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Microwave-assisted method investigation for the selective and enhanced leaching of manganese from low-grade pyrolusite using pyrite as the reducing agent

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Response to Reviewers:	We would like to thank the reviewers for their thoughtful review of the manuscript. They raise important issues and their inputs are very helpful for improving the manuscript. We agree with almost all their comments and we have revised our manuscript accordingly. We are already crafting a revised version of the paper that it states the hypothesis and

the implications of our work more clearly than before. Moreover, we are including all reviewers' suggestions and clarifying the text when needed. We respond below in detail to each of the reviewer's comments. We hope that the reviewers will find our responses to their comments satisfactory, and we are willing to finish the revised version of the manuscript including any further suggestion that the reviewers may have.
Please, find below the referees' comments repeated in italics and our responses inserted after each comment.
Looking forward hearing from you soon.

Sincerely,
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Reviewer #2:
1) How is the role of dielectric properties? Please explain the enhancement of heating pattern in terms of dielectric properties.

We appreciate this suggestion and the explanation for the role of dielectric properties is provided as follows:
(1) Li et al. in the paper entitled "Investigations on the microwave absorption properties and thermal behavior of vanadium slag: Improvement in microwave oxidation roasting for recycling vanadium and chromium" pointed that the dielectric properties refer to the ability of materials to absorb microwave energy and convert it into thermal energy.
(2) Haque et al. in the paper entitled "Microwave energy for mineral treatment processes-a brief review." reported that microwave heating reduced heating time for many mineral resources. With a microwave heating frequency of 2450 MHz, MnO_2 reached a temperature of 1287 °C within 6 min, and the heating characteristic of FeS_2 was 20 °C/s. For the common minerals of pyrolusite and pyrite, the heating characteristic of SiO_2 and Fe_2O_3 with microwave heating were 2-5 °C/s and 170 °C/min, respectively.
(3) Motohiko et al. in the paper entitled "Microwave heating of water, ice, and saline solution: Molecular dynamics study" pointed that the heating characteristic of water with microwave heating was 35°C/min.
Clearly, the mentioned enhanced heating characteristic of minerals and water are depending on the
dielectric properties, and leading to a enhancement of heating pattern.

2) Results are sloppily written. The microwave physics has to be addressed.
We appreciate this suggestion addressed by the reviewer. The "Results and Discussion" was rewritten in the revised manuscript, and microwave physics are now addressed in sections"Introduction" and "Results and Discussion".

3) The comparison of conventional and microwave heating has to be done in presence of identical heating rate. Otherwise, the comparison is not correct. This part has to be addressed. Figures have to be modified and results have to be rewritten.
We appreciate this suggestion addressed by the reviewer. The authors want to express our apology on the misleading description related to the mentioned part. Actually, the experimental data of conventional heating and microwave heating in the manuscript were all obtained at the same heating rate. We have revised the misleading description in the manuscript.

4) Please add benchmarking of experimental results and compare with existing literature data.
We appreciate this suggestion addressed by the reviewer. We fully agree that the literature data should be added as a benchmarking for the experimental data. As suggested by the reviewer, we tried our best to find the related literature data carried out with the same experimental conditions.
However, few literatures were found. In our future work, we will provide more data for

	the comparation purpose.

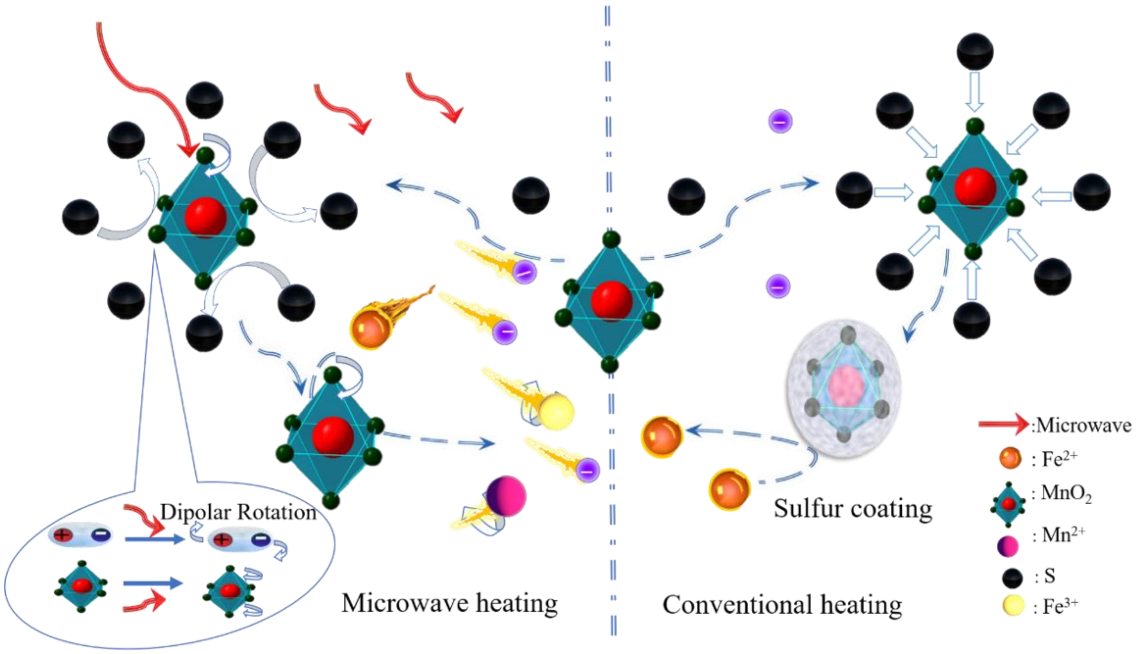
Highlights

(1) A novel microwave leaching method is proposed for manganese selective recovery.

(2) Microwave heating is proved to be more effective compared to conventional heating.

(3) The passivation layer detected during normal leaching was suppressed by MW heating.

Graphical Abstract



Microwave-assisted method investigation for the selective and enhanced leaching of manganese from low-grade pyrolusite using pyrite as the reducing agent

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Abstract

The recovery mechanism of manganese from low-grade pyrolusite was studied through microwave and conventional leaching, respectively, and pyrite was used as the reducing agent. An improvement on the manganese leaching rate with microwave heating was noticed which may be caused by the suppressing of the formation of sulfur passivation layer by the unique dipole rotation heating mechanism of microwave energy. To confirm this hypothesis, the leaching time, the amount of reducing agent, and the concentration of sulfuric acid were studied, and the surface compositions of the leaching residues were analyzed. The results evidenced that the sulfur content on the surface of residue produced by microwave leaching was significantly reduced compared to the results produced by conventional heating, which proved the rationality of the hypothesis. The recovery of leaching assisted with microwave heating was improved compared to that assisted with conventional heating under the same experimental conditions (liquid-solid ratio: 10:1, leaching temperature: 90 ℃, $M_{(pyrite)}/M_{(pyrolusite)}$: 0.2, sulfuric acid concentration: 1.2 mol/L, stirring speed: 400 rpm). The corresponding peak value of the leaching rate was 95.07% and 75.08%. Additionally, microwave leaching is very environmentally friendly since it significantly reduces the amount of reducing agent and sulfuric acid as well as reaction time.

Keywords: microwave heating; pyrolusite; enhanced leaching; dipole rotation; environmentally friendly

1. Introduction

Manganese(Mn) is a national strategic resource and is widely used in various industrial applications, wherein 90% of the Mn is applied in the iron and steel manufacturing process, and the rest is used in the production of fertilizers, non-ferrous metals, chemistry, glass and diet [1-3]. With the gradual exhaustion of high-quality manganese ore resources and the increasing demand for manganese resources in the world, a highly effective recycling approach for low grade manganese oxide ores is in urgent demand, which accounts about 60% of the world's manganese reserves, such as pyrolusite, the manganese source in which is MnO_2 [4-5].

At present, the main methods for the recovery of manganese are hydrometallurgical method (namely acid/alkaline leaching), and pyrometallurgy method (namely calcination) [6]. Compared with pyrometallurgical process, hydrometallurgical method is known to be environmentally friendly and endows the advantages including low energy consumption, however, has a disadvantage of time consuming; therefore, a new process for reducing reaction time is required [7]. In addition, it is noticed that manganese dioxide (MnO_2) in pyrolusite has strong stability in the absence of reducing agent during the leaching process, and hardly to be reduced to divalent manganese ion. Therefore, it is necessary to select suitable reducing agent in the process of hydrometallurgy for the recovery of MnO_2, such as pyrite (FeS_2) [8], scrap iron [9], SO_2 [10], potassium-oxalate [11] and so on. Pyrite (FeS_2) as one of the most abundant sulfides on the earth's surface, it has the advantages of low price and convenient access. Pyrite can be decomposed into Fe^{2+} and S_2^{2-}, which present strong reducibility in acidic solution [12]. Therefore, a new process is needed, which can reduce the formation of sulfur passivation layer in solution [15-17], and recover manganese from pyrolusite efficiently and environmentally friendly.

The pyrolusite (MnO_2) and pyrite (FeS_2) are polar molecules with good microwave absorption properties, resulting to a good ability to convert microwave energy into thermal energy [18, 45]. The heating characteristic of MnO_2 was 214.5 °C/min at 2450 MHz, and the heating characteristic of FeS_2 was 20 °C/s. Additionally, the heating characteristic of a common mineral of pyrolusite and pyrite, namely SiO_2, was 2-5 °C/s. Clearly, the application of microwave energy will enhance the heating pattern of pyrolusite and pyrite because of the corresponding enhanced heating characteristic of minerals[46-47].

According to Maxwell's electromagnetic radiation theory, the microwave field is mainly composed of changing electric field and magnetic field [19], and the change of electric field and magnetic field will affect the charge distribution in the molecule. Thus, polar molecules (ions) and polar molecular groups (ion groups) move directionally in the solution under the combined action of microwave electric field and magnetic field, while the collision of charged materials with neighboring molecules or atoms produces resistance and heats the sample. Under the action of high frequency electric field (2450 MHz), the dipole molecule oscillates 4.9×10^9 times per second with dipole rotation [20-22]. It is reported that the directional motion and dipole rotation of polar molecules in solution increase the friction heating between molecules, which leads to the heating of solution [23-24]. Considering the rotational motion of the dipole during microwave heating, the usage of microwave energy may be used to prevent the attachment of molecule S on the MnO_2 surface, thereby reducing the formation of sulfur passivation layer [16]. Thus, microwave-assisted leaching process could be a possible solution for highly efficient pyrolusite recovery.

Recently, microwave-assisted leaching process has many successful applications including the recovery of copper [25], nickel ores [26], and chalcopyrite [27]. Different from the traditional heating method, microwave energy directly acts in the object [28], so it endows the advantages including rapid and selective heating, and low energy consumption [29-31]. Besides, in order to prevent the interference between electromagnetic signals in the same frequency band, the available frequency of microwave heating is adjusted to 2450 MHz and 915 MHz with corresponding wavelengths of 335 mm and 122 mm, respectively. At present, the heating frequency commonly used in laboratory is 2450 MHz, which was selected in this experiment with a wavelength of 335 mm [32].

In this paper, considering the strong coupling effect of pyrolusite and pyrite under microwave energy, microwave heating was introduced as a new assisted process during the leaching process of pyrolusite to improve the recovery of manganese from low-grade pyrolusite, and save energy consumed. In addition, the mechanism of microwave-assisted leaching was discussed, and the possible heating principle of microwave in inorganic chemistry and the positive effect of microwave on sulphide ores were introduced in details. Moreover, the application prospect of microwave heating in the field of hydrometallurgy was also introduced.

2. Experimental

2.1. Materials

Pyrolusite samples were provided by Guangxi Chongzuo CITIC Dameng Mining Co., Ltd. (China). The pyrite used in the experiments was supplied by Yunnan Wenshan Dounan

Manganese Industry Co., Ltd. (China). Sulfuric acid (98% of purity) was purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. (China). Table 1 indicated the chemical composition of pyrolusite samples. The total manganese content of pyrolusite was 26.39%, which belongs to low grade pyrolusite (below 30%). Since the Mn/Fe was less than 3, the ore sample had a high iron content. Table 2 presented the chemical composition of pyrite samples. The total mass ratio of iron and sulfur was 41.58% and 38.20%, respectively, indicating that the iron sulfide in pyrite was in high content. The different concentrations of sulfuric acid used in the experiment were diluted by adding distilled water. All the chemicals were directly used without further purification.

Fig. 1 displayed X-ray diffraction patterns of pyrolusite and pyrite samples, and the results were compared with PDF cards provided by MDI Jade 6.5 software. Fig. 1(a) indicated that the main form of manganese in pyrolusite was MnO_2 phase, accompanied with a small amount of manganese ferrite. Fig. 1(b) signified that iron content in pyrite mainly existed in the form of FeS_2, and the minor amount of sulfur existed as zinc sulfide.

2.2. Instrument characterization

Powder X-ray diffractometer (rotating anode, Panaco) equipped with CuKα Radiation (λ=1.540598 Å) was used to analyze pyrolusite and pyrite samples. The working current and voltage of the instrument were 40 mA and 40 kV, respectively. The sample was scanned at a scanning speed of 1.6 °/min, and the XRD pattern of the sample was recorded in the 2-Thera range of 5 °-90 °. Scanning electron microscopy (SEM, Phenom prox, Netherlands) was used to observe the surface morphology of the leached sample under the working voltage of 10 kV. The elemental compositions of the leached samples under different heating methods were determined by energy dispersive scanning spectrometer (EDS, Phenom-world, Netherlands) matched with scanning electron microscope (SEM) with working voltage 15 kV. A Mastersizer 2000 laser diffraction particle size analyzer (Malvin, UK) was used to measure the particle size of pyrolusite and pyrite, and water was used as dispersant, with the refractive index of the dispersion medium, the refractive index of the sample and the imaginary refractive index of the sample set according to the recommended values of the system.

2.3. Experimental procedures

The experimental process was illustrated in Fig. 2. In order to select the optimum experiment conditions, single factor experimental conditions were carried out. Based on these single factor experiments, the optimum conditions were determined. Firstly, before the leaching experiments, pyrolusite and pyrite were dried in a constant temperature blast drying box at 105 ℃ for 2 h to remove moisture from the mineral surface, and then 20.00 g of pyrolusite and different quality of pyrite were weighed by analytical balance. Different volumetric concentrations of sulfuric acid were added to the mixed sample according to the liquid-solid ratio of 10:1. Then the sample was placed into the reaction container and poured it into sulfuric acid for reaction. In the heating stage, the heating time was automatically recorded, and the heating rate of microwave heating was synchronously controlled with the conventional heating till 90 ℃ (±0.2 ℃), resulting from the adjusting on the microwave output power.

After 2.5 h of reaction, the leaching residue and leaching solution were obtained by filtering the reaction products in the glass container. The leaching residue was washed with deionized water for 2-3 times to remove the possible residual manganese ions on the surface and dried in the constant temperature blast drying box at 50 ℃. According to the national standard (GB/T1506-2016), the content of Mn in the leaching solution was determined with 0.04 mol/L solution of $(NH_4)_2Fe(SO_4)_2$. The leaching rate of manganese ore in leaching solution was calculated by Eq. 1. The specific calculation formula of the manganese leaching rate was expressed as follows:

$$\eta = \frac{m}{M \times W} \times 100\% \tag{1}$$

where η means the leaching rate of manganese, *m* represents the mass of manganese in lixivium, *M* indicates the mass of manganese ore, *W* expresses the content of manganese in pyrolusite.

The experimental process was mainly composed of two identical mechanical agitators (DSX-120, Hangzhou instrument and Electrical Appliance Co., Ltd.). The constant temperature blast drying box used in the experiment was purchased in Shanghai Yiheng Scientific instrument Co., Ltd. The temperature measurement was consisted of two digital K-type thermocouples with accuracy of ±0.1 °C and fast response. A glass container made of quartz was used, which was a non-absorbing material to microwave energy [34]. The only difference between the two setups was the heating method. Microwave heating was dependent on microwave radiation, while conventional heating was mainly heated by water bath.

3. Results and discussion

3.1. Reaction principle

The reduction of manganese in the pyrolusite using pyrite in sulfuric acid medium mainly follows the following reaction equations (Eq.2-5) [8, 35,36]

$$2FeS_{2(s)} + 15MnO_{2(s)} + 14H_2SO_{4(aq)} = 15MnSO_{4(aq)} + Fe_2(SO_4)_{3(aq)} + 14H_2O_{(l)} \quad (2)$$

$$FeS_{2(s)} + H_2SO_{4(aq)} = FeSO_{4(aq)} + H_2S_{(g)} + S_{(s)} \quad (3)$$

$$2FeS_{2(s)} + 9MnO_{2(s)} + 10H_2SO_{4(aq)} = 9MnSO_{4(aq)} + Fe_2(SO_4)_{3(aq)} + 10H_2O_{(l)} + 2S_{(s)} \quad (4)$$

$$FeS_{2(s)} + Fe_2(SO_4)_{3(aq)} = 3FeSO_{4(aq)} + 2S_{(s)} \quad (5)$$

Under acidic conditions, Fe^{2+} and S_2^{2-} are used as reductants to reduce Mn (IV) to Mn (Ⅱ). In the reaction process, attributed to the oxidation of S_2^{2-}, elemental sulfur (S) may be formed. Therefore, thermodynamic analysis is needed to analyze the possibility for the formation of sulfur in the solution. The calculation of the thermodynamic parameters involved in the reaction depends on the calculation of Factsage® for Microsoft Windows, ver. 7.3, wherein the thermodynamic database is Thermfact/CRCT (Canada) and GTT-Technologies (Germany). The results of thermodynamic calculation were shown in Fig. 3(a) and the schematic diagram of the reaction process was presented in Fig. 3(b), respectively.

In Fig. 3(a), thermodynamic analysis denoted that the formation of sulfur elemental ($\triangle G<0$) during the reduction of pyrolusite by pyrite is very possible with the increase of temperature (273.15K-373.15K). The mechanism of the reaction process of ions in the solution is illustrated in Fig. 3(b). In addition, the formation of elemental sulfur was also reported in the leaching of similar sulfide ore [36]. It is attributed to the existence of free sulfur elements, which adsorbed on the mineral surface, resulting in the formation of a hydrophobic sulfur passivation layer, further inhibiting the reaction and reducing the leaching rate [13, 14]. Therefore, it is hoped that the dipole rotation mechanism of microwave heating on ionic solution can be used to reduce the formation of this passivation layer.

3.2. Effect of leaching time on Mn (II) leaching

The effect of leaching time (0 h-2.5 h) on the extraction efficiency of manganese was observed in Fig. 4, wherein the leaching temperature was 90 ℃, an initial sulfuric acid concentration was 1.2 mol/L with 240 mL sulfuric acid, the m(pyrite)/m(pyrolusite) = 0.2, liquid/solid (L/S) was 10:1, and the stirring speed was 400 rpm. It is demonstrated from Fig. 4 that the leaching rate of manganese has a positive relation with the reaction time, and the difference between the leaching rates responding to the different heating approach was enhanced with the increase of reaction time. When the manganese was leached under microwave heating for 2 h, the leaching rate of manganese was obtained at 80.04%.

The leaching rate obtained with microwave heating for 2 h was higher than leaching rate obtained with conventional heating for 2.5 h (75.08%), indicating that microwave heating enhanced the reaction process, shorten the reaction time and improved the leaching rate. Yuan et al. found that the low leaching rate of manganese under conventional heating conditions was mainly attributed to the dissolution of pyrite to produce elemental sulfur (Eq.2-5) [35,36]. The sulfur element produced during the reaction will accumulate and adsorb on the ore surface to form a passivation layer, and the reduction reaction (Eq.1) will be interrupted due to the hydrophobicity of the sulfur passivation layer [37-38]. However, microwave heating promotes the rotation of polar molecules (H_2O) in the solution with the changing electromagnetic field, which reduces the accumulation of sulfur elements in the solution and slows down the appearance of sulfur passivation layer on the ore surface.

Additionally, in order to verify this hypothesis, we carried out XRD characterization and elemental analysis of the leaching residue under conventional heating and microwave heating.

The XRD pattern and the elemental analysis of the leaching residue under the condition of conventional heating and microwave heating shows that there were few elemental sulfur in the leaching residue heated by microwave, but elemental sulfur was existed in the conventional leaching residue, and the experiment results are demonstrated in Fig. 5 and Fig. 6, respectively.

Both analysis techniques (XRD, SEM-EDS) indicated that the elemental sulfur appeared in the conventional leaching residue (as shown in Fig. 5 and Fig. 6). The sulfur was absented in the leaching residue of microwave heating. The results confirmed that the formation of elemental sulfur during leaching with conventional heating conditions [13-14, 38-39]. Fig. 7 indicated the schematic diagram of the formation of sulfur passivation layer during microwave radiation leaching and conventional leaching. During the conventional heating leaching process, free elemental sulfur was generated in the solution due to the presence of side reactions, the sulfur element was gradually accumulated and adsorbed on the surface of pyrolusite, resulting in the formation of hydrophobic passivation layer. Due to the existence of this passivation layer, pyrolusite was failed to contact with the reducing agent and was ineffectively reduced to bivalent manganese ions dissolved in the solution [36]. However, the unique dipole rotation in the process of microwave heating has led to the agitation of polarity. It inhibited the adsorption of free elemental sulfur as well as the formation of passivation layer, and the friction between polar molecules has led to serious ore corrosion, and the contact area was increased as a result of the formation of porous structure (as shown in Fig. 6) which further promoting the reaction speed. Finally, a high leaching rate was obtained.

3.3. Effect of the mass ratio of pyrite and pyrolusite on Mn (II) leaching

Fig. 8 illustrated the effect of different reductants quantity on the leaching efficiency of manganese, recovered with a leaching temperature of 90 ℃, a sulfuric acid volume of 240 mL with an initial concentration sulfuric acid of 1.2 mol/L, a liquid/solid (L/S) of 10:1, a stirring speed of 400 rpm, and a leaching time of 2.5 h. As shown in Fig. 8, the concentration of manganese ion in the solution increased gradually with the rise of reaction time. The leaching rate of manganese under microwave-assisted heating(95.07%) was optimized compared to that under conventional heating (75.08%). For the same manganese leaching rate (75%), the amount of reducing agent required for microwave-assisted leaching (10:1.5) is about 25% lower than that for conventional heating leaching (10:2). The low consumption of reducing agent is of great significance for saving resources and protecting the environment, and also provides a new direction for reduction reaction. Since the migration of ions in the solution was induced by microwave electromagnetic field, the convection in the solution was enhanced, resulting in an improved leaching rate[40]. Under the same conditions, the improved convection of H^+ will accelerate the dissolution of pyrite, and the released ions act in directional movement affected by electric field. Therefore, the leaching process was encouraged, and the leaching rate of microwave-assisted heating was higher than that of conventional heating.

Fig. 9 displayed the SEM images of the samples extracted by different heating approach, respectively. SEM images show that there are obvious cracks and irregular pore structure on the surface of the microwave leaching residue after 2.5 h of leaching, whilst the surface of the mineral is relatively smooth under conventional heating. The reason is that the absorption coefficient of microwave energy of different components (MnO_2, SiO_2, FeS_2, etc.) in the mineral is different, which leads to different heating rates and thus creating temperature gradient inside the mineral [33]. The existence of temperature gradient leads to cracks in the ore from the inside to the outside. Additionally, the unique heating mechanism caused by electromagnetic field in microwave field accelerates the effective collision of H^+, Fe^{2+} , and S_2^{2-} with MnO_2 in pyrolusite, and thus accelerates the chemical reaction, which leads to the formation of porous structure on the mineral surface. As a result, the detected porous structure of the mineral surface further increases the contact area between the mineral and the solution, which promotes the occurrence of the reaction.

3.4. Effect of sulfuric acid on Mn (II) leaching

The leaching degree of Mn at different sulfuric acid concentrations (0.6 mol/L to 1.2 mol/L) was depicted shown in Fig. 10. By keeping the other experimental factors at constant (leaching time of 2.5 h, 9 leaching temperature of 0 °C, m(pyrolusite)/m(pyrite) of 10:2, the ratio of liquid/solid was 10:1 and the corresponding stirring speed of 400 rpm). Fig. 10 indicated that the leaching rate of manganese has a positive relation with the sulfuric acid concentration. However, Fig.10 shows that the concentration of manganese ion in the leaching solution under the condition of microwave-assisted heating is higher than that under the condition of conventional heating. The reason for this phenomenon may be that microwave heating can promote the ionization of hydrogen ions in sulfuric acid (H_2SO_4), which was supported by Eq. 1. The dissolution of hydrogen ions will increase the impact and contact to metal minerals [41, 42], thus accelerating the leaching of manganese ions. The peak value for microwave-assisted leaching rate (95.07%) was much higher than that of conventional heating leaching (75.08%) under the same experimental condition. Moreover, it can be seen in Fig. 10 that under the condition of microwave-assisted heating, the leaching rate of manganese obtained through using 0.8 m concentration of sulfuric acid (79.58%) was slightly higher than that obtained through using 1.2 mol concentration of sulfuric acid under conventional heating conditions (75.08%). Therefore, microwave-assisted heating can significantly reduce the amount of required sulfuric acid [43,44]. These results also provide a novel idea for the experiment similar to those carried out under acidic conditions.

4. Conclusions and Outlook

In order to improve the leaching rate of manganese in pyrolusite, this study proposed a new process based on microwave-assisted method which was compared with conventional heating under the condition of single factor experiment, considering that pyrolusite has decent microwave absorbing ability. Moreover, the mechanism of microwave efficient leaching of manganese from low-grade pyrolusite was described. The following conclusions are drawn.

(1) With the optimized experimental conditions (L/S=10:1, 1.2 mol/L of sulfuric acid concentration, $M_{(pyrolusite)}$: $M_{(pyrite)}$=0.2, 2.5 h of leaching time), the leaching rate of Mn was 95.07% under microwave-assisted heating, while that was 75.08% under conventional heating. Advantaged from microwave heating, the leaching rate of manganese was improved, and the leaching period was effectively reduced.

(2) The mechanism of microwave dipole rotary heating has explained the advantage of microwave heating, which reduced the formation of passivation layer on the mineral surface, and thus guaranteed the efficient reaction rate.

(3) Additionally, the unique coupling mechanism of the microwave created cracks on the mineral surface and increased the reaction area during leaching, which accelerated the reaction rate.

Thus, microwave heating, as a new heating process, has great potential and advantages in the process of mineral extraction, such as reducing the reaction duration, reducing the addition cost of reducing agents, saving resources, improving extraction efficiency, and so on.

Acknowledgments

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Table 1 Chemical compositions of pyrolusite.

Compositions	Mn	Si	Fe	Al	Ca
Mass %	26.39	16.18	9.88	2.04	0.91

Table 2 Chemical compositions of pyrite.

Compositions	Fe	S	Zn	Si	Ca
Mass %	41.58	38.20	1.43	0.93	0.70

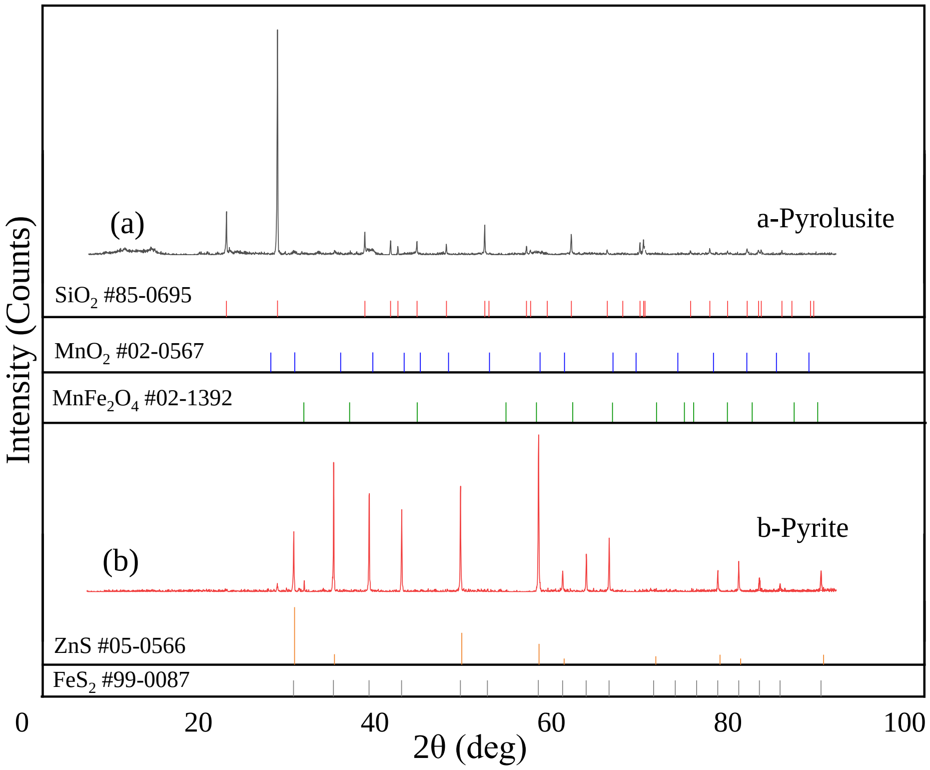

Fig. 1 The XRD patterns of pyrolusite (a) and pyrite (b).

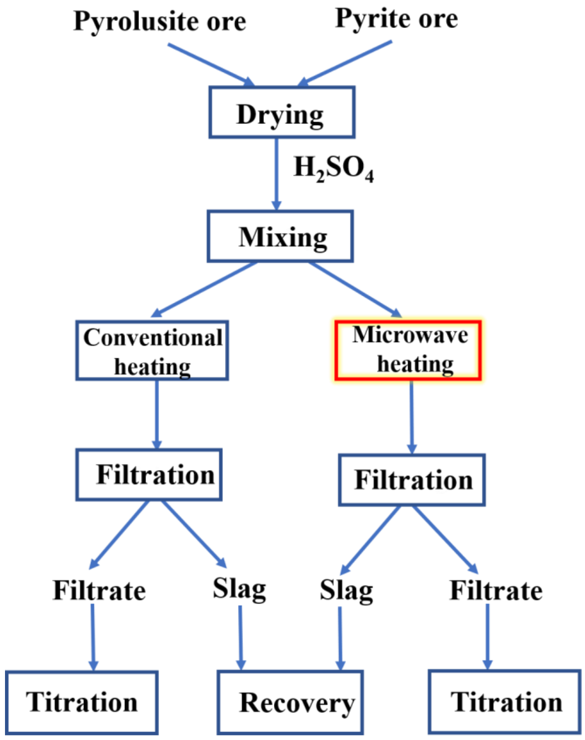

Fig. 2 Schematic diagram of the experimental sequence.

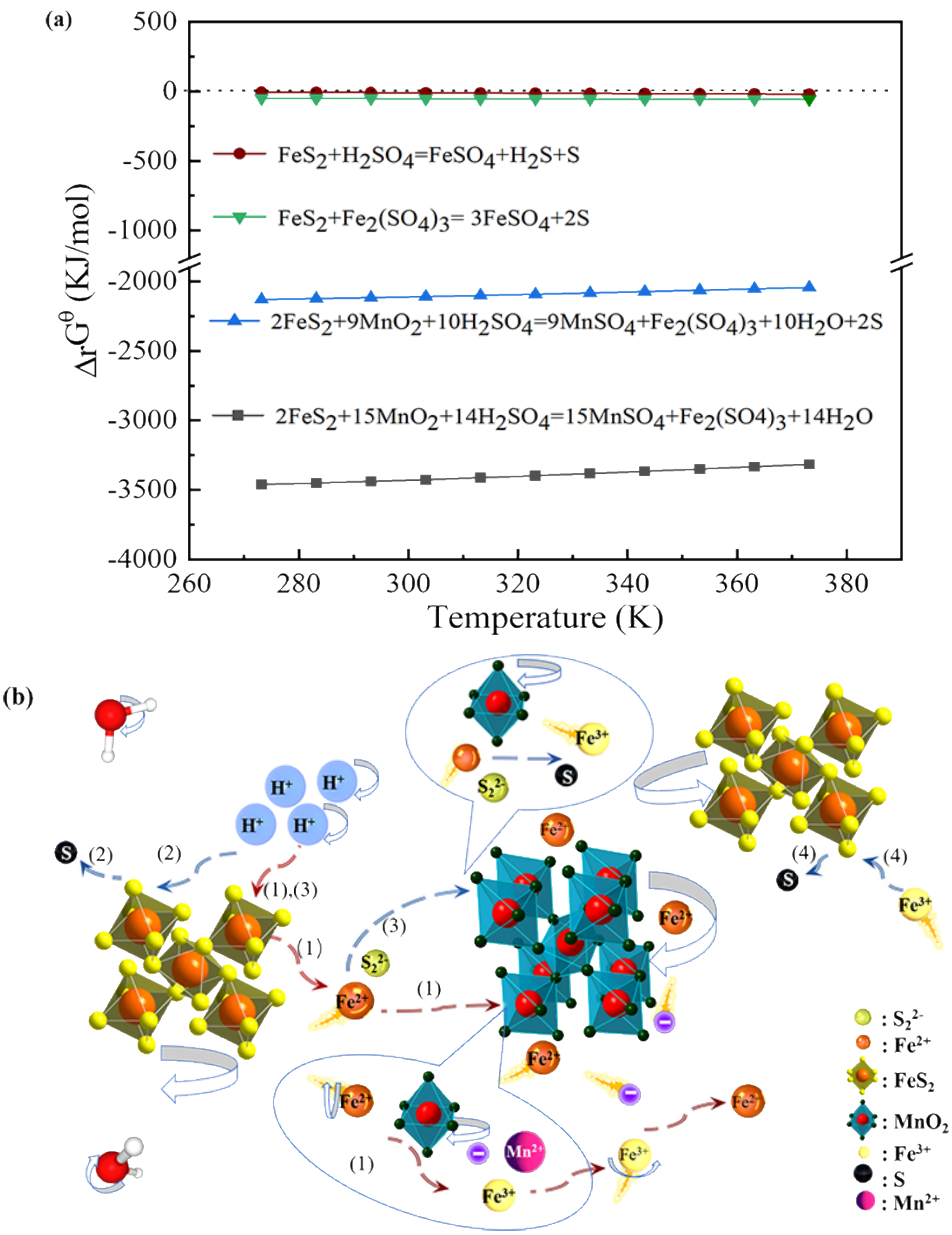

Fig. 3 Schematic diagram of reaction thermodynamics simulation (a) and schematic diagram of reaction process in solution (b).

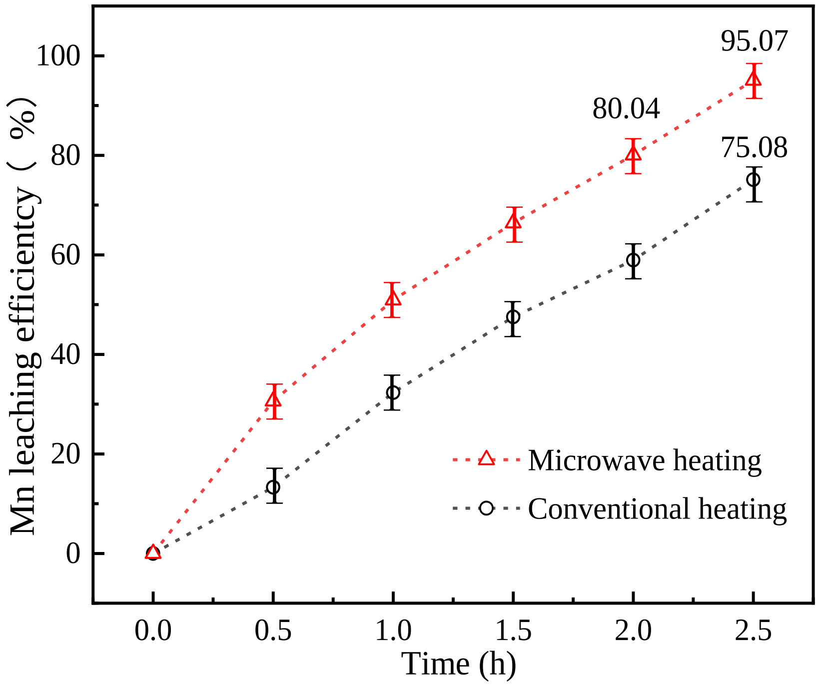

Fig. 4 Effect of leaching time on leaching of Mn.

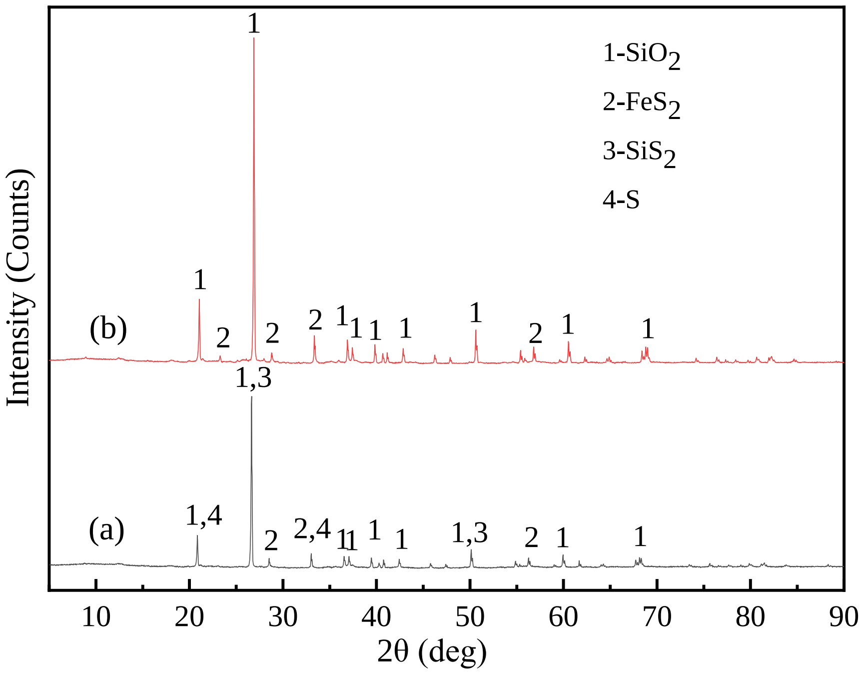

Fig. 5 The XRD pattern of leaching residue: conventional heating (a), microwave heating (b).

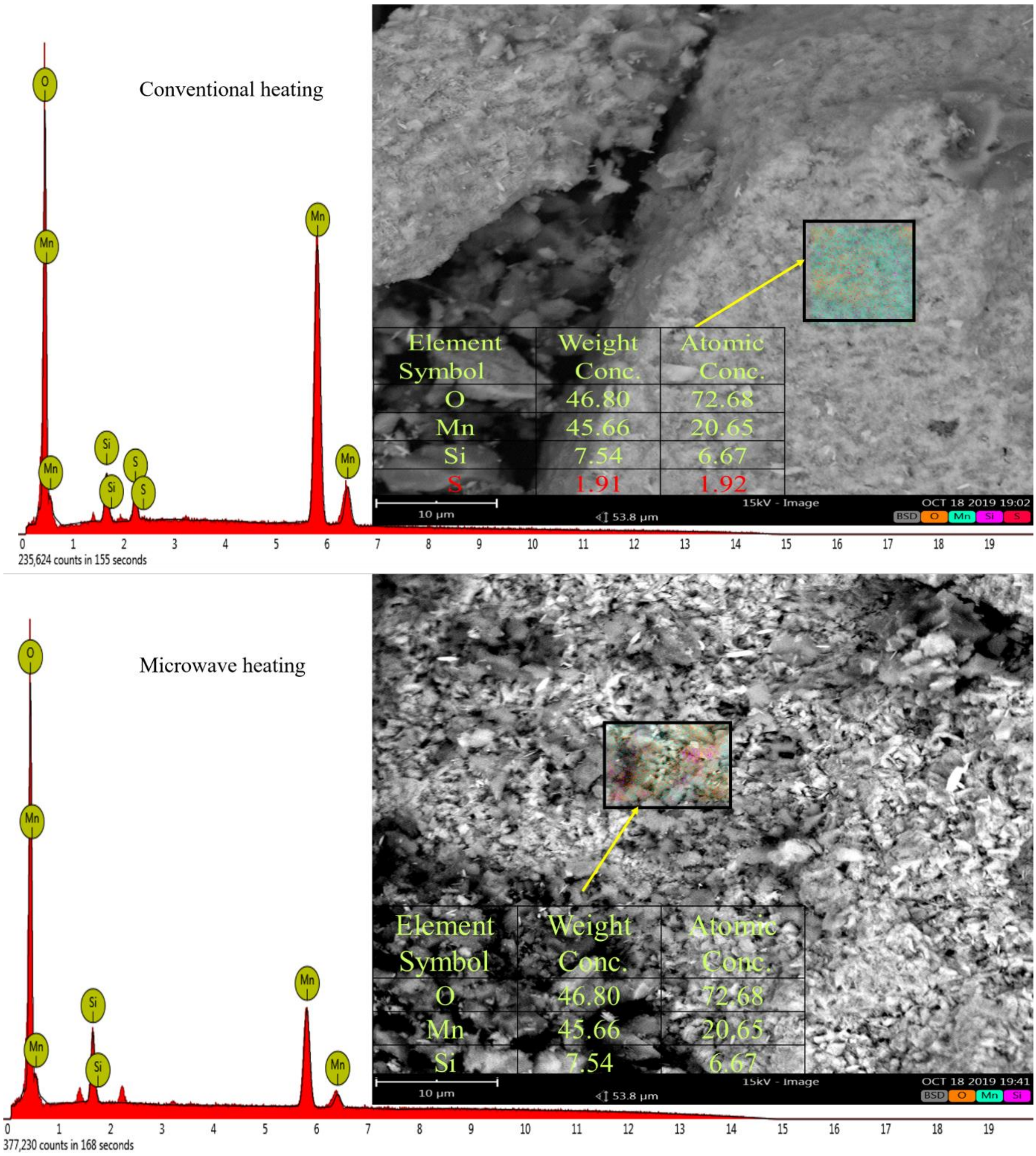

Fig. 6 SEM-EDS of leaching residue under microwave heating and conventional heating methods.

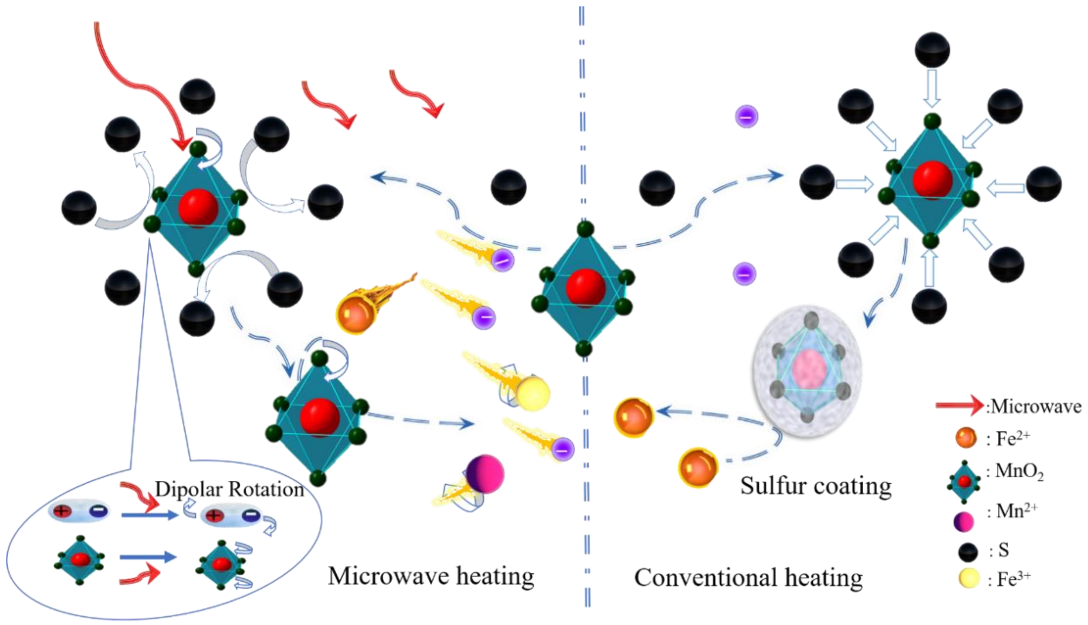

Fig. 7 Schematic diagram of the formation of the sulfur passivation layer under microwave heating and conventional heating methods.

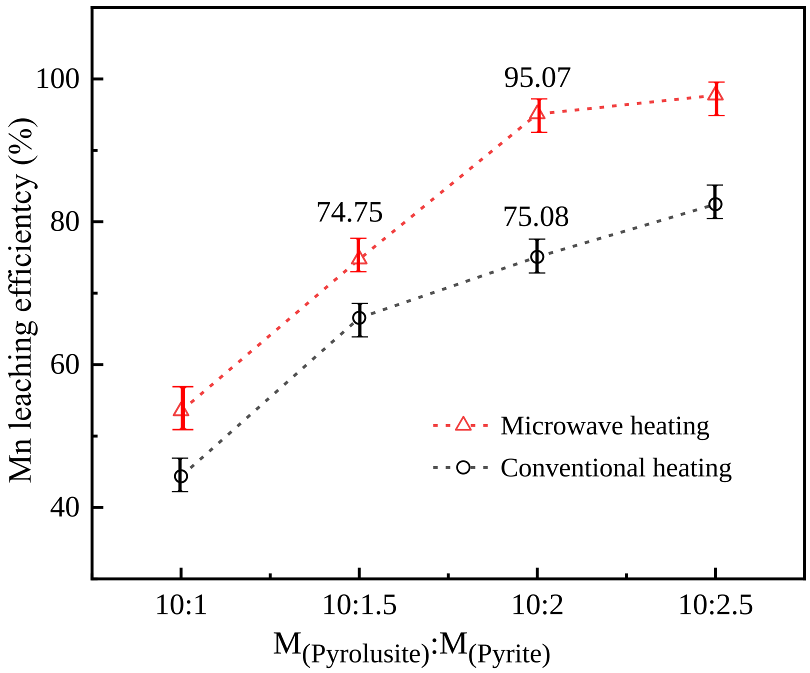

Fig. 8 Effect of the mass ratio of pyrite and pyrolusite on leaching of Mn.

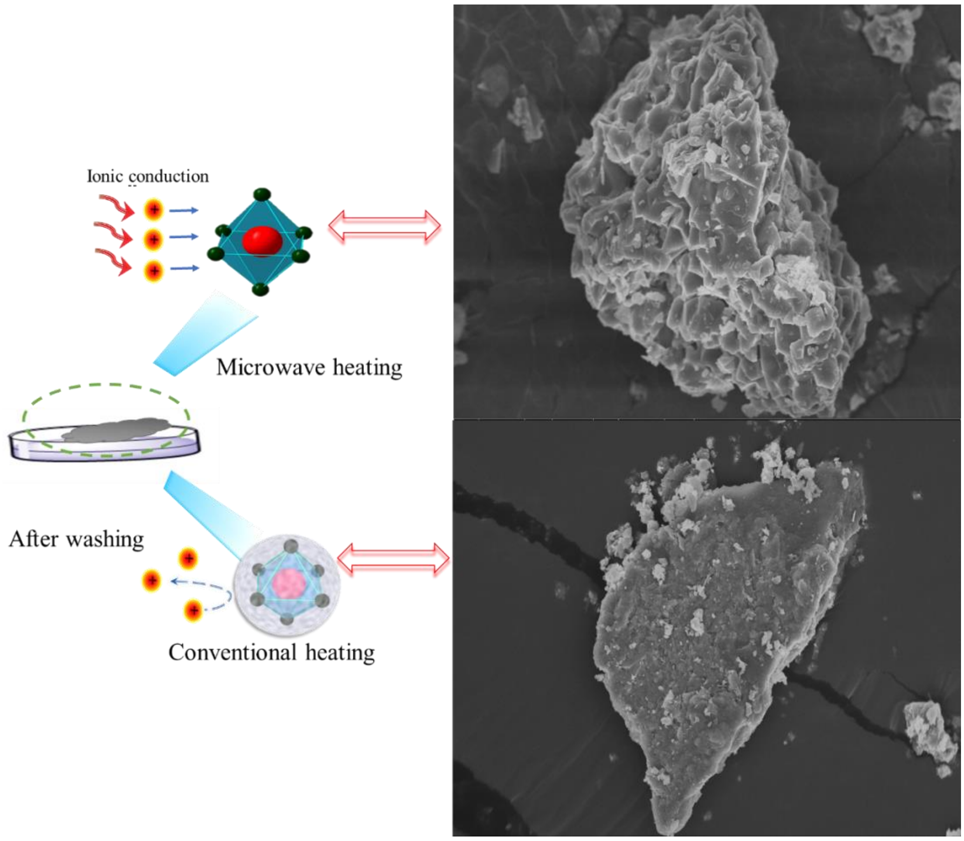

Fig. 9 Scanning diagram of surface morphology of leaching residue at 10000 times.

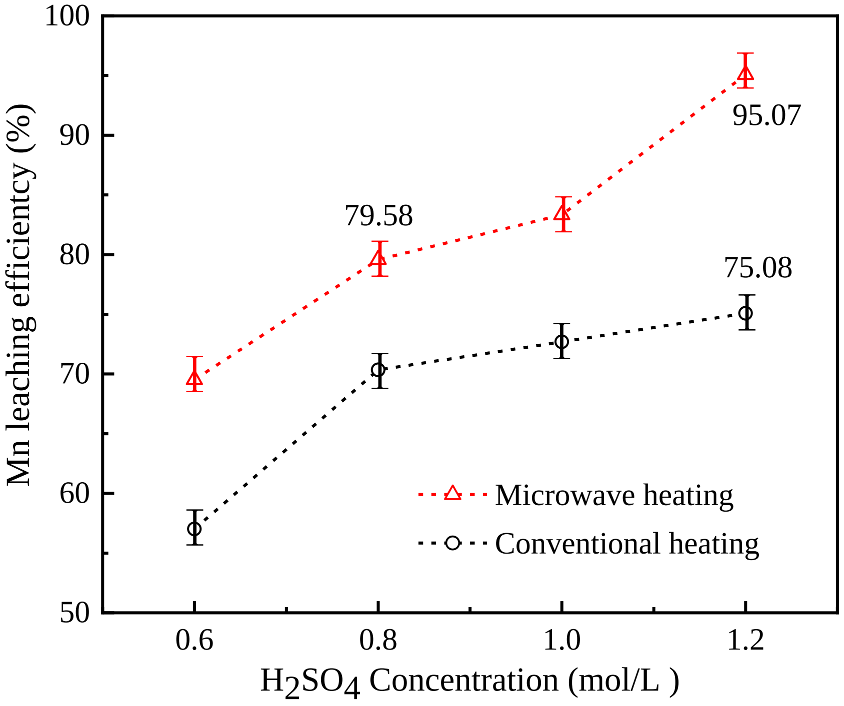

Fig. 10 Effect of sulfuric acid on leaching of Mn.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

Prof. Guo Chen, Prof. Jin Chen and Prof. Shenghui Guo conceived and designed the study. Mr. Shunda Lin, Mr. Yong Yang, Dr. Mamdouh Omran and Prof. Guo Chen performed the experiments. Prof. Guo Chen and Prof. Shenghui Guo provided the raw materials. Prof. Jin Chen, Prof. Guo Chen and Dr. Lei Gao provided the microwave high temperature furnace. Mr. Kangqiang Li, Mr. Shunda Lin, Dr. Lei Gao and Prof. Jin Chen wrote the paper. Mr. Shunda Lin, Mr. Kangqiang Li, Dr. Mamdouh Omran, Dr. Lei Gao and Prof. Guo Chen reviewed and edited the manuscript. All authors read and approved the manuscript.