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Reductive Leaching of Pyrolusite using Orange Peel as a Reducing Agent

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Abstract

In this research work, the reductive leaching of pyrolusite in a sulfuric acid medium with the aid of orange peel as a reductant was investigated. The important parameters affecting the leaching process include temperature in the range of 25 to 95 °C, the weight ratio of reducing agent to pyrolusite (R/P) in the range of 0 to 2 (w/w), and the concentration of sulfuric acid in the range of 0.05 to 0.25 M. According to the results, the parameters of temperature and the R/P are more significant in the reductive leaching process. With increasing temperature from 25 to 95 °C, Mn recovery increases from 0.5% to 52.5%. Also Mn recovery with a two-step increase in 0-0.1 and 0.1-1.5 of the R/P indicates a jump of 28.5% and 19.0%, respectively. Sulfuric acid concentration shows its effect by supplying sulfate and hydrogen ions in the leaching process. The successful use of orange peel as a reductant was confirmed by achieving a manganese dissolution efficiency of 98.1% under optimum conditions (temperature of 90 °C, sulfuric acid concentration of 0.1 M, and R/P ratio of 1.5 (w/w)). Kinetic investigations showed that the shrinking core model could not be used to determine the leaching mechanism of pyrolusite in the presence of fruit peel reductant. Avrami's kinetic model with very high fitting accuracy was used to determine the kinetic model of pyrolusite leachin..

1. Introduction

The widespread industrial use of manganese metal in various industries such as the production of steel alloys, batteries, glass making, catalysts, pigments, pharmaceuticals, and chemicals has made it considered a strategic metal [1]. The production and consumption of this metal in 2022 have been about 20 million tons, and about 90% of its consumption is related to iron alloy industries [2]. Most of the manganese concentrates are processed in South Africa and then in America, Australia, and China, and sold to global markets [3]. According to forecasts, the consumption of this metal will increase in the coming years due to the widespread production of lithium-ion batteries and the economic growth of developing countries [4]. On the other hand, with the reduction of high-quality mineral resources of this metal, the importance of complex mineral materials of manganese will become more apparent.

The most mineral sources of manganese include pyrolusite (MnO_2), manganite ($Mn_2O_3.H_2O$), romanchit (($(Ba,H_2O)_2$ $(Mn^{4+},Mn^{3+})_5O$), and hasmanite (Mn_3O_4) [1]. Mineral sources containing manganese carbonate are known as high-quality soils of this metal. However, due to the reduction of these resources and their limited distribution worldwide, manganese oxide soils such as pyrolusite (60% of the mineral resource reserves of this metal) have become more important [5].

Pyrulosite with the tetravalent combination of manganese is very resistant to dissolution in acidic or alkaline environments and does not dissolve. It is inevitable to use a reductant to change its capacity from tetra-valent to di-valent for its dissolution [6]. In this regard, inorganic and organic reductants have been used to dissolve pyrolusite [7]. By using inorganic solvents such as SO_2, iron-containing materials, and hydrogen

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peroxide, they were able to recover 95.5% [8], 96% [9], and 95.73% [10], respectively. Organic reducing agents have been recognized as efficient and "green" reducing agents for hydrometallurgical dissolution due to their advantages in terms of less harmful gas emissions during leaching and ease of leaching solution purification compared to inorganic reducing agents. From this group, sucrose [11,12], corn stalk [13], corn [6], tea pulp [14], sawdust [15], cellulose [16], glucose [17, 18] can be mentioned. Another option of reductant is the fruit peel, which has received a lot of attention recently due to the presence of cellulose in its structure and a much lower price than other reductants, as well as being environmentally friendly [19]. In a study conducted by Ali et al. [19] on low-grade manganese minerals using banana peel in sulfuric acid media, in optimal conditions (2 h leaching time, 4 g of banana peel, leaching temperature 120 °C, 15 % concentration of sulfuric acid and 5 g of pyrolusite) managed to recover 98% of the manganese content. The global demand for high-purity metal materials underscores the necessity for production methods that are both environmentally sustainable and aligned with the essentials of addressing global warming. In this study, the essential to adopt entirely green methodologies, which minimize environmental impact, is most important. Notably, among the critical metals determining to the landscape of new and renewable energy production, manganese occupies a vital position. Moreover, the utilization of sources characterized by a low-grade manganese content assumes particular significance in the context of this research work, as it facilitates the extraction of this metal. Against this backdrop, the strategic tracking of manganese production through green methodologies takes on pronounced importance. In this research work, orange peel has been used as a green reductant to dissolve the pyrolusite mineral in H_2SO_4 media. Analyzing tonnage data, oranges secure the fourth spot in global production following bananas, watermelons, and apples. In other words, the availability of this material in substantial quantities presents minimal challenges [20].

In this research work, pyrolusite reductive leaching in sulfuric acid media has been investigated for the first time with the incorporation of an environmentally friendly reducing agent devoid of any ecological concerns. The influencing parameters including time, acid concentration, temperature, and reducing agent to pyrolusite ratio (R/P) were evaluated. The kinetics of the leaching process of pyrolusite in a sulfuric acid medium with orange peel as a reducing agent was assessed using the shrinking core model and the Avrami model.

2. Methods and materials

2.1. Materials and chemicals

To conduct pyrolusite leaching experiments, laboratory-grade sulfuric acid (purity 98%, Mojalli Co.) was used as a leaching medium, and orange peel as a reducing agent. Figure 1 schematically shows how to prepare orange peel powder.

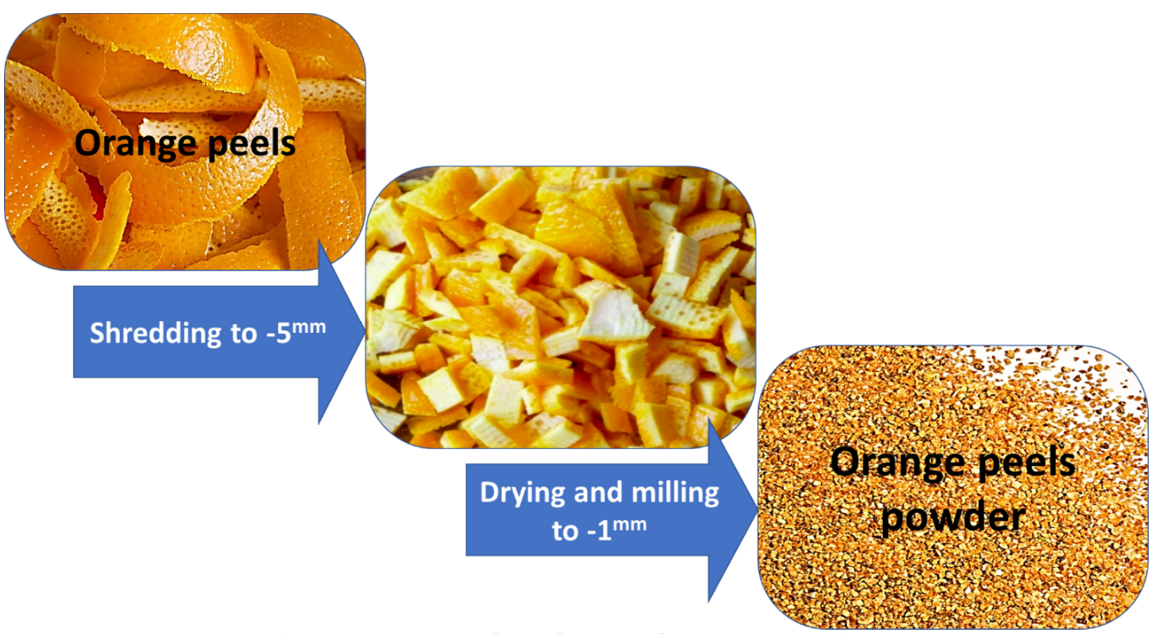

Figure 1. Orange peel powder (as reductant) preparation.

The pyrolusite used, which was obtained from the Kermanshah mine, in Iran, has the following analysis (Table 1):

Table 1. Chemical composition of pyrolusite used in this research work.

Element	Mn	Fe	Zn	Mg	Cu
Content (wt. %)	30.30	0.61	0.19	0.07	0.04

Philips PW-3710 XRD equipment with CuK_α beam and accelerating voltage of 400 kV was used to identify pyrolusite phase compounds. Also X'pert HighScore Plus software version 2.2b (2.2.2) was used to determine the phases. According to mineralogy, the concentration of solutions resulting from the leaching process was measured using an atomic absorption spectrometer (AAS, Varian 240).

2.2. Leaching experiments

In the pyrolusite leaching experiment, three parameters affecting the dissolution of manganese include the R/P in the range of 0.1 to 2 (w/w), temperature in the range of 25 to 90 °C, and sulfuric acid concentration in the range of 0.05 to 0.25 M in constant time (4 h) was investigated. The following formula was used to determine the Mn recovery:

$$R_{Mn} = \frac{C_{Mn} \times V}{P_{Mn} \times M} \times 100 \quad (1)$$

where R_{Mn} is the Mn recovery (%), C_{Mn} is the Mn concentration, V is the volume of leach liquor (L), P_{Mn} is the manganese grade in pyrolusite (%), and M is the mineral content (g). After optimizing the parameters, the final leaching test of pyrolusite was performed under optimal conditions including the R/P of 1.5, the temperature of 90 °C, sulfuric acid concentration of 0.1 M, and time of 4 h, to measure the highest Mn recovery. In the same conditions, the leaching test was performed without reducing agent to determine the effect of orange peel addition. To investigate the kinetics of the pyrolusite leaching process, leaching was conducted at three temperatures of 50, 70, and 90 °C, considering the acidity level of 0.1 M, and the R/P of 1.5. The experiments exhibited an error margin of approximately 10% in conjunction with performing tests and the measurement of concentrations.

3. Results and Discussion

3.1. Results of characterization

This section is dedicated to the comprehensive characterization of the pyrolusite raw material through the utilization of the X-ray diffraction (XRD) technique. Furthermore, a detailed investigation of the orange peel's characterization will be undertaken, drawing upon existing references within this specialized domain. This dual approach seeks to provide a thorough understanding of both the raw material and the reductant source, contributing to the holistic assessment of their applicability in the leaching process.

3.1.1. Identification of ore composition

The XRD analysis of the feed is shown in Figure 2. Accordingly, the dominant minerals were pyrolusite (MnO_2), calcite ($CaCO_3$), quartz (SiO_2), and anorthite (Ca ($Al_2Si_2O_8$)). Quartz, with a hexagonal crystal system (JCPDS: 01-083-2466), demonstrates its unique structural arrangement. Pyrolusite, characterized by a tetragonal crystal system (JCPDS: 01-072-1984), exhibits distinctive symmetry. Calcite's rhombohedral crystal system (JCPDS: 01-086-2341) underscores its geometric configuration. The anorthite mineral, belonging to the anorthic crystal system (JCPDS: 01-086-1707), further contributes to this comprehensive analysis of minerals and their crystallographic properties. According to Table 1, the content of manganese is prominent, constituting 30.30% of the composition, signifying its substantial presence. In contrast, iron contributes a minor portion, accounting for 0.61%. Zinc, magnesium, and copper constitute even smaller fractions, with their respective weights being 0.19%, 0.07%, and 0.04%.

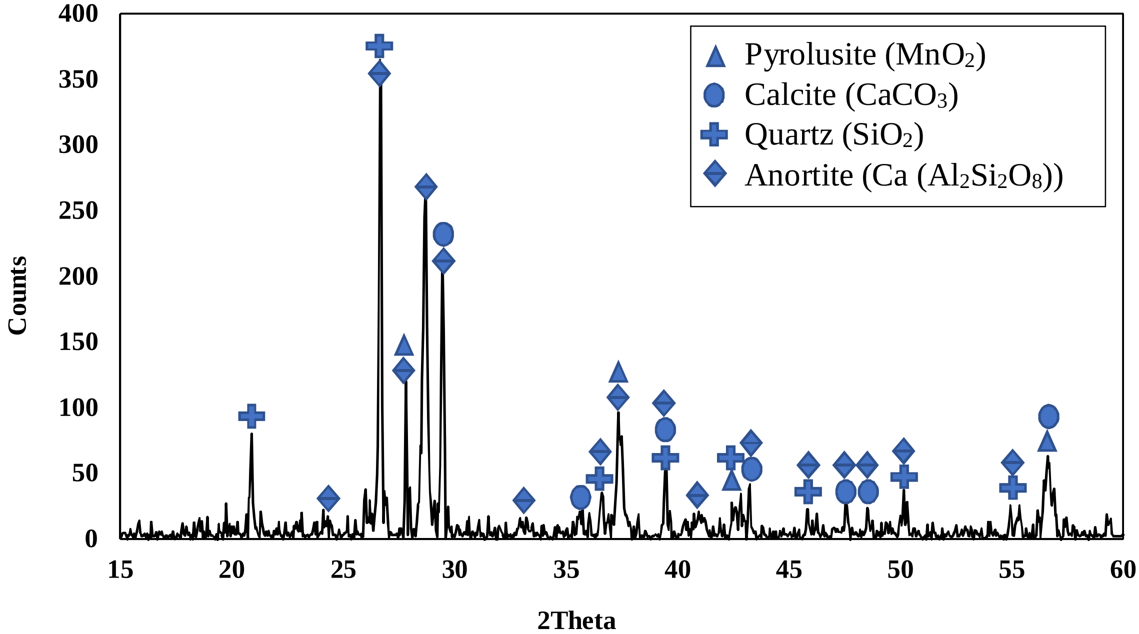

Figure 2. XRD pattern of Pyrolusite ore.

3.1.2. Composition of orange peel

Various studies have been conducted in pyrolusite leaching using organic reductants [21, 22]. Among them, citrus peel is a suitable and environmentally friendly option. In the composition of these materials, the three main components include cellulose, hemicellulose, and lignin in an average amount of 22-37%, 5-17%, and 7-9%, respectively. As it is known, the amount of lignin in these materials is lower than in other materials, and its high amount is related to carbohydrates [23]. Among citrus fruits, orange is the most consumed in the food industry, and about 75.6 million tons of it are produced annually [20, 24]. After dewatering, it can be used as an important resource for leaching industries. Lemon waste has been used in the leaching process of lithium-ion batteries in citric acid by Wu et al. [25]. According to the results, orange waste, having cellulosic and antioxidant compounds, and providing electrons causes the reduction of metals in the cathode of lithium-ion batteries [25]. When the orange peel is heated under acidic conditions, about 30% of cellulose can be degraded to glucose and more than 70% of hemicellulose can be rapidly converted to aldehyde-containing reducing sugars such as xylose, arabinose, and mannose. Therefore, these findings suggest that orange peel is a promising alternative to industrial reductants such as H_2O_2 because it contains multiple reductant compounds.

As previously explained, based on an orange peel analysis, it contains compounds such as cellulose, hemicellulose, and lignin. These compounds have reductant capabilities. In addition to another type of analysis, orange peel consists of about 40% moisture, 7% ash, 7-9% pectin, 5-9% fiber, and 10-15% of various sugar family compounds [26].

Some compounds of the family of monomolecular sugars (monosaccharides such as glucose, fructose, and galactose) or disaccharides (such as sucrose, lactose, and maltose) also have the ability to play a reductive role in the dissolution of manganese with sulfuric acid [1]. In this regard, some of the most common reactions suggested in the literature are presented. Cellulose, which is a linear polymer of glucose, can play as a reductant in an acidic solution with the following general form [27]:

$$(C_6H_{10}O_5)_n + 12nMnO_2 + 12nH_2SO_4 = 12nMnSO_4 + 6nCO_2 + 17nH_2O \quad (2)$$

Considering the conversion of cellulosic compounds to glucose, the following reaction can be written for the reductive leaching process of pyrolusite by glucose:

$$C_6H_{12}O_6 + 12MnO_2 + 12H_2SO_4 = 12MnSO_4 + 6CO_2 + 18H_2O \quad (3)$$

In the presence of sucrose, the reductive leaching of manganese can be proposed as the following reaction:

$$24MnO_2 + C_{12}H_{22}O_{11} + 48H^+ = 24Mn^{2+} + 12CO_2 + 35H_2O \quad (4)$$

In addition to the above reduction reactions, the sucrose decomposition into glucose and galactose can also intensify the reduction conditions:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6(Glucose) + C_6H_{12}O_6(Galactose) \quad (5)$$

3.2. Results of leaching experiments

3.2.1. Effects of sulfuric acid concentration

Figure 3 shows the effect of sulfuric acid concentration on reductive leaching of pyrolusite in the range of 0.05 to 0.25 M, while maintaining a constant temperature, R/P ratio, and leaching time at 70 °C, R/P of 0.5, and 4 h, respectively. The results indicated that manganese recovery increased from 19.7% at 0.05 M acid concentration to 34.15% at 0.10 M sulfuric acid concentration. Still, only a slight increase of 4% was observed within the range of 0.1 to 0.25 M. This suggests that after reaching the necessary sulfate ion level, sulfuric acid has minimal impact on the pyrolusite leaching process and increasing its concentration may lead to more impurities dissolving in the solution, which should be avoided. To enhance manganese recovery, sufficient reductant is required in the presence of sulfuric acid for electron transport between the reductant agent and pyrolusite. Similar findings were reported by Xue et al.'s research [28], where an increase in acid concentration up to 1.7 M resulted in higher manganese recovery rates without further improvement beyond this point. In the case of using divalent iron [29] and alcohol molasses [21] as reducing agents, the high concentration of sulfuric acid does not have much effect on the amount of manganese recovery from pyrolusite.

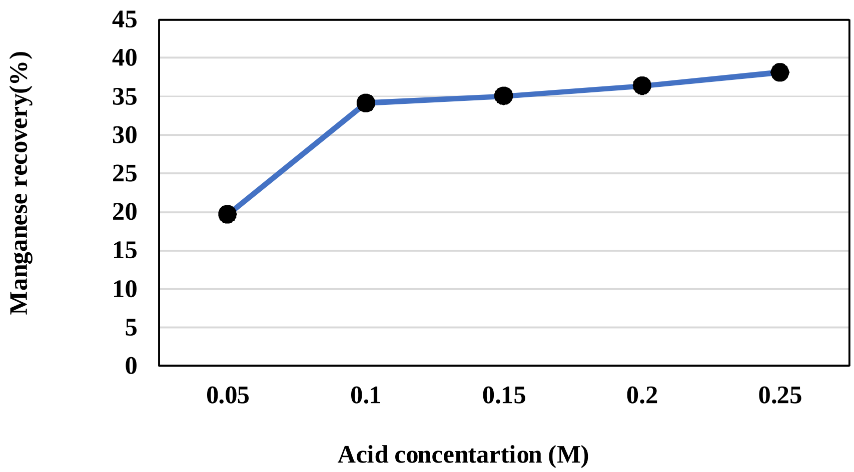

Figure 3. Effect of sulfuric acid concentration on manganese recovery from pyrolusite in 70 ˚C, R/P of 0.5 (w/w), and 4 h.

3.2.2. Effects of temperature

The effect of temperature on manganese recovery in pyrolusite reductive leaching was investigated in the range of 25 to 90 °C under the conditions of R/P of 0.5 (w/w), while maintaining a sulfuric acid concentration of 1.5 M, R/P ratio of 0.5 (w/w), and a leaching time of 4 h. The results, depicted in Figure 4, indicate that an increase in temperature has a significant effect on the recovery rate of manganese. Specifically, the recovery rate increased from 0.5% at 25 °C to 52.5% at 90 °C, representing a tenfold increase with a temperature rise of 65 °C. Temperature appears to be one of the most influential parameters affecting manganese recovery from pyrolusite reductive leaching. This result is due to its ability to provide the activation energy required for the reaction and increase the percentage of active agents and effective collisions between mineral particles and reducing agents [30]. In another study examining reductive leaching with sugarcane, temperatures ranging from 55 to 95 °C were investigated and results showed an increase in manganese recovery rate from 23.47% to 96.28%. According to their results, the effect of temperature shows the most significant impact at the beginning of the leaching process, due to the availability of raw materials. It has been reported that cellulose and hemicellulose are converted into glucose by increasing the temperature. Glucose as a reductant can reduce a more significant fraction of the pyrolusite and consequently, increase the recovery [31].

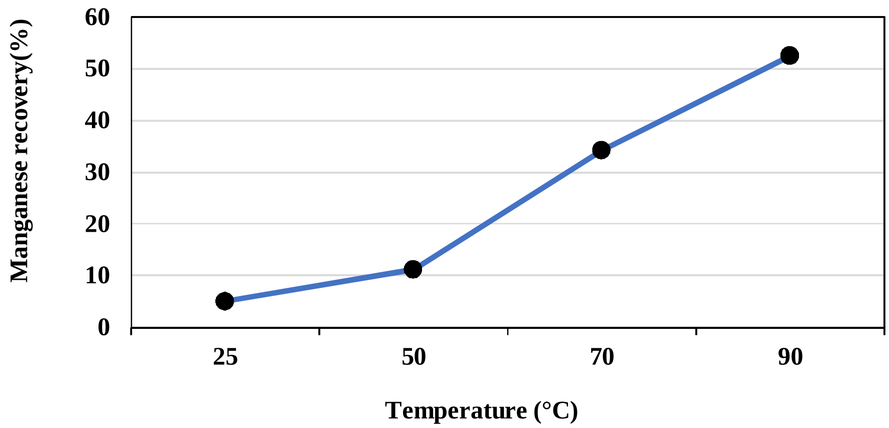

Figure 4. Effect of temperature on manganese recovery from pyrolusite in the sulfuric acid concentration of 1.5 M, R/P of 0.5 (w/w), and 4 h.

3.2.3. Effects of reducing agent to pyrolusite

In this study, a novel investigation was conducted into the pyrolusite dissolution mechanism in sulfuric acid, employing an environmentally benign reducing agent. This research work marks the first instance of such an examination. Additionally, from a production standpoint, pyrolusite occupies the fourth position globally within the category of fruits. Consequently, a substantial volume of byproducts is anticipated to be generated, presenting a valuable resource that could potentially serve as a reducing agent within the leaching process of manganese compounds. The results of reductive manganese acidic dissolution with the R/P in the range of 0 to 2 (w/w) are shown in Figure 5. In this figure, the values of sulfuric acid concentration, temperature and, dissolution time were considered equal to 0.15 M, 70 °C, and 4 h, respectively. Orange peel powder particles were below 300 microns. The levels of these values were taken into account so that the effect of the reductant is visible.

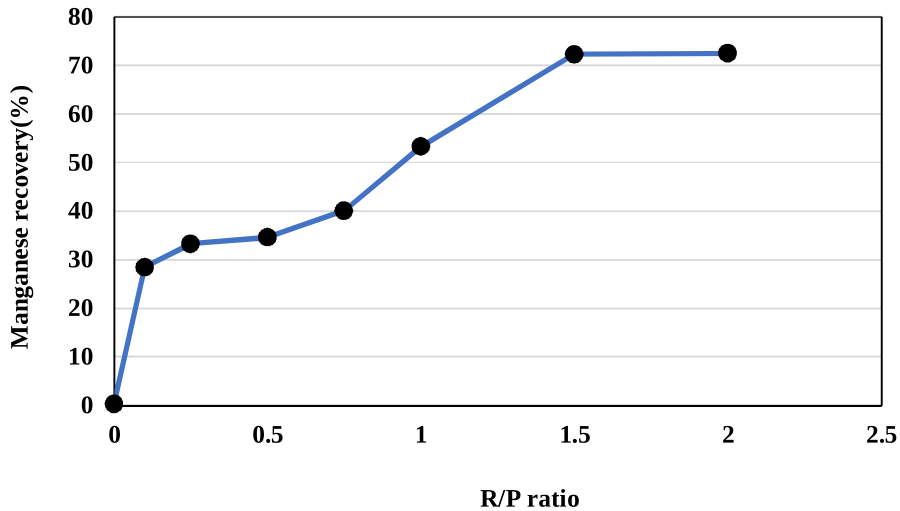

Figure 5. Effect of R/P on manganese recovery from pyrolusite in the sulfuric acid of 1.5 M, 70 °C, and 4 h.

As expected, without reductant, manganese dissolution was very slight and negligible. As a result, for the effective dissolution of manganese, a suitable magnitude reductant is essential. However, according to thermodynamic calculations based on HSC6 software, the Gibbs free energy changes for the manganese dissolution reaction from pyrolusite in the absence of reductant are negative:

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2 \quad \Delta G_{reaction} = -85.6\ kJ/mol \tag{6}$$

It means that there is a thermodynamic tendency for the dissolution of manganese in these conditions. Still, in practice, appreciable dissolution does not occur, and the dissolution efficiency is very low in the absence of a suitable reductant. A similar result in the reductive dissolution of manganese using other reductants in the studies of Ismail et al. [32] with lactose in 2004, Furlani et al. [17] with glucose in 2006, Hariprasad et al. [33] with sawdust in 2007, Sinha et al. [34] with ascorbic acid in 2020, Cheng et al. [13] in 2009, Tian et al. [6] with corn waste in 2010, Tang et al. [14] with tea pomace in 2014, and Vegilo and Toro [35] with sucrose in 1994 have reported.

As it is evident from Figure 5, orange peel has a high ability as a reductant in dissolving manganese from pyrolusite with sulfuric acid. In general, with the increase of reducing agents, the dissolution efficiency increased significantly, so that in the first step of increasing the ratio of R/P from 0 to 0.1 w/w, the recovery increased to 28.5%. This shows the significant effect of the amount of orange peel as a reductant. Further R/P increasing to 0.25, 0.5, and 0.75 led to a slight and gradual increase in manganese leaching recovery up to 40.1%. As a result, the presence of orange peel in the reduction dissolution of manganese from pyrolusite in sulfuric acid is a more important factor than its amount in the range of R/P = 0-0.75 w/w. By further increasing of R/P ratio to 1 and 1.5, a significant increase in manganese leaching recovery was observed to the values of 53.33% and 72.33%. This increase can be due to the rise in the concentration of lignin compounds present in the orange peel and, high concentrations, have a positive effect on the dissolution of manganese [36]. But finally, with the further increase of the R/P ratio to 2, the efficiency does not show a significant impact. Thus, the optimal amount of R/P ratio was considered equal to 1.5. Since orange peel is one of the cheapest and most abundant organic wastes and is environmentally friendly, it can be expected to achieve high manganese leaching recoveries by applying optimal levels of other effective factors in dissolution.

3.2.4. Optimization of leaching conditions

The study on the factors that affect the process revealed that the leaching test was carried out under optimum conditions of 90 °C temperature, 0.1 M sulfuric acid concentration, and R/P ratio of 1.5 (w/w) for 4 h. The successful use of orange peel as a reductant was confirmed by achieving a manganese dissolution efficiency of 98.1% under these conditions. In order to advance the research work, it is advisable to undertake a concurrent examination of various fruit peels' effects. Additionally, assessing the concentration of dissolved sugars throughout the leaching process could serve as a dependable parameter for further scrutinizing the experimental procedures.

3.2.5. Kinetics of reductive leaching

The mechanism of the pyrolusite reductive leaching process can be understood using kinetic models. Among the different kinetic models, the shrinking core model has been commonly used in leaching processes [30, 37, 38]. But it may not always be accurate as it investigates the total time of reductive leaching, including diffusion through the film layer, diffusion through the product layer, or chemical reaction. In Figure 6, the kinetic data at three temperatures of 50, 70, and 90 °C are plotted with diffusion through the product layer and chemical reaction. However, both models had minimal linear correlation, indicating that neither model accurately represents the kinetics of the reductive leaching process as it does not purely follow diffusion through the product layer and chemical reaction.

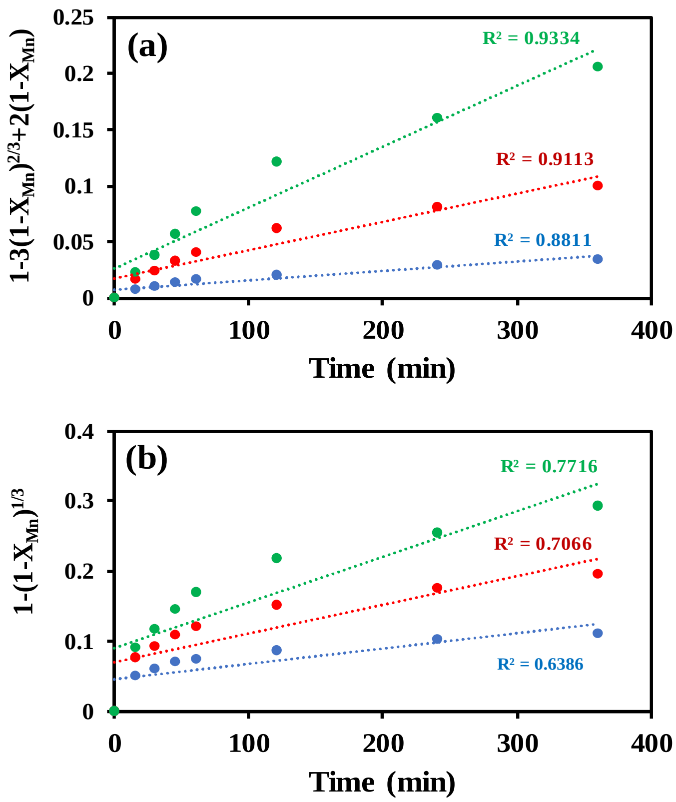

Figure 6. Kinetic data plot based on the shrinking core model at three temperatures of 50 ˚C (blue line), 70 ˚C (red line) and 90 ˚C (green line) (a) diffusion through the product layer, (b) chemical reaction.

To achieve better accuracy, two sections were utilized in the leaching process: one with high kinetic (0 to 60 minutes) and the other with low kinetic (60 to 360 minutes). Figure 7 illustrates the outcomes of modeling kinetic data at three different temperatures (50, 70, and 90 °C) using diffusion through the product layer and chemical reaction in these two sections. The coefficient value for diffusion control through the product layer in the high-kinetic section (0-60 minutes) ranged from 0.9496 to 0.9957, which is relatively appropriate. However, for chemical reaction control in the same section, it was between 0.7993 and 0.9037. In contrast, for the slow-kinetic section (60-360 minutes), linear correlation coefficients were not very precise and ranged from 0.8155 to 0.9345 for diffusion control and from 0.7859 to 0.9243 for chemical reaction control. This fluctuation of data made it impossible to determine a suitable kinetic model for the whole process, which is consistent with Xiong et al.'s research work [36]. The shrinking core model cannot be used to identify the leaching mechanism of pyrolusite recovery based on their findings.

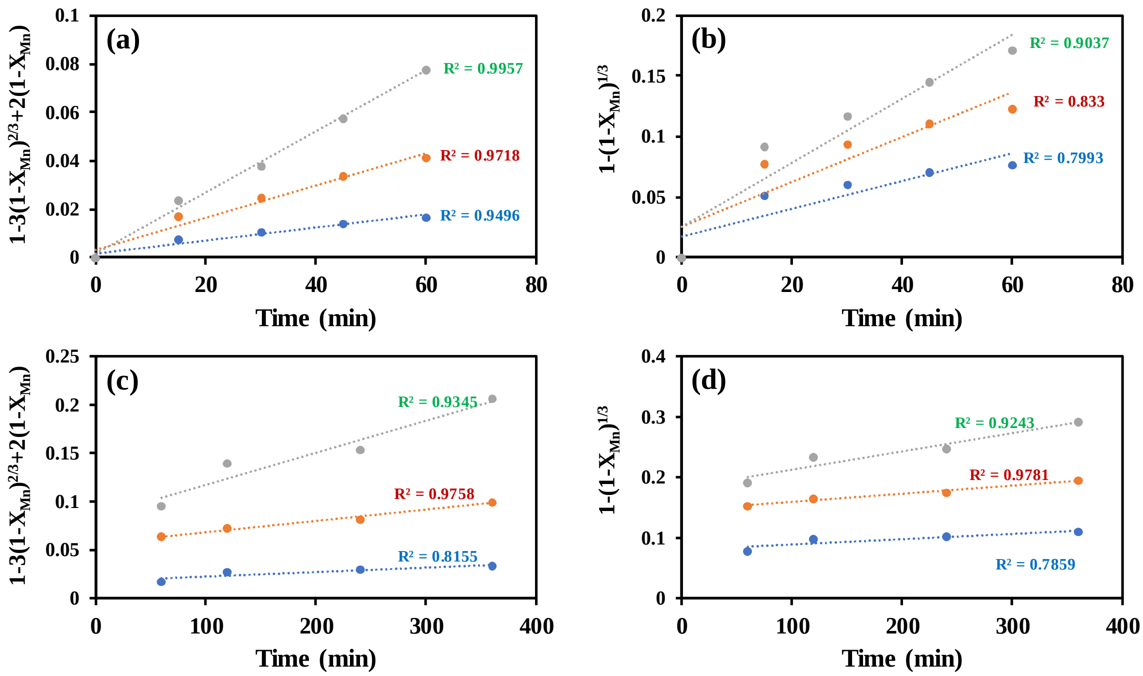

Figure 7. Kinetic data plot based on the shrinking core model at three temperatures of 50 °C (blue line), 70 °C (red line), and 90 °C (green line) in the range of 0 to 60 min (a) diffusion through the product layer, (b) chemical reaction, and the range of 60 to 360 min (c) diffusion through the product layer, (d) chemical reaction.

Table 2 presents a summary of the R^2 values for SCM model in one and two stage. A comparison of the acquired values leads to the deduction that the SCM model is incapable of forecasting the leaching mechanism of pyrolusite in H_2SO_4 when utilizing an orange peel as reducing agent. In other words, the observed mechanism does not align with SCM kinetic model.

Table 2. Summary of the R^2 values for SCM model in one and two stage.

Stage	Model	Time duration (min)	50 °C	70 °C	90 °C
Single stage	SCM-Diffusion	0-360	0.8811	0.9113	0.9334
	SCM-Chemical	0-360	0.6386	0.7066	0.7716
Two stage	SCM-Diffusion 1	0-60	0.9496	0.9718	0.9957
	SCM-Diffusion 2	60-360	0.8155	0.9758	0.9345
	SCM-Chemical 1	0-60	0.7993	0.8330	0.9037
	SCM-Chemical 2	60-360	0.7859	0.9781	0.9243

Most studies on pyrolusite leaching have proposed that the chemical reaction occurring on the surface is the critical factor controlling the leaching kinetics. Additionally, the accuracy of kinetic data obtained from the commonly used shrinking core model and the Avrami model in leaching processes has been questioned. The Avrami kinetic model equation is typically employed to fit such data.

Most studies on pyrolusite leaching have proposed that the chemical reaction occurring on the surface is the controlling step in the kinetics of reductive leaching [19, 31, 36]. Also the uncertainty in the kinetic data of the shrinking core model caused another model to be used. Therefore, Avrami model, which is one of the most used models in leaching processes, was used to fit the kinetic data. The Avrami kinetic model equation is defined as follows [36]:

$$Ln(-Ln(1-y)) = LnK + nLnt \quad (7)$$

The leached weight fraction is represented by y, while K denotes the kinetic constant value, n represents the degree of reaction, and t signifies the leaching time. Figure 8 illustrates the Avrami model-based kinetic data plotted at three different temperatures of 50, 70, and 90 °C. The correlation coefficient values for these temperatures are 0.9926, 0.9928, and 0.9869, respectively, indicating a highly accurate data fit. Previous studies on pyrolusite reductive leaching using organic reductants such as sucrose [39], sawdust [40], lignin [36], water containing xanthan gum [41], oat straw [42] have also shown that chemical reaction on the surface is the controlling mechanism of leaching. Additionally, the value of n being less than one at all temperatures indicates that the kinetics of the process decreases over time, which aligns with experimental results. The activation energy obtained from this model is approximately 5.5 kJ/mol.

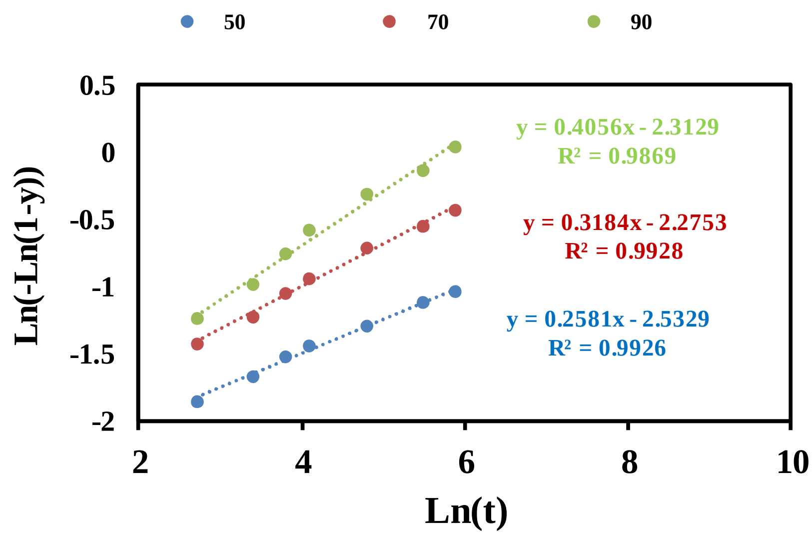

Figure 8. Plotting kinetic data based on the Avrami model at three temperatures of 50 °C (blue line), 70 °C (red line), and 90 °C (green line).

4. Conclusions

This study undertook a pioneering examination of the pyrolusite dissolution mechanism in sulfuric acid, employing an environmentally benign reducing agent, which constitutes an innovative approach. The culmination of this investigation yields the following conclusions:

- Examined leaching process under different temperatures (25-95 °C), showing a remarkable ten-fold increase in manganese recovery from 25 °C to 95 °C, resulting in 52.5% recovery.
- Investigated the impact of sulfuric acid concentration (0.05-0.25 M), revealing a rise in manganese recovery from 19.7% to 34.15% as concentration increased from 0.05 M to 0.10 M, with subsequent increments showing no significant effect.
- Explored the role of R/P ratio (0-2 w/w), demonstrating substantial effects on manganese recovery - a rise of 28.5% within the 0-0.1 range and 0.19% within the 0.1-1.5 range.
- Achieved 98.1% manganese dissolution efficiency under optimal conditions (90 °C temperature, 0.1 M sulfuric acid concentration, and 1.5 (w/w) R/P ratio), affirming the effective utilization of orange peel as a reductant.
- Examined pyrolusite leaching kinetics with fruit peel reductant, finding the shrinking core model inadequate; Avrami's kinetic model employed with high accuracy.

Conflict of Interest Statement

The authors declare no competing financial interests.

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انحلال احیایی پیرولوزیت با استفاده از پوست پرتقال به عنوان یک عامل کاهنده

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چکیده:

در این کار تحقیقاتی، انحلال احیایی پیرولوزیت در محیط اسید سولفوریک با کمک پوست پرتقال به عنوان احیاکننده مورد بررسی قرار گرفت. در این راستا، اثر پارامترهای دما در محدوده 25 تا 95 درجه سانتی گراد، نسبت وزنی احیاکننده به پیرولوزیت (R/P) در محدوده 0 تا 2 (w/w) و غلظت اسید سولفوریک در محدوده 0/05 تا 0/25 مولار مورد مطالعه قرار گرفت. با توجه به نتایج، پارامترهای دما و R/P در فرآیند لیچینگ کاهشی تاثیر بیشتری در انحلال احیایی منگنز دارند. با افزایش دما از 25 به 95 درجه سانتی گراد، بازیابی منگنز از 0/5% به 52/5% افزایش می یابد. همچنین بازیابی انحلال منگنز با افزایش دو مرحله ای R/P در محدوده 0-0/1 و 0/1-1/5 به ترتیب جهش 28/5% و 19% را نشان داد. اثر غلظت اسید سولفوریک هم بررسی شد و نقطه بهینه آن 0/1 مولار تعیین شد. بر اساس نتایج، استفاده موفق از پوست پرتقال به عنوان یک ماده احیاکننده سبز در انحلال منگنز از پیرولوزیت با دستیابی به راندمان انحلال منگنز 98/1% در شرایط بهینه (دمای 90 درجه سانتیگراد، غلظت اسید سولفوریک 0/1 مولار و نسبت R/P برابر 1/5 (وزنی/وزنی)) تایید شد. بررسی‌های سینتیکی نیز نشان داد که مدل هسته کوچک‌شونده نمی‌تواند برای تعیین مکانیسم انحلال منگنز از پیرولوزیت در حضور احیاکننده پوست پرتقال بکار گرفته شود. به همین علت، برای تعیین مدل سینتیکی لیچینگ پیرولوزیت از مدل سینتیکی آورامی با دقت برازش بسیار بالا استفاده شد.

کلمات کلیدی: پیرولوزیت، انحلال احیایی منگنز، پوست پرتقال، بررسی سینتیکی، مدل آورامی.