sulfuric acid addition (**b**), temperature (**c**), particle size of manganese–silver concentrate (**d**), pulp density (**e**), Fe(III) concentration (**f**), stirring speed (**h**) and leaching time (**g**).

As shown in Figure 2, the best amount of silver-bearing pyrite addition is 500 kg/t with a Mn leaching efficiency of 97.84%, the best amount of sulfuric acid addition is 500 kg/t with a Mn leaching efficiency of 99.11%, the best reaction temperature is 90 °C with a Mn leaching efficiency of 99.01%, the best particle size of manganese–silver concentrate is 80% less than 74 μ m with a Mn leaching efficiency of 99.29%, the best pulp density is 25 wt% with a Mn leaching efficiency of 98.19%, the best Fe(III) concentration is 4 g/L with a Mn leaching efficiency of 97.21%, the best stirring speed is 500 rpm with a Mn leaching efficiency of 97.94%. The leaching efficiency of manganese is significantly enlarged with the increase of the amount of silver-bearing pyrite addition, amount of sulfuric acid addition, temperature, stirring speed and leaching time. Within the experimental research scope, the amount of

silver-bearing pyrite addition, the amount of sulfuric acid addition, temperature, stirring speed and leaching time had a greater influence on the leaching efficiency of manganese compared with the particle size of manganese–silver concentrate, pulp density and Fe(III) concentration. The reaction between manganese–silver concentrate, silver-bearing pyrite and sulfuric acid involves two solid phases and one liquid phase with effective contact [26] among reactants determining the rate and efficiency of manganese dissolution. Therefore, the leaching rate and efficiency of manganese are highly-related to the reactant concentration, pulp density and stirring speed. Moreover, the particle size has a slight influence on the leaching reaction as a small particle size is beneficial for the dissolution of metal ions.

3.2. Plackett–Burman Design

The Plackett–Burman design (PBD) was employed to screen out and evaluate the relative importance of factors on the Mn leaching efficiency. The studied factors were selected based on the results of the single factor test and the Plackett–Burman design, and the values are shown in Table 2. The contribution of different variation factors for Mn leaching efficiency was screened and shown in Table 3. A large gap ranging from 12.31% to 67.45% suggested that various factors with different levels had a significant influence on the leaching efficiency of Manganese. The estimated effects of eight parameters via the Plackett–Burman design on Mn leaching efficiency are summarized in Figure 3.

Table 2. Experimental parameters in t	wo levels designed by Placket	t–Burman design model.
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Factors	Symbol Code	Plackett–Burma Lower	n Design Values Higher
Amount of silver-bearing pyrite addition (kg/t)	а	100	500
Amount of sulfuric acid addition (kg/t)	b	100	500
Temperature (°C)	с	30	90
Particle size of manganese–silver concentrate $(-74 \ \mu m \text{ content} account)$	d	40%	80%
Pulp density/wt%	e	10	30
Fe(III) concentration (g/L)	f	0	4
Stirring speed (rpm) Leaching time (h)	g h	100 1	500 5

Table 3. Twelve-trial Plackett–Burman design matrix for eight parameters with actual values along with observed Mn leaching efficiency.

Run	Amount of Silver- Bearing Pyrite Addition (kg/t)	Amount of Sulfuric Acid Addition (kg/t)	Temperature (°C)	Particle Size of Manganese– Silver Concentrate (–0.074 mm Content Account%)	Pulp Density (%)	Fe(III) Concentration (g/L)	Stirring Speed (rpm)	Leaching Time (h)	Mn Leaching Efficiency (%)
1	500	100	90	80	30	0	100	1	39.7
2	100	100	90	40	30	4	100	5	32.6
3	100	100	30	40	10	0	100	1	12.3
4	500	500	30	40	10	4	100	5	37.7
5	100	100	30	80	10	4	500	1	19.4
6	100	500	90	80	10	0	100	5	43.8
7	500	500	90	40	10	0	500	1	59.4
8	500	500	30	80	30	4	100	1	46.6
9	500	100	30	40	30	0	500	5	41.9
10	500	100	90	80	10	4	500	5	67.5
11	100	500	90	40	30	4	500	1	54.1
12	100	500	30	80	30	0	500	5	47.8



Figure 3. Estimated effects of eight parameters via Plackett–Burman design on Mn leaching efficiency.

According to Figure 3, all the factors had a positive effect on the leaching efficiency of manganese. The results suggested that the amount of silver-bearing pyrite addition, the amount of sulfuric acid addition, temperature and stirring speed have relative significant for Mn leaching efficiency while the particle size of manganese–silver concentrate, pulp density, Fe(III) concentration and leaching time showed less influence.

As the reducing agent, silver-bearing pyrite showed a significant effect on the decomposition of manganese-silver concentrate, promoting reactions in Equations (1) and (2). At the same time, the total amount of Fe^{2+} ions released from pyrite increased with the increase of the addition amount of silver-bearing pyrite, which accelerated the reaction shown in Equation (4). Sulfuric acid is also a critical reagent in the reductive leaching of manganese oxide mineral, providing an acidic environment for manganese-silver concentrate and silver-bearing pyrite. Particularly, the effect of temperature was clearly more critical in terms of manganese dissolution kinetics. This can be explained by the fact that the determining step for Mn dissolution is reaction rate k—as previously reported in the literature [27]—and is strongly related to temperature via the Arrhenius equation [28]. In addition, the effect of stirring speed was also found to be substantial as the efficient reaction relied on sufficient contact between manganese-silver concentrate, silver-bearing pyrite and sulfuric acid. Conversely, leaching time shows less effect than other factors, even though a remarkable promotion was observed in Figure 2h. As suggested in Figures 2 and 3, employing Fe(III) and fine grinding will also benefit the manganese dissolution. However, due to the increasing energy consumption and amount of leaching residual, the over-grinding and Fe(III) addition may not be economical and eco-friendly. The results summarized in Figures 2 and 3 also reveal that the minimal increase of Mn leaching efficiency was achieved with the increase of pulp density, and a slight influence was observed.

3.3. Chemical Leaching Parameter Optimization Using CCD

According to Equations (3), (5) and (6), as the major reaction reagents, ferrous ion and sulfuric acid can be generated from the dissolution and oxidation of pyrite. Afterward, the generation of sulfuric acid from pyrite increases the concentration of sulfuric acid in the pulp, contributing to the decomposition of manganese–silver concentrate and reducing the amount of added sulfuric acid. Additionally, it is also worth noting that the increase of temperature will accelerate the process of pyrite oxidation and manganese– silver concentrate decomposition, which are acid generation and the consumption process, respectively. The above discussions indicate that the interactive effects may exist in the reaction among manganese–silver concentrate, silver-bearing pyrite and sulfuric acid. With the aim of investigating the main and interactive effects, the leaching tests were accompanied by the central compound design (CCD), which is based on response surface processes. Through RSM study, the regression model equations were adjusted and interactions were improved via designing a surface response with five levels and six central points in order to conclude the greatest factors for the Mn leaching efficiency. From the final results of PBD, the amount of silver-bearing pyrite addition, the amount of sulfuric acid addition, temperature and stirring speed were carefully considered as four substantial factors for further CCD optimization study.

Experiments were completed to scrutinize the combined effect of four parameters on the Mn leaching efficiency. The Design Expert software 12 was used to determine the second-order polynomial coefficients for each term of the equation through multipleregression analysis. The 30 runs with suggested parameters and the experimental value of Mn leaching efficiency are shown in Table 4. All levels such as independent factors, interactions and linear relationships affecting the sensitive factors are shown in Table 5. It is revealed that the effects of factors on Mn leaching efficiency at a quadratic level were shown to be highly significant.

Table 4. Central composite design values for different experimental parameters.

Run	A: Amount of Silver-Bearing Pyrite Addition (kg/t)	B: Amount of Sulfuric Acid Addition (kg/t)	C: Temperature (°C)	D: Stirring Speed (rpm)	Y: Mn Leaching Efficiency (%)
1	300	300	90	300	80.4
2	200	200	75	200	38.8
3	400	400	75	200	85.7
4	300	300	30	300	31.5
5	300	500	60	300	66.1
6	200	400	75	200	55.8
7	300	300	60	500	59.9
8	300	100	60	300	33.2
9	300	300	60	300	60.4
10	200	400	45	200	27.3
11	200	200	75	400	45.0
12	400	400	45	400	48.5
13	500	300	60	300	67.3
14	400	200	45	200	29.1
15	300	300	60	300	57.4
16	200	400	45	400	31.6
17	300	300	60	300	58.7
18	400	400	75	400	99.2
19	200	200	45	400	22.0
20	400	200	75	200	59.6
21	400	200	75	400	69.0
22	200	400	75	400	64.7
23	300	300	60	100	19.0
24	400	200	45	400	33.7
25	200	200	45	200	19.0
26	300	300	60	300	59.2
27	300	300	60	300	59.4
28	100	300	60	300	23.0
29	300	300	60	300	59.0
30	400	400	45	200	41.9

Source	Sum of Squares	df	Mean Square	F-Value	<i>p</i> -Value
Model	11,954.61	14	853.9	35.71	< 0.0001
А	2629.55	1	2629.55	109.98	< 0.0001
В	1738.71	1	1738.71	72.72	< 0.0001
С	5483.04	1	5483.04	229.32	< 0.0001
D	794.96	1	794.96	33.25	< 0.0001
AB	53.36	1	53.36	2.23	0.1559
AC	195.26	1	195.26	8.17	0.012
AD	8.87	1	8.87	0.371	0.5516
BC	141.68	1	141.68	5.93	0.0279
BD	6.44	1	6.44	0.2692	0.6114
CD	23.55	1	23.55	0.9851	0.3367
A ²	309.42	1	309.42	12.94	0.0026
B^2	139.02	1	139.02	5.81	0.0292
C^2	12.2	1	12.2	0.5103	0.486
D^2	628.75	1	628.75	26.3	0.0001
Residual	358.65	15	23.91		
Lack of Fit	353.79	10	35.38	36.41	0.0005
Pure Error	4.86	5	0.9717		
Cor Total	12,313.26	29			
Standard deviation	4.89		R-Squared	0.9	709
Mean	50.17		Adj R-Sq	0.9	437
C.V. (%)	9.75		Pred R-Sq	0.8	339
Press	2044.85	5	Adep Precision	23.0	0500

Table 5. The quadratic model of ANOVA analysis for the Mn leaching efficiency.

The improved model equation was used to estimate the response values, and the polynomial equation coefficients were determined using experimental values. Suggested using ANOVA, the quadratic polynomial equations representing the final reduced models for Mn leaching efficiency are shown as Equation (11).

$$Y = 59.02 + 10.47A + 8.51B + 15.11C + 5.76D + 1.83AB + 3.49AC + 0.7466AD + 0.746AD + 0.746AD + 0.746AD + 0.7466AD + 0.746AD +$$

 $2.98BC + 0.6343BD + 1.21CD - 3.36A^2 - 2.25B^2 - 0.6670C^2 - 4.79D^2$ (11)

where Y is the Mn leaching efficiency (%); A, B, C and D are the coded values of the amount of silver-bearing pyrite addition (kg/t), the amount of sulfuric acid addition (kg/t), temperature ($^{\circ}$ C) and stirring speed (rpm).

Table 5 revealed the ANOVA of the resulting quadratic polynomial equations for Y. For the polynomial equation, the significance of the coefficients of regression was expressed by the *p*-value. The smaller *p*-value shows the related coefficients are of crucial importance. The amount of silver-bearing pyrite addition (A), the amount of sulfuric acid addition (B), temperature (C) and stirring speed (D) terms (p < 0.0001) had the most significant influence on Y. The interactive effect between the amount of silver-bearing pyrite addition and the temperature (AC) (with p < 0.05), and the interactive effect between the amount of sulfuric acid addition Y. Throughout the whole RSM study, other interactive effects were not significant.

The response surface and contour plots of the interactive effects of AC (the amount of silver-bearing pyrite addition and the temperature) and BC (the amount of sulfuric acid addition and the temperature) were shown in Figure 4. It can be observed that with the temperature increased, the blue color (negative values of Y) reduced and gradually moved to the red region (positive values), and this was in accord with the PBD test. A similar trend appeared with both factor A (the amount of silver-bearing pyrite addition) and factor B (the amount of sulfuric acid addition). Another noteworthy fact is that when operating at a higher temperature, Mn leaching efficiency can be achieved at an equal level with a smaller amount of silver-bearing pyrite addition and sulfuric acid addition compared with operating at a lower temperature. The result shown in Figure 4 implies that temperature

played a crucial and beneficial role in the decomposition of manganese–silver concentrate and oxidation of silver-bearing pyrite. The positive effect of temperature was mostly attributed to the facilitation of pyrite oxidation and sulfuric acid generation. With the significant influence of the oxidation of sulfur contained in pyrite, the decomposition and oxidation of silver-bearing pyrite are of vital importance in opening the package of silverbearing pyrite and reducing the dosage of pyrite and sulfuric acid. However, overheating is neither eco-friendly nor economical. Therefore, a novel method to promote the oxidation efficiency of pyrite is of increasing importance.



Figure 4. Contour and 3D response surface plots for Mn leaching efficiency (**a**); interaction plots of amount of silver-bearing pyrite addition and temperature on Mn leaching efficiency; (**b**) interaction plots of amount of sulfuric acid addition and temperature on Mn leaching efficiency.

3.4. Two-Stage Method Study

With the advantages of low production costs, simple equipment, mild reaction conditions and reduced environmental impact, bioleaching technology has been employed to reduce the usage of additional reagents [29] and enhance the oxidation efficiency of silverbearing pyrite. Moreover, in order to accelerate the leaching rate, the leaching process was divided into two parts: the chemical leaching stage and the bioleaching stage. The main objective of the chemical leaching stage was to reduce and leach most manganese with the acceptable usage of pyrite and sulfuric acid. Afterward, the bioleaching stage was carried out to dissolve the residual manganese and open the package of unoxidized silver-bearing pyrite. To determine the detailed parameters of chemical leaching, numerical optimization was carried out with the improved model equation constructed in the RSM study. The goal of multi-objective optimization was to determine the optimum points of four variables, namely, the amount of silver-bearing pyrite addition, the amount of sulfuric acid addition, temperature and stirring speed, which satisfied the multiple objectives to minimize the addition of pyrite and sulfuric acid with a target goal of Mn leaching efficiency. In order to achieve an efficient connection with the bioleaching stage, six desired goals of Mn leaching efficiency were assigned at the targeted values. Additionally, all independent variables were assigned as "within range". The desired goals for all independent factors with ranges and the importance for optimization are presented in Table 6.

Table 7 shows the optimal values for four variables with different targeted Mn leaching efficiency. According to Table 7, chemical leaching experiments were performed under the suggested conditions, and the experimental results revealed that the developed model could accurately predict the leaching efficiency. After chemical leaching, further bioleaching experiments with residuals from experiments No. 1~5 were conducted at 45 °C to screen the most suitable chemical leaching conditions and validate the feasibility of the two-stage co-leaching method. A controlled experiment for No. 3 was conducted without leaching bacteria inoculation.

No.	Mn Leaching Efficiency (%)	Amount of Silver-Bearing Pyrite Addition (kg/t)	Amount of Sulfuric Acid Addition (kg/t)	Temperature (°C)	Stirring Speed (rpm)
1	target→50	in range (150~250)	in range (150~250)	in range (30~90)	in range (100~500)
	(*****)	(****)	(****)	(***)	(**)
2	target→60	in range (200~300)	in range (200~300)	in range (30~90)	in range (100~500)
	(*****)	(****)	(****)	(***)	(**)
3	target→70	in range (250~350)	in range (250~350)	in range (30~90)	in range (100~500)
	(*****)	(****)	(****)	(***)	(**)
4	target→80	in range (300~400)	in range (300~400)	in range (30~90)	in range (100~500)
	(*****)	(****)	(****)	(***)	(**)
5	target→90	in range (350~450)	in range (350~450)	in range (30~90)	in range (100~500)
	(*****)	(****)	(****)	(***)	(**)
6	target→95	in range (400~500)	in range (400~500)	in range (30~90)	in range (100~500)
	(*****)	(****)	(****)	(***)	(**)

Table 6. The desired goals for all independent factors with ranges and importance (shown with the number of "*", the more "*", the more importance) on Mn leaching efficiency.

Table 7. Potential optimization conditions based on CCD for Mn leaching efficiency.

ŊŢ	Mn Leaching	Amount of Silver-Bearing	Amount of Sulfuric Acid	Temperature	Stirring Speed	Mn Leaching	hing Efficiency (%)	
N0.	Efficiency (%)	Pyrite Addition (kg/t)	Addition (kg/t)	(°C)	(rpm)	n) Predicted	Experimental	
1	target \rightarrow 50	203.45	196.32	83.15	345.87	50.00	51.6	
2	target $\rightarrow 60$	227.63	231.61	82.19	352.13	60.00	59.0	
3	target \rightarrow 70	284.94	277.44	77.73	287.76	70.00	71.3	
4	target $\rightarrow 80$	336.91	321.51	80.20	242.69	80.00	81.0	
5	target \rightarrow 90	388.04	385.24	80.19	223.82	90.00	88.7	
6	target \rightarrow 95	425.64	426.80	75.29	254.26	95.00	94.1	

Figure 5 presents the changes in ORP, Mn leaching efficiency, pH and acid consumption during the bioleaching stage. As seen in Figure 5, after the inoculation of leaching bacteria, Mn leaching efficiency increased rapidly even with a small amount of pyrite remaining in the chemical leaching residual. This can be explained by the fact that the adsorption of bacteria on pyrite particles accelerates the cleaving of the Fe–S bond, and the releasing of ferrous ions as pyrite particles are affirmed as the major energy resource for the leaching bacteria. Furthermore, the presence of sulfur-oxidizing microorganisms promoted the generation of sulfuric acid, which is in agreement with the decrease in pH in Figure 5c. Another remarkable sign of the bio-oxidation effect was shown in Figure 5a with experiments No. 4 and No. 5. During the bioleaching process of No. 4 and No. 5, the ORP values decreased sharply at the early stage (day 0–2) with the reductive leaching of manganese and releasing of ferrous ions. Yet, with the process going on, the ORP values raised with the bio-oxidation (Equation (7)) of ferrous ions. The leaching results of the controlled experiment of No. 3 also suggested an efficient dissolution of manganese minerals which was caused by the bio-decomposition of pyrite. As shown in Figure 5b, the reduction of acid consumption is also evidenced by the bio-oxidation of pyrite. Meanwhile, it is obvious that Mn leaching efficiency increased with the increase of the additional amount of silver-bearing pyrite. Nevertheless, with the prominent effect of the leaching bacteria, the influence of the pyrite amount on the Mn leaching efficiency decreased. Figure 5b also implied that equal Mn leaching efficiency could be achieved with the two-stage method of co-leaching. For instance, with the chemical leaching method, as the result of experiment No. 6, 94.1% of Mn leaching efficiency was realized with 425.64 kg/t consumption for silver-bearing pyrite and 426.80 kg/t for sulfuric acid. In contrast, an equal Mn leaching efficiency of 95.3% could be achieved with a reduced consumption of 284.94 kg/t consumption for silver-bearing pyrite and 277.44 kg/t for sulfuric acid. With the promotion of leaching bacteria on the bio-oxidation of silver-bearing pyrite, a higher silver recovery with a two-stage method is predictable.



Figure 5. Changes of ORP (**a**), Mn leaching efficiency through the whole two leaching stages (**b**), pH (**c**) and acid consumption (**d**) with leaching time during bioleaching stage.

3.5. Cyanidation Leaching

Cyanidation leaching tests for residues of different leaching experiments were carried out to verify the leaching efficiency of silver at room temperature. Thereby, the oxidation efficiency of silver-bearing pyrite could be further illustrated. The cyanidation leaching tests for samples of manganese–silver concentrate, silver-bearing pyrite and mixed ore were conducted to show the influence of chemical and bio treatments on the leaching efficiency of silver. The cyanidation leaching tests were carried out in triplicate.

Figure 6 shows that the direct cyanidation of manganese–silver concentrate and silverbearing pyrite is inefficient with a silver leaching efficiency of 19.7% and 33.9%, respectively. Similarly, the recovery of silver from mixed ore with manganese–silver concentrate and silver-bearing pyrite was poor. In contrast with the poor leaching efficiency of unprocessed samples, the silver recovery efficiency increased with the increase of Mn leaching efficiency. It can be concluded that the dissolution of manganese is in fact beneficial for the dissolution of silver in both manganese–silver concentrate and silver-bearing pyrite. The comparison details of different leaching methods are shown in Table 8. As the results show in Figure 5 and Table 8, it can be confirmed that the efficient recovery of manganese and silver can be achieved with the reduced addition of pyrite and sulfuric acid via a two-stage method.

Table 8. Comparison of chemical leaching and two-stage method.

Leaching Method	Chemical Leaching	Two-Stage Method		
Experiment number in cyanidation leaching tests	6	8	10	
Mn leaching efficiency (%)	99.2%	95.3%	98.1%	
Ag leaching efficiency (%)	96.3%	96.3%	95.9%	
Amount of silver-bearing pyrite addition (kg/t)	400	284.94	336.91	
Amount of sulfuric acid addition (kg/t)	400	277.44	321.51	
Stirring speed (rpm)	400	287.76 & 150	242.669 & 150	
Temperature (°C)	75	77.73 & 45	80.20 & 45	



Figure 6. Silver leaching efficiency of different samples: 1. Manganese–silver concentrate; 2. Silverbearing pyrite; 3. Mixed ore used in single factor test (amount of silver-bearing pyrite addition-level 5); 4. Leaching residual of single factor test (amount of silver-bearing pyrite addition-level 5); 5. Leaching residual of PB test (Run 7); 6. Leaching residual of RSM-CCD test (Run 18); 7. Leaching residual of two-stage method (No. 2); 8. Leaching residual of two-stage method (No. 3); 9. Leaching residual of two-stage method (No. 3-controlled); 10. Leaching residual of two-stage method (No. 4).

3.6. Mechanism Study: Mineral Behaviors

As suggested in Figure 7 and Table 9, oxygen was detected on the surface of pyrite from the bioleaching leaching residual. This can be explained by the formation of ironbased precipitates such as Fe_2O_3 or $Fe(OH)_3$ phases which were confirmed as a crucial passivation product by many previous studies [30,31]. During the reaction, ferric ions have a prominent effect on the oxidation of S_2^{2-} and S^{2-} and the reduzate ferrous ions could be re-oxidized back to Fe^{3+} by the oxidation of MnO_2 minerals. Ferric ions are continuously consumed, caused by the oxidation and participation of iron, which will further hinder the decomposition of pyrite as the coverage of the passivation layer is unfavorable for the settlement of leaching bacteria.

Table 9. Element content of selected area in (a) and (b).

Element Content/wt%	S	Fe	0	Si
(a)	52.9	48.1	-	-
(b)	39.6	53.3	5.7	1.4



Figure 7. SEM micrographs and EDS analysis of (**a**) silver-bearing pyrite, (**b**) pyrite in the leaching residual of bioleaching test (No. 9), (**c**) spectrum analysis of selected area in (**a**,**d**) spectrum analysis of selected area in (**b**).

Another fact supporting the oxidation of pyrite is the sharp decrease of sulfur element content from 51.9% to 39.6%. The oxidation of sulfur species consists of two categories: the formation of S^0 during the oxidation of S_2^{2-} and S^{2-} , and the oxidation of S^0 . The reduced sulfur species (S^{2-} and S_2^{2-}) could be oxidized by both Fe³⁺ and the leaching bacteria, and ferric ions could accelerate the oxidation of S_2^{2-} and S^{2-} . However, as a nonconductor, elemental sulfur could hardly be oxidized by ferric ions or dissolved oxygen, and the oxidation of S⁰ is only remarkable when the sulfur-oxidizing microorganisms are presented. Many previous studies have confirmed S⁰ as a crucial passivation product in the oxidation of sulfide minerals [32]. The X-ray diffraction pattern with the detection of sulfur phases shown in Figure 8 suggests that the presence of leaching bacteria benefits from the transformation from S_2^{2-}/S^{2-} to S^0 . Moreover, the formation of S^0 stimulates the growth of the leaching bacteria, especially the sulfur-oxidizing bacteria, which further promote the generation of sulfuric acid. As the common phases shown in general bioleaching residuals [33], jarosite was undetectable within this study. Instead, Fe_2O_3 was performed as the major iron-based product, and this may be due to the high ORP value caused by the presence of the strong oxidant MnO₂.



Figure 8. XRD pattern of leached residual of two-stage study (No. 1 bioleaching stage).

The SEM-EDS analysis of both chemical leaching residual and two-stage co-leaching residual was shown in Figure 9. According to Figure 9c,d, no significant evidence of manganese was found with the bioleaching residual while manganese minerals in larger clusters can be observed within the chemical leaching residual. The comparison results indicated a more thorough reaction between manganese–silver concentrate and silverbearing pyrite during the two-stage co-leaching. As suggested in Figure 9e,f, with the adsorption and acidolysis effects of leaching bacteria, a decomposition trend was shown with the major silicon-bearing gangue minerals, further supporting the bio-decomposition effect. Silver-bearing pyrite is the reducing reagent and major energy resource for leaching bacteria in the two-stage co-leaching process. Hence, it is of vital importance to verify the mineral behaviors of pyrite. Despite the oxidation product (spectrum 2) being detected in the residual, the Fe-S-O map in Figure 9g still shows the un-oxidized pyrite grains (spectrum 1) in the chemical residual, supporting the statistical analysis and observation results that pyrite is overloaded and insufficiently oxidized in the chemical leaching system. On the contrary, no significant evidence of pyrite was obtained in the bioleaching residual.



Figure 9. SEM micrographs with EDS element maps for chemical leaching residual of single factor test (amount of silver-bearing pyrite addition-level 5) (**a**,**c**,**e**,**g**) and two-stage leaching residual (No. 3) (**b**,**d**,**f**,**h**).

Another fact that supports the bio-decomposition effect was shown in Figure 10, with larger particles agglomerated from smaller particles produced in the disruption of mineral particles in the bioleaching stage. As shown in Figure 10, the mineral aggregate

mainly comprises silicon-bearing gangue minerals (Figure 10c), iron-based oxide precipitation (Figure 10b,f), fine pyrite particles and sulfate (Figure 10). According to Figure 10e, no noticeable sign of manganese was observed, which is in agreement with the leaching result and X-ray diffraction analysis.



Figure 10. SEM micrographs with EDS layered map for two-stage leaching residual (a-f).

4. Conclusions

A comprehensive study of the effect of the amount of silver-bearing pyrite addition, the amount of sulfuric acid addition, temperature, particle size of manganese–silver concentrate, pulp density, Fe(III) concentration, stirring speed and leaching time on the Mn leaching efficiency was carried out. It is suggested that these parameters had a positive enhancement on the reductive leaching of manganese. With the use of the Plackett–Burman design, the amount of silver-bearing pyrite addition, the amount of sulfuric acid addition, temperature and stirring speed were screened as the four most sensitive factors of leaching conditions for further optimization study.

The RSM study with CCD implied the interactive effects of the amount of silverbearing pyrite addition and the temperature and the amount of sulfuric acid addition and temperature. The discussion with the interactive effects elaborated the crucial role of sulfur element oxidation, which further inspired us on a novel two-stage method to save the usage of pyrite and sulfuric acid.

With the combination of the parameter optimization of the chemical leaching stage, bioleaching stage and cyanidation test, the bioleaching and decomposition effects of leaching bacteria were confirmed with a lower consumption of pyrite and sulfuric acid. The corresponding mineral behaviors were also identified with the XRD and SEM/EDS analysis. Furthermore, the bioleaching of silver-bearing pyrite also benefited the recovery of silver, which confirmed the applicability of bio-hydrometallurgy technology in the collaborative utilization of manganese–silver ore and silver-bearing pyrite.

Author Contributions: Conceptualization, J.S. and J.W.; Data curation, J.S. and H.Y.; Formal analysis, J.S. and H.S.; Funding acquisition, J.S., X.L. and Q.Z.; Investigation, J.S.; Methodology, J.S. and L.C.; Project administration, H.S. and X.L.; Resources, H.S.; Software, J.S.; Supervision, J.W.; Validation, X.L.; Visualization, H.S.; Writing—original draft, J.S.; Writing—review & editing, J.S., L.C. and Q.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key R&D Program for Young Scientists (No. 2022YFC2900151) and the Youth Fund Project of GRINM.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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