A green preparation of Mn-based product with high purity from low-grade rhodochrosite

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Abstract. The low-grade rhodochrosite, the main resources for exploitation and applications in China, contains multiple elements such as iron, silicon, calcium and magnesium. So the conventional preparation of manganese sulphate and manganese oxide with high purity from electrolytic product is characterized by long production-cycle, high-resource input and high-pollution discharge. In our work, a sustainable preparation approach of high pure MnSO₄ solution and Mn₃O₄ was studied by employing low-grade rhodochrosite (13.86%) as raw material. The repeated leaching of rhodochrosite with sulphuric acid was proposed in view of the same ion effect, in order to improve the solubility of Mn²⁺ and inhibit the dissolution of the impurities Ca²⁺ and Mg²⁺. With the aid of theoretical calculation, BaF₂ was chosen to remove Ca²⁺ and Mg²⁺ completely in the process of purifying. The results showed that the impurities such as Ca²⁺, Mg²⁺, Na⁺ were decreased to less than 20ppm, and the Ni- and Fe- impurities were decreased to less than 1ppm, which meets the standards of high pure reagent for energy and electronic materials. The extraction ratio and the recovery ratio of manganese reached 94.3% and 92.7%, respectively. Moreover, the high pure Mn₃O₄ was one-step synthesized via the oxidation of MnSO₄ solution with the ratios of OH⁻/Mn²⁺=2 and Mn²⁺/H₂O₂=1.03, and the recovery rate of manganese reaches 99%.

1. Introduction
Low-grade manganese carbonate ores (≤14%) becomes gradually the main resources for exploitation and applications in China according to national mineral resources survey [1, 2]. Therefore, the electrolytic deposition technique of rhodochrosite faces great challenges including low electrolysis efficiency, high-resource input and high-pollution discharge [3-5]. Recently, more and more amount of manganese series with high or super high purity such as MnSO₄, MnO₂, Mn₃O₄ and MnO is demanded with the development of energy and electronic materials. Due to low-grade rhodochrosite containing multiple elements such as iron, silicon, calcium and magnesium, conventional preparation process of manganese oxide such as Mn₃O₄ with high purity from electrolytic manganese metal is characterized by long production-cycle, high-pollution discharge and high energy consumption [6, 7]. By contrast, hydrometallurgical method combined with thermal decomposition, hydrothermal synthesis and sol-gel processes has been widely studied because of its high efficiency, low consumption and low cost [8]. But the key problem in direct preparation of manganese series from low-grade rhodochrosite is to remove completely the multiple impurities such as iron, silicon, calcium and magnesium [9]. So it is urgent to develop a sustainable alternative approach of high pure Mn-based products with characters of short process, high efficiency and environmental friendly.
In our work, the preparation technique of manganese sulphate with high purity directly from low-grade rhodochrosite ore (containing 13.86\% Mn) was studied and improved intensively. In detail, the repeated leaching of rhodochrosite with sulfuric acid was proposed herein to improve the solubility of Mn$^{2+}$ and inhibit the dissolution of the impurities Ca$^{2+}$ and Mg$^{2+}$, simultaneously. Additionally, the short purifying process was also explored with the aid of theoretical calculation. The recovery ratio of manganese and removal ratio of the impurity were evaluated via chemical titration and inductively coupled plasma (ICP) analysis, respectively. Furthermore, the high pure Mn$_2$O$_4$ was synthesized via the oxidation of MnSO$_4$ solution. Finally, the proposed green preparation directly from low-grade rhodochrosite has also been compared herein with the conventional technique from electrolytic manganese from the point of view of energy-efficiency and environmental friendly.

2. Experimental

The rhodochrosite samples were provided by BaoJingTianhe Manganese Industry Company, Hunan province, China. The samples were ground to powder with ≤2 mm in diameter. Firstly, the repeated leaching approach for rhodochrosite was performed herein, 10 g rhodochrosite powder, 3.6 ml sulfuric acid solution (98 \%) and deionized water were added into a 150 ml conical flask with solid-liquid ratio of 1:7 in weight and reacted for 2 h at 85 °C under vigorous stirring (300 r/min) [10-12]. Then 10 g rhodochrosite powder together with X ml sulfuric acid solution (98\%) and deionized water were added into the initial leaching solution with stirring. Then the residues were filtered to get the first repeated leaching solution. And the aforementioned procedures were repeated 0-4 times, so the total leaching times disperse in the range of 1-5. Moreover, the amount of sulfuric acid solution for each addition was calculated as the following formula:

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X=0.0779a-b/38.25
\]  

where X is the volume of sulfuric acid solution (ml), a is the total volume of the leaching solution (ml) and b is the concentration of H$^+$ in the leaching solution (mol/l).

In the purification process, the coarse manganese sulphate solution was adjusted to pH=4.0 using Ba(OH)$_2$ solution. After standing for 24 h, the precipitate was filtered. Subsequently, BaF$_2$ powder was introduced in the solution and stirred at 25 °C for 3 h. Then the precipitate was separated and the filtrate was adjusted to pH=8.0 using Ba(OH)$_2$ solution. Finally, the precipitate was filtered repeatedly and pure MnSO$_4$ solution was expected to be obtained.

In the synthesis of Mn$_2$O$_4$ process, 10ml pure MnSO$_4$ solution were put in 150ml conical flask, and a certain amount of KOH solution (1 mol/l) was added with the continuous stirring. Then the certain amount of H$_2$O$_2$ solution (30 wt.\%) was added dropwise. After stirring for 10 minutes, the solution was filtered and the precipitation was washed repeatedly with deionized water. Mn$_2$O$_4$ powder was obtained after dried in 120 °C.

The chemical composition of the rhodochrosite samples was chemically analyzed via chemical titration. While, the mineral composition of the samples was investigated by X-ray diffraction (XRD) on a Rigaku D/max (Japan) diffractometer. The data were collected at a scan speed of 5°/min on the 2θ range from 10° to 100°. The recovery ratio of manganese was evaluated via chemical titration with ammonium ferrous sulfate. The concentration of impurities such as calcium and magnesium ions was determined by ICP analysis (Spectroflame ICP, 2.5 kW, 27 MHz).

3. Results and Discussions

3.1. The composition of rhodochrosite samples

The chemical compositions of rhodochrosite samples are listed in table 1. The concentration of manganese is only 13.86 \%, which is typical low-grade manganese carbonate ores. In addition, the rhodochrosite samples are mainly composed of MnCO$_3$, SiO$_2$, CaMg(CO$_3$)$_2$ and FeSO$_4$ et al as shown in figure 1.
Table 1. The major chemical compositions of the rhodochrosite sample (wt.%).

|     | Mn  | Ca  | K   | Mg  | Ni  | Zn  | Na  | Fe  | Si  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| %   | 13.86 | 3.80 | 1.80 | 1.32 | <0.005 | 0.023 | 0.86 | 3.10 | 16.63 |

Figure 1. XRD patterns of the low-grade rhodochrosite.

3.2. The preparation of high pure MnSO₄ solution

In the repeated leaching process, the accumulative content of impurity in the leaching solution and the extraction ratio of Mn were characterized by ICP. The total recovery ratio of manganese is 94.3% after 5 leaching times. The standard deviation for the four parallel experiment results is below 0.73%, and the average concentration values are given in table 2.

Figure 2 demonstrates that the concentration of manganese is enhanced significantly and the accumulative content of Ca²⁺ is reduced obviously with the increase of the repeated leaching times. Though the absolute concentration of Mg²⁺ still increases, its extraction ratio is reduced in the repeated leaching process. Based on the same ion effect, the repeated leaching approach not only improves the concentration of Mn²⁺ but also inhibits the dissolution of the impurities Ca²⁺ and Mg²⁺.

The main impurities in the coarse manganese sulphate solution obtained from the leaching process consist of Al³⁺, Fe²⁺, Fe³⁺, Mg²⁺, Ca²⁺ and a small quantity of heavy metals. Among them, a large proportion of Ca²⁺ ions could be precipitated with SO₄²⁻ and removed with insoluble silica. Moreover, Ca²⁺ and Mg²⁺ cations are removed further by adding BaF₂ as the precipitant at pH=4.0. Finally, the iron, aluminium and heavy metals could be removed in hydrolysis via adjusting pH=8.0 with Ba(OH)₂.

According to ICP analysis of the manganese sulphate solution in Table 3, the removal rates of most impurities are above 99%. The Fe element and heavy metal impurities including Ni have been decreased to less than 1 ppm, and the contents of calcium, magnesium and sodium have been decreased to less than 20 ppm, which meets the standards of high pure reagent for energy and electronic materials. Mn content in the manganese sulphate solution is determined by titration with ammonium ferrous sulphate. It is confirmed that the recovery ratio of manganese reaches 92.7% in the purifying process.

Table 2. The average value of ICP analysis of ionic concentration in the repeated leaching solution.

| Total leaching times | 1    | 2    | 3    | 4    | 5    |
|---------------------|-----|-----|-----|-----|-----|
| Mn²⁺ (g/L)          | 19.42 | 38.49 | 56.02 | 71.44 | 84.05 |
| Ca²⁺ (mg/L)         | 540.2 | 533.7 | 522.2 | 504.0 | 486.0 |
| Mg²⁺ (mg/L)         | 1027.3 | 1165.0 | 1277.6 | 1425.0 | 1687.2 |
Figure 2. Effect of the leaching times on the ionic concentration.

Table 3. ICP analysis of the manganese sulphate solution.

| Elements | Mn  | Ca  | Mg  | Ni  | Fe  | Al  | Na  |
|----------|-----|-----|-----|-----|-----|-----|-----|
| Before purifying/ppm | 84050 | 486 | 1687 | 188 | 4060 | 3210 | 650 |
| After purifying/ppm | 77910 | 2.599 | 15.82 | 0.187 | 0.083 | 0.006 | 15.82 |
| Recovery ratio/% | 92.7 | 0.5348 | 0.9378 | 0.0995 | 0.0020 | 0.0002 | 2.434 |

In comparison with conventional technique from electrolytic manganese, the power consumption has been reduced to ≤2000 kWh/t(product) in our short-process approach. Moreover, comprehensive recovery rate of manganese increases significantly. As known, the quality of wastewater occurred in the process of electrolytic deposition is complex, containing toxic substances and high content of ammonia/nitrogen. By contrast, the wastewater generated from our short-process approach shows low content of ammonia/nitrogen about 500 mg/t(product) and no toxic emissions. Our study contributes to the sustainable application of low-grade rhodochrosite.

3.3. The preparation of high pure Mn₃O₄
Mn₃O₄ was synthesized from the oxidation of MnSO₄ by employing H₂O₂ as oxidant. The one step preparation process at room temperature could significantly reduce the energy consumption in the comparison of the traditional preparation of Mn₃O₄ from electrolytic manganese. The reaction
mechanism of Mn$_3$O$_4$ in the alkaline solution is shown as follow. The effects of OH$^{-}$ and oxidant are analysed as seen in figure 3 and 4.

$$3\text{Mn}^{2+} + \text{H}_2\text{O}_2 + 6\text{OH}^- = \text{Mn}_3\text{O}_4 + 4\text{H}_2\text{O}$$  \hspace{1cm} (2)

Figure 3. XRD patterns of samples with different rations of OH$^{-}$/Mn$^{2+}$.

Figure 4. XRD patterns of oxidative products with different rations of Mn$^{2+}$/H$_2$O$_2$.

Figure 3 shows that the oxidative products depends on the concentration of OH$^{-}$ in the solution. In detail, pure Mn$_3$O$_4$ is obtained when OH/Mn$^{2+}$ ratio is adjusted to be 2.00. While, MnO(OH) and $\gamma$-MnO$_2$ become the major phases with the decrease of OH$^{-}$ concentration. By contrast, $\beta$-MnO(OH) instead of Mn$_3$O$_4$ appears at the much higher pH value.

With a certain concentration of Mn$^{2+}$ and OH$^{-}$ in the solution, the content of H$_2$O$_2$ is responsible for the oxidative products as seen in figure 4. In view of the self-decomposition of H$_2$O$_2$ (in formula 3), additional H$_2$O$_2$ is introduced to guarantee the complete synthesis of Mn$_3$O$_4$.

$$\text{H}_2\text{O}_2 = \text{H}_2\text{O} + 1/2\text{O}_2$$  \hspace{1cm} (3)
According to Figure 3 and 4, γ-Mn$_3$O$_4$ (JCPDS No. 24-0734) is obtained with high purity when the ratios of OH/Mn$^{2+}$ and Mn$^{3+}$/H$_2$O$_2$ are controlled to be 2.00 and 1.03, respectively. In the short process of Mn$_3$O$_4$ preparation, the recovery rate of manganese increases to 99%. Unlike the conventional preparation of Mn$_3$O$_4$ from electrolytic manganese, the synthesis of Mn$_3$O$_4$ directly from low-grade rhodochrosite is a green technique with character of short process, low energy consumption and environmental friendly.

4. Conclusions

The preparation of high pure MnSO$_4$ and Mn$_3$O$_4$ with the sustainable, short and effective process from low-grade rhodochrosite ore (13.86%) has been developed in the paper. The results demonstrate that the extraction ratio and the recovery ratio of manganese in purifying process reach 94.3% and 92.7%, respectively. The concentration of manganese is accumulated in the repeated leaching solution, and simultaneously the extraction ratio of impurities of Ca$^{2+}$ and Mg$^{2+}$ is reduced significantly. The repeated leaching method provides an approach to the effective use of the low-grade rhodochrosite and the reduction of the wastewater discharge. In addition, BaF$_2$ is chosen as precipitant to remove Ca$^{2+}$ and Mg$^{2+}$ completely. The purification process is combined with adjustment of the pH value of manganese sulfate solution using Ba(OH)$_2$, which contributes to an effective remove of impurities and a short process for purification. Based on the preparation of the high pure MnSO$_4$ solution, Mn$_3$O$_4$ is one-step synthesized at room temperature via the oxidation of Mn$^{3+}$ by employing H$_2$O$_2$ as oxidant, which is more efficient and less energy consumed than the conventional preparation of Mn$_3$O$_4$ from electrolytic manganese. Our study contributes to the sustainable application of low-grade manganese ore.

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