Preparation of nano manganese oxides by H$_2$O$_2$ in-situ oxidation: effect of regulation mechanism on physical and chemical properties

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Abstract

Manganese oxides showed many special physicochemical properties in many fields such as electrochemistry, adsorption and catalysis. They were widely used in cathode materials for lithium batteries, molecular sieves, catalytic materials and adsorbents. In this paper, in situ oxidation of manganese sulfate solution was conducted with H$_2$O$_2$ as oxidant, and the characterization means of XRD, SEM and BET were used. The purpose was to study the effects of different regulation mechanisms on the physical and chemical properties of manganese oxides such as morphology, phase composition, surface properties and specific surface area. The adsorption properties of $\gamma$-MnO$_2$ for Co and Ni in manganese ore leaching solution were tested. The results showed as follows. Under alkaline conditions, the main product of manganese sulfate solution oxidized by H$_2$O$_2$ was Mn$_3$O$_4$ spherical particles with a radius of about 50 nm, these particles had micropores or mesopores, the oxidation reaction rate was rapid, and the specific surface area and N$_2$ adsorption capacity changed with the change of reaction conditions. The temperature had a great influence on the micro morphology of the product. The micro morphology was slender nanorod when the temperature was 20 °C. With the increase of temperature, the length of nanorod became shorter. When the temperature rises to 50 °C, the rod became spherical. When the pH value decreased from 9 to 7, the diffraction peak of each crystal plane in the product Mn$_3$O$_4$ decreased gradually. The diffraction peak of $\gamma$-MnO$_2$ appeared when the pH value decreased to 5. All the products were $\gamma$-MnO$_2$ when the pH value decreased to 3. With the increase of Mn$^{2+}$ concentration, the grain size decreased and agglomeration was easy to occur. The optimum conditions were obtained as follows: the temperature was 30 °C, pH was 3, reaction time was 90 min, the mole ration of H$_2$O$_2$ to Mn$^{2+}$ was 1:1, and Mn$^{2+}$ concentration was 10 g l$^{-1}$. Under the optimum conditions, $\gamma$-MnO$_2$ with high specific surface area (172.41 m$^2$ g$^{-1}$) was prepared. This $\gamma$-MnO$_2$ has a good adsorption effect on Co and Ni in manganese ore leaching solution, and the adsorption efficiency could be reached 94.75% and 95.67%. This study would provide a reference for the preparation of manganese oxides with different physical and chemical properties.

1. Introduction

As a multifunctional material, manganese oxides (Mn$_3$O$_4$, MnO$_2$, etc) had shown many special physicochemical properties in many fields such as electrochemistry, adsorption and catalysis [1–4]. Manganese oxide had good ion exchange and molecular adsorption characteristics, and manganese was a multivalent metal so that electrons were easy to be transferred. In addition, it had the advantages of low price, rich resources, changeable crystal form and controllable valence state. Therefore, manganese oxide was widely used in the field of battery materials, sieves, catalytic materials and adsorbents [5–9]. It was known that the size, structure, morphology and chemical composition of manganese oxides had a great influence on the physical and chemical properties of the materials.
So it had become a research hotspot of manganese materials to improve their characteristics and broaden their application fields by adopting simple and fast experimental methods to regulate the valence state, lattice defects, morphology, grain size and composite structure of manganese oxides in recent years [12, 13]. The preparation methods of manganese oxides were various, mainly including hydrothermal [14, 15], sol-gel [16], chemical precipitation [17], thermal decomposition [18, 19] and solid phase synthesis methods [20]. However, due to the synthesis process, manganese oxide mainly entered the application field with the cheap features, and the added value of goods was not high [21]. In order to improve the application value of manganese oxide, the traditional synthesis method must be improved to prepare new functional materials with novel structure and outstanding properties of meeting the needs of modern industry [22]. There had been a lot of reports on the preparation of manganese oxide nanocrystals by hydrothermal method, but it is still a difficult problem in this field to find a cheap, environment-friendly and safe production process [23]. The method of in situ oxidation of manganese sulfate solution with H₂O₂ as oxidant proposed in this paper had many advantages. It would not introduce new impurities, the obtained product was more pure, it did not need to be carried out at high temperature, the reaction time was short, and the waste of resources was greatly reduced. The literature research shows [24] that the manganese oxide generated in situ in the solution has rich hydroxylated surface and more porosity, and more active adsorption sites could be provided. The interface properties and structural characteristics show that it has excellent adsorption of pollutants. MnO₂ has shown great potential in the field of adsorption, and has good adsorption effect on heavy metal ions in aqueous solution, but it has been a difficult problem for the adsorption of heavy metal ions in high concentration metal salt solutions [25]. In this study, the effects of different regulation mechanisms on the physical and chemical properties of manganese oxides such as morphology, structure, phase composition, surface properties and specific surface area were investigated, Mn₃O₄ and γ-MnO₂ with different physical and chemical properties were prepared in a controlled way. The control technology of preparing high purity manganese oxide could be controlled for the purpose of high adsorption performance, and then the adsorption of cobalt and nickel heavy metal ions was verified. It laid the theoretical foundation for the subsequent application of manganese series materials.

2. Experiment

2.1. Reagents and equipments
Analytical pure sulfuric acid, H₂O₂, NaOH and MnSO₄·H₂O were produced by Tianjin Kemio company. Digital pH meter (AZ8601) was produced by Shanghai Yidian Scientific Instrument Co., Ltd, Constant temperature drying oven (DHG-9005A) was produced by Shanghai Yiheng Scientific Instrument Co., Ltd, Constant temperature water bath pot (HH-3), electric mixer (JJ-1) and vacuum suction filter pump (P4Z) was produced by Shanghai lichen Instrument Technology Co., Ltd, electronic analytical balance (PL2002) was produced by METTLER TOLEDO group.
2.2. Preparation process of manganese oxides
Firstly, a certain concentration of manganese sulfate solution was prepared, and then 500 ml of it was taken into a beaker. It was heated to a certain temperature by a constant temperature water bath and stirred at the speed of 200 r min\(^{-1}\). After that, the pH value of the solution was adjusted with 30 g l\(^{-1}\) NaOH solution, and a certain amount of 30% analytical pure H\(_2\)O\(_2\) was slowly dropped. After a certain reaction time, the stirring was stopped, the solution was filtered, then the filter residue was washed with deionized water for many times. Finally, the slag was dried at 80 °C for 6 h, and was ground for various analysis.

2.3. Experimental theory
The E-pH diagram of Mn-H\(_2\)O system could be drawn according to HSC thermodynamic software, it was shown in figure 1. According to the standard electrode potential meter, the oxidation potential of H\(_2\)O\(_2\) was 1.763V in the acidic system, and the electrode reaction was as follows.

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{H}_2\text{O} \quad \phi_{\text{H}_2\text{O}_2}^\circ = 1.763\text{V}
\]

The oxidation potential of H\(_2\)O\(_2\) was 0.867V in alkaline system, and its electrode reaction was as follows.

\[
\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e} \rightarrow 2\text{OH}^- \quad \phi_{\text{H}_2\text{O}_2}^\circ = 0.867\text{V}
\]

The relationship between oxidation potential of H\(_2\)O\(_2\) and pH under acidic conditions at 40 °C was as follows:

\[
\phi_{\text{H}_2\text{O}_2}^\circ = 1.79369 - 0.062 \text{pH}
\]

The relationship between oxidation potential of H\(_2\)O\(_2\) and pH under alkaline conditions at 40 °C was as follows:

\[
\phi_{\text{HO}_2^-}^\circ = 0.31161 + 0.04046 \text{pH}
\]

According to the figure 1, under alkaline conditions, Mn\(^{2+}\) reacted with OH\(^-\) to form Mn(OH)\(_2\). After H\(_2\)O\(_2\) being dropped, Mn(OH)\(_2\) was oxidized into a variety of complex manganese oxides, such as Mn\(_3\)O\(_4\), MnOOH and MnO\(_2\). The reaction formula was as follows.

\[
3\text{Mn(OH)}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Mn}_3\text{O}_4 + 4\text{H}_2\text{O}
\]

\[
\text{Mn}_3\text{O}_4 + [\text{O}] + \text{OH}^- \rightarrow 3\text{MnOOH}
\]

\[
\text{Mn}_3\text{O}_4 + [\text{O}] \rightarrow 3\text{MnO}_2
\]

\[
\text{MnOOH} + [\text{O}] \rightarrow \text{MnO}_2
\]

Therefore, manganese oxides such as Mn\(_3\)O\(_4\), MnOOH and MnO\(_2\) could be prepared by H\(_2\)O\(_2\) in situ oxidation method in theory. The physical and chemical properties of manganese oxides, such as phase composition, micro morphology, specific surface area and surface properties, were related to reaction conditions, such as reaction temperature, pH, time, Mn\(^{2+}\) concentration, H\(_2\)O\(_2\) dosage, etc.
manganese oxides with different physical and chemical properties could be obtained theoretically by controlling the preparation conditions.

2.4. Characterization of manganese oxides
The morphology and structure of manganese oxide were analyzed by Hitachi su8020 ultra-high resolution field emission scanning electron microscope. XRD analysis was done by D8 ADVANCE x-ray diffractometer of Brooke company. The specific surface area and mesoporous analysis were carried out by ASAP 2460 physical adsorption instrument of American Mike company.

3. Results and discussion

3.1. Effect of H2O2 dosage
When the reaction temperature was 40 °C, the reaction pH was 8, the reaction time was 90 min, the concentration of Mn2+ in the solution was 30 g l−1, and the molar ratio of H2O2 to Mn2+ was 0.5:1, 0.7:1, 1:1, 1.5:1 and 2:1 respectively, the properties of the prepared products were characterized as follows.

3.1.1. XRD patterns
XRD patterns of MnO2 prepared at different H2O2 dosage were shown in figure 2.
It could be seen from figure 2 that the phase of the product prepared at different H$_2$O$_2$ dosage was Mn$_3$O$_4$. According to Nernst formula, when the temperature was 40 °C and pH = 8, the oxidation potential of H$_2$O$_2$ was 0.63529, the main components under this condition were Mn$_3$O$_4$ and MnOOH from figure 1. But Mn$_3$$^+$ would not exist stably, so the main component was Mn$_3$O$_4$. When the molar ratio of H$_2$O$_2$ to Mn$^{2+}$ was 0.5:1, 0.7:1 and 1:1, the XRD diffraction peak was relatively high. When the molar ratio of H$_2$O$_2$ to Mn$^{2+}$ continues to be increased, the diffraction peak tended to decrease. Because excessive oxidant accelerated the oxidation rate and increases the oxidation degree, Mn$_3$O$_4$ may be oxidized excessively, resulting in the decrease of crystallinity [26].

3.1.2. SEM images
SEM images of MnO$_2$ prepared at different H$_2$O$_2$ dosage were shown in figure 3.

It could be seen from figure 3 that the micro morphology of the products with different amounts of oxidant was aggregated by nano pellets of about 50 nm, and the whole was cora. A small amount of rod-shaped crystals appeared when the molar ratio of H$_2$O$_2$ to Mn$^{2+}$ was 0.5:1, which was caused by Mn(OH)$_2$ not completely oxidized. When the molar ratio of H$_2$O$_2$ to Mn$^{2+}$ was 0.7:1, it could be found that the agglomeration between...
Figure 6. XRD patterns of products prepared with different reaction times.

Figure 7. SEM images of products prepared with different reaction times.

a--30min; b--60min; c--90min; d--120min; e--150min; f--180min
grains was more serious. With the increase of oxidant, the grain became uniform and grew gradually, and the compactness of the product increased gradually.

3.1.3. BET analysis
The product was characterized by BET under different oxidant dosage. The N₂ adsorption-desorption curve of the product was shown in figure 4. The specific surface area calculated from the N₂ adsorption-desorption curve by t-plot formula was shown in figure 5.

It could be seen from figures 4 and 5 that with the increase of oxidant dosage, the adsorption capacity of N₂ by the product increased first and then decreased, and the specific surface area of the product also showed the same trend. It showed that the high specific surface area of the product was favorable for adsorption. According to the IUPAC system model [27], the adsorption-desorption curves of these products belonged to class V adsorption-desorption isotherms. When the molar ratio of H₂O₂ to Mn²⁺ was 0.5:1, the hysteresis loop belonged to H3 type, which indicated that the adsorption presented unlimited adsorption capacity under relatively high pressure, and the adsorption capacity increased with the increase of pressure. This type of hysteresis loop usually appeared in materials with narrow and long cracks. When the molar ratio of H₂O₂ to Mn²⁺ increased to 1:1, the adsorption capacity reached the highest value, and the hysteresis loop changed from H3 type to H1 type, which was caused by the regular pore structure of the product. With the continuous increase of H₂O₂, it was still H1 type hysteresis loop, but the N₂ adsorption capacity decreased. Therefore, with the increase of H₂O₂, the specific surface area of the product first increased and then decreased, which was consistent with the change trend of N₂ adsorption capacity. The most suitable molar ratio of H₂O₂ to Mn²⁺ was 1:1.

3.2. Effect of reaction time
When the reaction temperature was 40 °C, the reaction pH was 8, the molar ratio of H₂O₂ to Mn²⁺ was 1:1, the concentration of Mn²⁺ in the solution was 30 g l⁻¹, and the reaction time was 30 min, 60 min, 90 min, 120 min, 150 min and 180 min respectively., the properties of the prepared products were characterized as follows.

3.2.1. XRD patterns
XRD patterns of MnO₂ prepared at different reaction times were shown in figure 6.

It could be seen from figure 6 that the phase of the product prepared at different reaction times was Mn₃O₄. The diffraction peak of 30 min was relatively low, and the diffraction peak intensity remained basically unchanged after 60 min. This indicated that the oxidation reaction was a relatively rapid process, and it could be completely oxidized within 60 min, so it was of little significance to continue to increase the reaction time.

3.2.2. SEM images
SEM images of MnO₂ prepared at different reaction times were shown in figure 7.

It could be seen from figure 7, the products prepared at different reaction times were nano pellets in micro morphology, and the diameter of the particles changed slightly, they were about 50 nm. When the reaction time
was 90 min, the diameter of the nanoparticles was the smallest, and the average diameter was only about 20 nm. It indicated that the reaction was completed in a short time, and the grains could grow rapidly. Increasing the reaction time had little effect on the microstructure of the product.

3.2.3. BET analysis

Adsorption-desorption isotherm and specific surface area of products prepared at different reaction times were shown in figures 8 and 9.

It could be seen from figures 8 and 9 that with the increase of reaction time, the adsorption capacity of N₂ by the product increased first and then decreased, and the specific surface area of the product also showed the same trend. Compared with the isothermal adsorption desorption curve, the adsorption curves of the products were class V isotherms, so the products are microporous or mesoporous solids. When the reaction time was from 30 min to 180 min, the change trend of the specific surface area of the product was consistent with that of the particle diameter. They all increased first and then decreased. When the reaction time was 90 min, the maximum specific surface area was 82.0376 m² g⁻¹. It showed that the specific surface area of the product was related to the particle diameter, the smaller the diameter of nano spherical particles was, the larger the specific surface area was, and the greater the adsorption potential was. Overall, the better reaction time was 90 min.

Figure 9. Specific surface area of the products.

Figure 10. XRD patterns of products prepared with different reaction temperatures.
3.3. Effect of reaction temperature

When the reaction pH was 8, the molar ratio of H₂O₂ to Mn²⁺ was 1:1, the concentration of Mn²⁺ in the solution was 30 g l⁻¹, the reaction time was 90 min, and the reaction temperature was 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C and 90 °C respectively. The properties of the prepared products were characterized as follows.

3.3.1. XRD patterns

XRD patterns of MnO₂ prepared at different reaction temperatures were shown in figure 10.
It could be seen from figure 10 that the phase composition of the products prepared at different reaction temperatures was Mn$_3$O$_4$. The diffraction peaks increased and became sharp with the increase of reaction temperature. It showed that with the increase of temperature, the crystallinity increased and the crystal development was more perfect. However, when the temperature was increased to 60°C, the impurity peak gradually increased when 2θ was between 20° and 30°. Which indicated that as the temperature continued to rise, the Brownian motion of ions in the solution was also intense, the reaction was more intense, and the oxidizability of hydrogen peroxide was also enhanced, and the Mn$_3$O$_4$ phase had a tendency to change. Therefore, Mn$_3$O$_4$ with better crystallinity and higher purity could be obtained at 50°C.

3.3.2. SEM images

SEM images of MnO$_2$ prepared at different reaction temperatures were shown in figure 11. It could be seen from figure 11 that under the condition of low temperature of 15°C, the product was composed of nanorods with a length of about 400 nm and a diameter of about 20 nm. With the increase of temperature, the length of nanorods became shorter and a small amount of spherical grains appeared. When the temperature rose to 50 °C, the rod shape particles were completely transformed into spherical particles with a diameter of about 50 nm. Because the reaction temperature had affect on the speed of crystal nucleation and the time of crystal nucleus maturation. The higher the temperature was, the shorter the time of crystal nucleus maturation was. The grain growth had the characteristic of growing along one-dimensional direction. The lower the reaction temperature was, the longer the nucleation maturation time was. Therefore, the micro morphology...
of the product was nano rod at low temperature, and the higher reaction temperature would lead to the acceleration of crystal ripening, the its micro morphology was nano spherical particles [28].

3.3.3. BET analysis
Adsorption-desorption isotherm and specific surface area of products prepared at different reaction temperatures were shown in figures 12 and 13.

It could be seen from figures 12 and 13 that with the increase of reaction temperature, the adsorption capacity of N$_2$ by the product increased first and then decreased, and the specific surface area of the product also showed the same trend. The adsorption curves of different products were type V isotherms. When the reaction temperature was 30 °C, the maximum specific surface area was obtained and it was 74.89 m$^2$ g$^{-1}$. The change of specific surface area was affected by the morphology of products. The Mn$_3$O$_4$ of rod-like structure had more space structure and crystal defects than the Mn$_3$O$_4$ of spherical structure, Mn$_3$O$_4$ of rod-like would had larger specific surface area and higher adsorption potential. The appropriate reaction temperature was 40 °C considering XRD, SEM and BET analysis.

3.4. Effect of pH
When the reaction temperature was 40 °C, the reaction time was 90 min, the concentration of Mn$^{2+}$ in the solution was 30 g l$^{-1}$, the molar ratio of H$_2$O$_2$ to Mn$^{2+}$ was 1:1, and the reaction pH was 3, 5, 7, 9 and 11 respectively. The properties of the prepared products were characterized as follows.

3.4.1. XRD patterns
XRD patterns of MnO$_2$ prepared at different pH were shown in figure 14.

As shown in figure 14, the main product was Mn$_3$O$_4$ under alkaline conditions, and the diffraction peaks of each crystal plane gradually increased and the impurity peaks decreased with the increase of alkaline. Mn$_3$O$_4$ with good crystallinity and high purity was obtained when pH was equal to 11. The main product was MnO$_2$ under acidic condition., When the pH decreased to 5, the diffraction peaks of γ-MnO$_2$ began to appear. When the pH decreased to 3, strong diffraction peaks appeared on the crystal planes such as (120), (131), (300) and (160), and the product phases were all γ-MnO$_2$. According to the standard electrode potential meter, the oxidation potential of H$_2$O$_2$ was 0.867v in alkaline system, and it was 1.763v in acidic system. According to Nernst equation, the electrode potential would change with the change of reaction conditions. The oxidation potential of H$_2$O$_2$ was higher under acidic conditions than that under alkaline conditions. According to the E-pH diagram, Mn$^{2+}$ could only be oxidized to Mn$_3$O$_4$ by H$_2$O$_2$. Under alkaline conditions. If the pH is adjusted to acidic, the electrode potential of H$_2$O$_2$ would increase, part of Mn$^{2+}$ could be further oxidized to MnO$_2$, and the new Mn$_3$O$_4$ may also decompose into Mn$^{2+}$ and MnO$_2$. So MnOOH and γ-MnO$_2$ appeared in the product at low pH. The products were all γ-MnO$_2$ phase when pH decreased to 3. The γ-MnO$_2$ was a very disordered tunnel type, it had a large number of defects, vacancies and non ideal ratio., Which made γ-MnO$_2$ have better electrochemical and adsorption characteristics [29].
Figure 15. SEM images of products prepared with different pH.

- a–pH=3;  b–pH=5;  c–pH=7;  d–pH=9;  e–pH=11

Figure 16. Adsorption-desorption isotherm of products.
3.4.2. SEM images
SEM images of MnO₂ prepared at different pH were shown in figure 15.
It could be seen from figures 14 and 15 that γ-MnO₂ was polymerized by clusters of nano spherical particles when the reaction pH was 3. This small and porous morphology could be obtained more adsorption sites [30]. The product was mainly composed of nano spherical γ-MnO₂ and MnOOH of nanorods when the reaction pH rises to 5. The rod-like structure, especially the nanotubular structure, was more conducive to the application in the field of catalysis [31]. As the pH continued to rise, Mn₃O₄ with slender nano rod structure appears. When the pH rises to 11, Mn₃O₄ with uniform nano spherical particles was formed.

3.4.3. BET analysis
Adsorption-desorption isotherm and specific surface area of products prepared at different pH were shown in figures 16 and 17.
It could be seen from figure 17 that the isothermal adsorption curve of the products belonged to class IV isotherm, and its hysteresis ring was H1 type. This showed that the products were mesoporous structure, and the appearance of hysteresis ring was due to capillary shrinkage in mesoporous solids. H1 type hysteresis ring indicated that the hole had a regular shape, which was different from the size distribution of narrow hole. With the decrease of pH, the adsorption capacity for nitrogen and the specific surface area of the products increased gradually, so the adsorption potential also increased gradually. The maximum specific surface area was 90.81 m²
It was obvious that MnO₂ had a larger specific surface area than Mn₃O₄. The appropriate pH was 3 considering XRD, SEM and BET analysis.

3.5. Effect of Mn²⁺ concentration
When the reaction pH was 3, the molar ratio of H₂O₂ to Mn²⁺ was 1:1, the reaction time was 90 min, the reaction temperature was 40 °C, and the concentration of Mn²⁺ in the solution was 10 g l⁻¹, 20 g l⁻¹, 30 g l⁻¹, 40 g l⁻¹, 50 g l⁻¹ and 60 g l⁻¹ respectively. The properties of the prepared products were characterized as follows.

3.5.1. XRD patterns
XRD patterns of MnO₂ prepared at different Mn²⁺ concentrations were shown in figure 18.

It could be seen from figure 18 that the phase of the product would not change with the change of Mn²⁺ concentration, under the study conditions, all of them were γ-MnO₂. However, the diffraction peak at the (101) interface and the half peak width increased gradually with the increase of Mn²⁺ concentration. The preferential orientation phenomenon occurred on this interface. According to the Oswald ripening process mechanism [32], the grains would nucleate rapidly at high concentration, they could grow slowly only below the critical concentration. Therefore, a large number of crystal nuclei were formed in a short time when Mn²⁺ concentration was high, which would lead to the lower average size of crystal nuclei and more defects.
3.5.2. SEM images
SEM images of MnO2 prepared at different Mn$^{2+}$ concentrations were shown in figure 19.

The nano spherical particles of MnO2 were dispersed, evenly when the Mn$^{2+}$ concentration was below 30 g l$^{-1}$, and they became smaller with the increase of Mn$^{2+}$ concentrations. The fine MnO2 particles agglomerate seriously when the Mn$^{2+}$ concentration was higher than 40 g l$^{-1}$. The reasons were as follows, when the concentration of Mn$^{2+}$ in the reaction system was too large, the generation trend of crystal nucleus would be greater than that of crystal nucleus. The number of crystal nuclei increased rapidly in a short time, adhere to the formed nuclei to grow$^{[33]}$ and the grains squeezed each other to form cluster agglomerates$^{[34]}$.

3.5.3. BET analysis
Adsorption-desorption isotherm and specific surface area of products prepared at different Mn$^{2+}$ concentrations were shown in figures 20 and 21.

It could be seen from figure 20 that the adsorption potential of the product decreased first and then increased with the increase of Mn$^{2+}$ concentration, their isothermal adsorption curves belonged to class IV isotherm, and these hysteresis ring were H1 type. With the increase of Mn$^{2+}$ concentration, the specific surface area of the products also decreased first and then increased from figure 21. When the Mn$^{2+}$ concentration was 10 g l$^{-1}$, the maximum specific surface area was was obtained and it was 172.41 m$^{2}$ g$^{-1}$. It could be found that there were many voids in MnO2 prepared at higher or lower Mn$^{2+}$ concentrations considering the SEM images, which was beneficial to the increase of N$_2$ adsorption capacity and specific surface area. The appropriate Mn$^{2+}$ concentration was 10g l$^{-1}$ considering XRD, SEM and BET analysis.
In the evaluation of adsorption performance, the specific surface area of adsorbent was a key factor, generally MnO₂ specific surface area was about 100 m² g⁻¹. The prepared γ-MnO₂ has a large surface area and more binding sites for adsorption, thereby improving the adsorption performance.

3.6. Adsorption performance test of MnO₂

For the purpose of high adsorption performance, the optimum conditions were obtained as follows. The temperature was 30 °C, pH was 3, reaction time was 90 min, the mole ration of H₂O₂ to Mn²⁺ was 1:1, and Mn²⁺ concentration was 10 g l⁻¹, the γ-MnO₂ with richer pores and high specific surface area (172.41 m² g⁻¹) could be prepared under these conditions. The MnO₂ has good adsorption potential and could provide more binding sites and better adsorption conditions for ionic groups in solution. Therefore, γ-MnO₂ was used to test the adsorption properties of Co and Ni in manganese ore leaching solution.

100 ml manganese ore leaching solution was taken as a beaker, stirred with a stirrer at 200 r min⁻¹, and heated to 60 °C in a water bath. After pH regulator was adjusted to 6, 1 g γ-MnO₂ was added as adsorbent, and the reaction time was 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, respectively. The solution was filtered, and the filtrate was taken for ICP detection. The composition of manganese ore leaching solution were shown in table 1, and the adsorption percentage of Co and Ni in manganese ore leaching solution were shown in figure 22.

It could be seen from figure 22 that γ-MnO₂ with high specific surface area and high porosity has good adsorption effect on Co and Ni in manganese ore leaching solution, and the adsorption reaction rate was fast. Co and Ni were adsorbed by 52.71% and 65.08% respectively in 10 min. With the increase of adsorption time, more Co and Ni were adsorbed by MnO₂. When the adsorption time reaches 40 min, the adsorption percentage of Co and Ni tends to be stable, and the adsorption efficiency of Co and Ni could reached 94.75% and 95.67%.

Table 1. Composition of manganese ore leaching solution.

| Ions | Concentration (mg l⁻¹) | Ions | Concentration (mg l⁻¹) | Ions | Concentration (mg l⁻¹) |
|------|------------------------|------|------------------------|------|------------------------|
| Mn   | 46913.2                | Cu   | 2                      | Co   | 12.2                   |
| Fe   | 2.75                   | Na   | 93.5                   | Al   | 5.6                    |
| Ni   | 30.3                   | K    | 32.95                  | Cd   | 1.15                   |
| Mg   | 628.4                  | As   | 1.05                   | Mo   | 32.64                  |
| Ca   | 750                    | Cr   | 0.35                   | V    | 0                      |

In the evaluation of adsorption performance, the specific surface area of adsorbent was a key factor, generally MnO₂ specific surface area was about 100 m² g⁻¹. The prepared γ-MnO₂ has a large surface area and more binding sites for adsorption, thereby improving the adsorption performance.
adsorption process of MnO₂ in manganese ore leaching solution was a dynamic process, and the adsorption and desorption were carried out simultaneously. When the adsorption rate was equal to the desorption rate, the dynamic equilibrium was achieved. In the initial stage of the reaction, there are a large number of adsorption sites on the surface of MnO₂, Ni and Co were quickly adsorbed on the surface of MnO₂. After a period of reaction, the adsorption sites and pores on the MnO₂ surface were largely occupied, and the adsorption rate gradually decreased. When the adsorption sites were all occupied, the adsorption amount of Ni and Co reaches saturation, and the number of adsorption sites depends on the specific surface area and porosity of MnO₂. Therefore, γ-MnO₂ with high specific surface area and porosity was the key to high adsorption performance.

4. Conclusion

Different manganese oxides were prepared by in situ oxidation of manganese sulfate solution with H₂O₂ as oxidant. The effects of reaction conditions on the physicochemical properties of manganese oxidation were investigated.

The phase and microstructure of the product were not changed by oxidant dosage and reaction time under alkaline conditions, the main component of the products was Mn₃O₄, which were a spherical particles with a diameter of 50 nm. However, the specific surface area and adsorption potential increased first and then decreased with the increase of oxidant dosage and reaction time. The adsorption curves of products were all the V-type isotherms, and there were micropores or mesopores in the products. The increase of temperature was beneficial to improve the crystallinity of Mn₃O₄, reduce the specific surface area and adsorption potential, and have a great influence on the microstructure of the products. When the temperature was 20 °C, the micro morphology of the product was slender nanorod. With the increase of temperature, the length of nanorod became shorter, and they became spherical when the temperature rises to 50 °C.

The phase composition of the product was influenced by reaction pH greatly. When the pH decreased from 9 to 5, Mn₃O₄ gradually disappeared by two ways. On one hand, some Mn²⁺ was further oxidized, and the phases of MnOOH and γ-MnO₂ began to appear. On the other hand, the new Mn₃O₄ was decomposed into Mn²⁺ and MnO₂. The product were γ-MnO₂ with high specific surface area and adsorption potential when pH was 3. With the increase of Mn²⁺ concentration, the grain size decreased and agglomeration was easy to occur. The optimum conditions were obtained as follows. The temperature was 30 °C, pH was 3, reaction time was 90 min, the mole ration of H₂O₂ to Mn²⁺ was 1:1, and Mn²⁺ concentration was 10 g l⁻¹, and the γ-MnO₂ with high specific surface area (172.41 m² g⁻¹) could be prepared under these conditions. When preparing manganese oxide mesoporous materials, pH was the key to affect the product structure. The controllable preparation of manganese oxide could be realized by combining with other control methods.

This γ-MnO₂ has a good adsorption effect on Co and Ni in manganese ore leaching solution, and the adsorption efficiency could be reached 94.75% and 95.67%. γ-MnO₂ with high specific surface area and porosity was the key to high adsorption performance.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

There are no conflicts to declare including any competing financial interest.

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