Study on the Adsorption Mechanism of Cobalt and Nickel in Manganese Sulfate by $\delta$-MnO$_2$

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ABSTRACT: Manganese has excellent performance in removing metal ions from aqueous solutions, but there are few studies on the adsorption and removal of heavy metal impurities in metal salt solutions. In this paper, the adsorption of cobalt and nickel ions in MnSO$_4$ solution by $\delta$-MnO$_2$ prepared from two different manganese sources was studied. The optimum adsorption conditions were as follows: When the concentration of Mn$^{2+}$ was 20 g/L, $\delta$-MnO$_2$ addition was 10 g/L, Co$^{2+}$ concentration was 80 mg/L, Ni$^{2+}$ concentration was 80 mg/L, reaction time was 60 min, reaction temperature was 80 °C, and pH value was 7, the adsorption rate of Co$^{2+}$ and Ni$^{2+}$ reached more than 80%. The manganese dioxide adsorbed by heavy metals was analyzed and detected. The results showed that MnOOH appeared in the phases of both kinds of $\delta$-MnO$_2$, and their morphologies were dense rod-like structures with different lengths and flake-like structures of fine particles. Co and Ni were distributed on the surface and gap of MnO$_2$ particles, and the atomic percentage of Co was slightly higher than that of Ni. The new vibration peaks appeared near wave numbers of 2668.32, 1401.00, and 2052.19 cm$^{-1}$, which were caused by the complexation of cations such as Co$^{2+}$ and Ni$^{2+}$ with hydroxyl groups. Some cobalt and nickel appeared on the surface of $\delta$-MnO$_2$, and the surface oxygen increased after adsorption. The above characterization revealed that the adsorption of cobalt and nickel in manganese sulfate by $\delta$-MnO$_2$ was realized by the reaction of its surface hydroxyl with metal ions (M) to form $\equiv$SOMOH.

1. INTRODUCTION

Manganese sulfate is the most important and basic manganese source material for manganese-based lithium battery cathode materials. $^{1−3}$ It is also the raw material for the preparation of manganese oxides, so it is of great significance to prepare high-purity manganese sulfate. $^{5−9}$ In manganese ore, heavy metal cobalt and nickel often exist in the form of association. Therefore, when manganese ore is leached to obtain manganese sulfate, the impurity metals Co and Ni will also be leached one after another, resulting in the high content of heavy metal ions in the leached manganese sulfate solution, which seriously affects the quality of subsequent products. For example, the purity of manganese-based materials, especially the content of heavy metal impurities, is directly related to the specific capacity of the battery and the number of charge and discharge times. $^3$ Battery-grade manganese sulfate has strict requirements on various metal impurity ions. The key to preparing high-purity manganese sulfate is to remove impurities. To obtain high-quality manganese-based battery materials, the purity of manganese-based raw materials must first be ensured. Whether it is manganese sulfate directly used to produce ternary materials or manganese oxide used to produce lithium manganate, it is necessary to first obtain manganese sulfate with high purity. Manganese sulfate is the most important and basic manganese source material for cathode materials of manganese-based power lithium batteries. So it is necessary to remove impurities in the manganese sulfate solution to obtain high-purity manganese sulfate products. $^{10,11}$ The common impurity removal methods include the sulfide precipitation method, $^{12−14}$ fluorination method, $^{15−17}$ carbonation method, $^{18,19}$ extraction method, $^{20}$ and crystallization method. $^{21,22}$ There are many shortcomings such as the long procedure, many control nodes, high requirements, high cost, large amount of slag, and low efficiency in the above processes. Therefore, developing an effective, short process with low environmental harm, low cost, and low slag removal has become a research hotspot in manganese sulfate production.

The adsorption method has been more and more widely used because of its simple process, good economic benefit, high treatment efficiency, and environmental friendliness, $^{23−27}$ and the heavy metal ions in the adsorbent could be recycled by resolution so as to realize the regeneration and recycling of the adsorbent. $^{28,29}$ Adsorption is the phenomenon of automatic

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diffusion and enrichment of molecules or ions between solid-liquid interfaces. According to this principle, the target molecules or ions are removed from the solution by using adsorbents with large specific surface area and high surface energy.\textsuperscript{35, 39} MnO\textsubscript{2} is an excellent adsorbent because of its rich surface hydroxyl, many defects, large specific surface area, and strong ion exchange capacity.

Manganese dioxide is mainly used in the field of adsorption to adsorb heavy metal ions in wastewater and alleviate the pressure of heavy metal pollution on the environment.\textsuperscript{51–37} Wang\textsuperscript{38} studied the adsorption properties of heavy metals antimony and thallium. \(\delta\)-MnO\textsubscript{2} had the best adsorption properties for Sb(III) and Tl(I), and its maximum adsorption capacities reached 120 and 498 mg g\(^{-1}\), respectively. \(\delta\)-MnO\textsubscript{2} was prepared by Kong and Zhu\textsuperscript{39} in a laboratory method, and its adsorption properties for Zn\textsuperscript{2+}, Cd\textsuperscript{2+}, Cu\textsuperscript{2+}, Pb\textsuperscript{2+}, Ni\textsuperscript{2+}, and Co\textsuperscript{2+} in the mixed metal ion system was studied. The initial pH and adsorption time of the solution were investigated. Effect of coexisting ions and ionic strength on adsorption. The results showed that when the initial pH > 3.2, the adsorbent showed good removal effects on Zn\textsuperscript{2+}, Cd\textsuperscript{2+}, Cu\textsuperscript{2+}, Pb\textsuperscript{2+}, Ni\textsuperscript{2+}, and Co\textsuperscript{2+}. The manganese oxide prepared by Kanungo et al.\textsuperscript{40} by the method of reducing potassium permanganate had a high adsorption capacity for heavy metal ions. Oscarson and Huang\textsuperscript{41} studied the removal of As(III) by \(\delta, \alpha, \beta\) state manganese dioxide. The results showed that the removal effect was related to the degree of crystallization and surface characteristics of manganese dioxide, indicating that \(\delta\), \(\alpha\) state manganese dioxide with high activity can alleviate the toxicity of As(III) in the natural environment. Chen and Ye\textsuperscript{42} found that manganese dioxide had a strong adsorption effect on As(III) in the oxidation adsorption test of wastewater containing As(III) by pyrosulphite, and the adsorption capacities of different forms of manganese oxides were also different. Two kinds of manganese dioxide, \(\alpha\)-MnO\textsubscript{2} and \(\delta\)-MnO\textsubscript{2}, were prepared by Li.\textsuperscript{43} By controlling the single factor conditions, the main factors affecting the adsorption of nickel by manganese oxides were analyzed and studied. When the dosage was above 10 mmol, the adsorption rate of a 100 mL nickel solution with a 2 mmol/L concentration was close to 100%.

Although manganese dioxide has a good adsorption effect on heavy metal ions in water, the adsorption of heavy metal ions in high concentration metal salt solutions has been a difficult problem in the field of adsorption, and the related research is scarce. Some researchers investigated the effect of salt concentration (potassium salt, sodium salt, etc.) on the adsorption performance of manganese dioxide in the study of heavy metal ion adsorption. It was found that the adsorption amount of heavy metals was greatly weakened when there was a small amount of salt in the solution, and the adsorption amount was seriously slowed down with the increase of salt concentration. For the anion form of heavy metal impurity ions, the interference of salt solution was weak. In the mixed solution system of 80 g/L NaCl and 15 g/L Na\textsubscript{2}SO\textsubscript{4}, Yao\textsuperscript{44} studied the adsorption properties of flower-like manganese dioxide and sea-urchin-like manganese dioxide for trivalent arsenic. When the additive dosage was 30 g/L, the arsenic removal rates of the two adsorbents were 97.60 and 96.06%. The adsorption behavior of manganese dioxide on molybdenum ion in a manganese sulfate solution had been discussed by Xia et al.\textsuperscript{45, 46} and Chen et al.\textsuperscript{47, 48}. Through in-depth analysis, it was found that the reason why arsenic ions and molybdenum ions can overcome the influence of high concentration salts mainly depends on the fact that both ions exist in the form of anionic groups such as \(\text{H}_5\text{AsO}_3^-\), \(\text{HAsO}_2^{2-}\), \(\text{MoO}_4^{2-}\), and \(\text{HMnO}_4^-\) in a certain pH range to be adsorbed by MnO\textsubscript{2}, while a large number of metal cations in high concentration salt solutions had limited obstacles to their anionic groups, so molybdenum ions in the manganese sulfate solution could be better adsorbed by manganese dioxide. However, there was no obvious effect on the metal ions in the cation form in the manganese sulfate solution.

To solve the problem of manganese dioxide adsorption of metal ions in the manganese sulfate solution, the adsorption mechanism of manganese dioxide was further studied. There are many studies on adsorption mechanism considering the influence of surface charge. The isoelectric point and zero charge of manganese dioxide are proposed,\textsuperscript{49} but the influence of surface defects and surface hydroxyl is less mentioned.\textsuperscript{50} Due to more or less defects, vacancies, and impurities in MnO\textsubscript{2}, oxygen coordination around manganese vacancies was unsaturated, resulting in the presence of a large number of hydroxyl groups. When MnO\textsubscript{2} adsorbed heavy metal ions by surface hydroxyl complexation, the first effect was on pH.\textsuperscript{51} Therefore, Li Mingdong, of our research group, did the determination of different crystal MnO\textsubscript{2} acid point pH,\textsuperscript{52} and he compared different crystal manganese dioxide adsorption of cobalt and nickel in manganese sulfate solution. He did the analysis of its influencing factors and explored the interaction between manganese dioxide and manganese sulfate solution.\textsuperscript{53} On this basis, this paper explored the process conditions of manganese dioxide adsorption of metal ions in heavy metal salt solutions, analyzed the surface hydroxyl complexation mechanism, and further studied the adsorption characteristics of MnO\textsubscript{2} surface hydroxyl ion on heavy metal ions. The adsorption mechanism of impurity ions in high-salt solutions was theoretically clarified to solve the difficult removal of heavy metal ions in the manganese sulfate solution, the raw material of manganese battery. Using manganese dioxide to adsorb cobalt and nickel impurities in manganese sulfate, on the one hand, can provide a reference method for manganese sulfate impurity removal to achieve battery-level requirements; on the other hand, it can recycle the adsorbed nickel and cobalt metal impurities, which has important economic significance. In this paper, the mechanism of manganese dioxide adsorbing cobalt and nickel in the manganese sulfate solution had been studied. Adsorption conditions were explored only in a simpler manganese sulfate solution system. It is hoped that, in the future, this study can be used to adsorb cobalt and nickel in a more complex manganese sulfate solution system and provide reference for adsorbing other impurity ions in heavy metal salt solutions.

2. RESULT AND DISCUSSION

2.1. Study on the Adsorption Process. Researchers in our group had done a lot of preliminary work,\textsuperscript{53} and through the comparison of different crystal forms of manganese dioxide, the best adsorption performance was by \(\delta\)-MnO\textsubscript{2}. \(\delta\)-MnO\textsubscript{2} prepared with different manganese sources was further studied, and the equi-acidity point pH,\textsuperscript{53} specific surface area, pore size, and pore volume of the isoacid point were detected. Studies had shown that when the pH of the electrolyte solution is higher than the equi-acidity point pH of MnO\textsubscript{2}, the surface hydroxyl groups undergo deprotonation reaction and complex with metal ions to release H\textsuperscript{+}, reducing the pH value of the solution. When the pH of the solution was lower than the equi-acidity point pH, the protonation reaction of the surface hydroxyl mainly consumed H\textsuperscript{+}, which increased the pH value. When the pH of the solution
was the same as the equi-acidity point pH, the H⁺ was released by the surface hydroxyl complexation reaction and the protonation reaction consumed H⁺ in a dynamic equilibrium, and the pH value did not change. The pH value of the equi-acidity point of MnO₂ is essentially the equilibrium pH value of the adsorption and desorption of the surface hydroxyl and metal ions, and the pH value of the equi-acidity point depends on the content of the surface hydroxyl and the complexation ability. Both δ₁-MnO₂ and δ₂-MnO₂ have abundant surface hydroxyl groups, but the pH values at the equi-acidity point are quite different. δ₁-MnO₂ is much higher than δ₂-MnO₂, indicating that δ₂-MnO₂ has a stronger surface hydroxyl complexing ability, so it is speculated that it has a greater adsorption potential. It can be seen from Figure 1 that the isoelectric points of δ₁-MnO₂ and δ₂-

![Figure 1. Surface zeta potential of δ-MnO₂.](image)

MnO₂ are 3.7 and 3.4, respectively. When the solution pH was lower than the equi-acidity point pH, the surface of MnO₂ was positively charged. When the solution pH was higher than the equi-acidity point pH, the surface of MnO₂ was negatively charged, and the heavy metal cations in the solution could be adsorbed by charge attraction.

The two kinds of δ-MnO₂ have a pore structure, and the average pore diameter is large. The pore volume and average pore diameter of δ₂-MnO₂ are higher than those of δ₁-MnO₂. It can be seen from Figure 2 that the adsorption and desorption isotherms of the two kinds of δ-MnO₂ show the fourth type, and there is an obvious hysteresis loop. δ₁-MnO₂ belongs to the H1 hysteresis loop, which is caused by the difference in the regular shape of the pores and the size distribution of the narrow pores. The pore size distribution can be found to be mainly in the range of 2–10 nm. δ₂-MnO₂ belongs to the H3 type hysteresis loop, and the MnO₂ is composed of disc-shaped particles. The pores are slit-shaped. It can be found from the pore size distribution that most of the pores are distributed in the range of 2–10 nm, and there are still some pores in the range of 10–100 nm. The macropore structure is more abundant than δ₁-MnO₂.

From Table 1 and the above analysis, the adsorption performance of δ₂-MnO₂ should be slightly better than that of δ₁-MnO₂. It can also be found from the study of Li et al. that the adsorption efficiency of δ₂-MnO₂ on cobalt and nickel is higher than that of δ₁-MnO₂. In this paper, based on the two δ-MnO₂ adsorption conditions of Li et al., 20 g/L Mn²⁺ concentration and 10 g/L MnO₂ addition were obtained as the better conditions. The optimal reaction time, reaction temperature, reaction pH, Co²⁺ concentration, and Ni²⁺ concentration were further explored; the adsorption efficiency of MnO₂ for Co²⁺ and Ni²⁺ was determined; and the influence of process conditions on the adsorption performance of MnO₂ was analyzed.

2.1.1. Effect of Reaction Time. When the Co²⁺ concentration was 80 mg/L; the Ni²⁺ concentration was 80 mg/L; the reaction temperature was 80 °C; the reaction pH was 7; and the reaction time was 5, 10, 20, 30, 60, 90, and 150 min, respectively, the adsorption rate of Co²⁺ and Ni²⁺ in manganese sulfate by δ-MnO₂ was as shown in Figure 3.

It can be seen from Figure 3 that with the increase of reaction time, the adsorption of δ-MnO₂ on Co²⁺ and Ni²⁺ first increased and then decreased. When the reaction time was 60 min, the adsorption rate reached the highest. The adsorption reaction of the two kinds of δ-MnO₂ in the first 30 min was faster due to the fact that the surface hydroxyl of δ-MnO₂ adsorption sites have not been occupied. Co²⁺ and Ni²⁺ adsorption probability is the largest, the surface complex reaction is intense, and the solution pH decreased rapidly. When the reaction time was 30–60 min, the adsorption sites were gradually occupied, the complexation reaction decreased, the pH of the solution decreased slowly, the pH adjustment times were less, and the adsorption rate of Co²⁺ and Ni²⁺ slowed down. At 60 min, the adsorption amount reached saturation. At this time, the adsorption and desorption maintained a dynamic equilibrium. The pH of the solution no longer decreased and remained stable at about 7. The adsorption amounts of Co²⁺ and Ni²⁺ reached the maximum. After 60 min, the adsorption rate decreased due to the shedding of Co²⁺ and Ni²⁺ adsorbed in MnO₂ pores and attracted by charge, and the

![Figure 2. Nitrogen adsorption—desorption curve of δ-MnO₂.](image)

| Table 1. Partial Performance Parameters of Two Kinds of δ-MnO₂ |
|-----------------|-------------------|-------------------|-------------------|-------------------|------------------|
| MnO₂ crystal form | specific surface area (m²/g) | equi-acidity points pH | isopotential point | aperture (nm) | pore volume (cm³/g) |
| δ₁-MnO₂ | 217.42 | 3.85 | 3.7 | 5.2627 | 0.323685 |
| δ₂-MnO₂ | 223.46 | 1.40 | 3.4 | 8.5211 | 0.417930 |
ion exchange reaction between other ions and adsorbed Co\(^{2+}\) and Ni\(^{2+}\). So the appropriate reaction time was 60 min.

The adsorption rate of \(\delta_1\)-MnO\(_2\) is higher in 10 min, and that of \(\delta_2\)-MnO\(_2\) is higher in 10–60 min. The above phenomenon is due to the slit-like shape of the internal pores of \(\delta_2\)-MnO\(_2\), and the ion diffusion in the interlayer needs a longer time to diffuse to the corresponding adsorption point, so the adsorption rate is lower. After 10 min, the diffusion adsorption process is no longer a limitation of the adsorption rate. More binding sites will have a higher adsorption rate. \(\delta_2\)-MnO\(_2\) has larger specific surface area, pore size, and pore volume, which can provide more adsorption sites, so the adsorption rate is higher.

2.1.2. Effect of Temperature. When the Co\(^{2+}\) concentration was 80 mg/L; the Ni\(^{2+}\) concentration was 80 mg/L; the reaction time was 60 min; the reaction pH was controlled at 7; and the reaction temperature was 20, 35, 50, 65, 80, and 95 °C, respectively, the adsorption rate of Co\(^{2+}\) and Ni\(^{2+}\) in manganese sulfate by \(\delta\)-MnO\(_2\) was as shown in Figure 4.

It can be seen from Figure 4 that the adsorption rate of \(\delta\)-MnO\(_2\) for Co\(^{2+}\) and Ni\(^{2+}\) increased with the increase of reaction temperature. Since the adsorption of \(\delta\)-MnO\(_2\) was mainly due to the complexation reaction of surface hydroxyl, the higher the reaction temperature was, the more intense the movement of Co\(^{2+}\) and Ni\(^{2+}\) in the solution was, the higher the possibility of binding with hydroxyl was, and the faster the reaction was. When the temperature reached 80 °C, the adsorption rate was basically unchanged, the adsorption amount and desorption amount were in a dynamic equilibrium, and the adsorption of manganese dioxide reached saturation. It was of little significance to continue to increase the temperature. When the temperature was lower than 65 °C, the adsorption rate of \(\delta_1\)-MnO\(_2\) for the two ions was higher. When the temperature was higher than 65 °C, the adsorption rate of \(\delta_2\)-MnO\(_2\) for the two ions was higher, and \(\delta_2\)-MnO\(_2\) was more affected by temperature, indicating that, at lower temperatures, the slit pore structure of \(\delta_2\)-MnO\(_2\) limited the binding of Co\(^{2+}\) and Ni\(^{2+}\) with internal adsorption sites, and the adsorption rate of \(\delta_1\)-MnO\(_2\) with a regular pore structure was higher. At higher temperatures, Co\(^{2+}\) and Ni\(^{2+}\) were more active, and the adsorption rate of \(\delta_2\)-MnO\(_2\) with a larger pore volume was higher. Therefore, the increase of temperature is beneficial to the reaction, and the adsorption reaction belongs to the endothermic reaction, which is mainly affected by the surface hydroxyl complexation. There are differences in the adsorption rate of two kinds of \(\delta\)-MnO\(_2\) with different pore structures and sizes.

2.1.3. Effect of pH Value. When Co\(^{2+}\) concentration was 80 mg/L; Ni\(^{2+}\) concentration was 80 mg/L; reaction time was 60 min; reaction temperature was 80 °C; and reaction pH value was
controlled at 1, 2, 3, 4, 5, 6, 7 and 8, respectively, the adsorption rate of Co\(^{2+}\) and Ni\(^{2+}\) in manganese sulfate solution by δ-MnO\(_2\) was as shown in Figure 5.

It is obvious from Figure 5 that the adsorption rate of δ-MnO\(_2\) for Co\(^{2+}\) and Ni\(^{2+}\) increased with the increase of pH value of the manganese sulfate solution. The change trend of the adsorption rate of the two kinds of δ-MnO\(_2\) was similar. When the solution pH increased from 1 to 5, the adsorption rate of the two ions increased slowly, mainly because the concentration of H\(^+\) was high at low pH, and the surface hydroxyl was more likely to react with H\(^+\) to form SOH\(^-\). At the same time, the solution pH was less than the isoelectric point and the surface of δ-MnO\(_2\) was positively charged, so the adsorption of Co\(^{2+}\) and Ni\(^{2+}\) was mainly affected by the structural defects and voids of δ-MnO\(_2\). However, when pH increased from 5 to 8, the adsorption rate increased rapidly. When pH reached 8, the adsorption rates of Co\(^{2+}\) and Ni\(^{2+}\) by δ-MnO\(_2\) reached the highest. This was because the pH of the solution was obviously higher than the isoelectric point, the negative charge on the surface of MnO\(_2\) increased, the hydroxyl was deprotonated to form SO\(^-\), and then it reacted with Co\(^{2+}\) and Ni\(^{2+}\) in the solution, so it was easier to adsorb Co\(^{2+}\) and Ni\(^{2+}\) in the solution. At the same time, when pH = 8, Mn\(^{2+}\) in manganese sulfate would be partially consumed and converted to Mn(OH)\(_2\). So the appropriate pH value was 7.

2.1.4. Effect of Co\(^{2+}\) and Ni\(^{2+}\) Concentration. When reaction time was 60 min; reaction temperature was 80 °C; pH value was controlled at 7; the concentration of Ni\(^{2+}\) was 100 mg/L; and the concentration of Co\(^{2+}\) was 0, 20, 40, 60, 80, 100, and 120 mg/L, respectively, the effect of Co\(^{2+}\) concentration on the adsorption of Ni\(^{2+}\) in the manganese sulfate solution by δ-MnO\(_2\) was as shown in Figure 6a. When the other conditions were the same; the concentration of Co\(^{2+}\) was 100 mg/L; and the concentration of Ni\(^{2+}\) was 0, 20, 40, 60, 80, 100, and 120 mg/L, respectively, the effect of Ni\(^{2+}\) concentration on the adsorption of Co\(^{2+}\) in the manganese sulfate solution by δ-MnO\(_2\) was as shown in Figure 6b.

Figure 6 shows that there is an obvious competitive relationship between Co\(^{2+}\) and Ni\(^{2+}\) in the adsorption process. The adsorption rate of Ni\(^{2+}\) decreases gradually with the increase of Co\(^{2+}\) concentration, and the adsorption rate of Co\(^{2+}\) decreases gradually with the increase of Ni\(^{2+}\) concentration. Co\(^{2+}\) is stronger in the adsorption competition. The affinity of hydroxyl to Co\(^{2+}\) is relatively large, and there is a difference in the adsorption capacities of two δ-MnO\(_2\) to two ions. δ\(_1\)MnO\(_2\) is more inclined to adsorb Ni\(^{2+}\), and δ\(_2\)MnO\(_2\) is more inclined to
adsorb Co^{3+}. The affinity and adsorption capacity of manganese dioxide for different metal ions are different. The adsorption order is generally Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > Na^+, which is basically consistent with the order of ionic hydrolysis constants. This is also the reason why Co^{2+} is preferentially adsorbed and Co^{2+} and Ni^{2+} could be adsorbed in the manganese sulfate solution. Considering the adsorption efficiency and adsorption competition, Co^{2+} and Ni^{2+} were set at 80 g/L.

2.2. Study on the Adsorption Mechanism of MnO_2. The optimal adsorption conditions were obtained through the above adsorption experiments, and they were as follows: the Co^{2+} concentration was 80 mg/L, Ni^{2+} concentration was 80 mg/L, reaction time was 60 min, reaction temperature was 80 °C, and pH value was 7. On the basis, products before and after adsorption were characterized by XRD, SEM, EDS surface scanning, IR, and XPS, and the adsorption mechanism of δ-MnO_2 was analyzed in depth.

2.2.1. Phase. The XRD analysis of manganese dioxide before and after Co and Ni adsorption is shown in Figure 7.

According to the XRD pattern analysis, Mn_3O_4 and MnOOH both appear in manganese dioxide after adsorption under the above conditions. This is because the adsorption process is affected by acid points of MnO_2, and the pH could be stabilized only by repeatedly adjusting the pH. In this process, a small amount of Mn^{2+} in the MnSO_4 solution became Mn(OH)_2 at pH = 7. Mn(OH)_2 was oxidized by oxygen to MnOOH in the air, and some MnOOH was further oxidized to Mn_3O_4. These two substances were filtered out together in the adsorbed product, so they appeared in the phase.

2.2.2. Microstructure and Surface Elements. The SEM images of manganese dioxide before and after Co and Ni adsorption are shown in Figure 8.

As shown in Figure 8, δ_1-MnO_2 before adsorption is stacked by nanoparticles with a diameter of 150 nm, forming a cluster of layered structures with large voids. The morphology after adsorption is shown in Figure 8c, which changes from the large pore structure of nanoparticles before adsorption to the dense structure of nanorods with different lengths. The δ_2-MnO_2 before adsorption is aggregated by nanorods and has a rich pore structure with a diameter of 700 nm. δ_2-MnO_2 after adsorption transforms into a compact accumulation structure.

EDS diagrams of two kinds of δ-MnO_2 before adsorption are shown in Figures 9 and 10. The higher the O/Mn ratio of MnO_2 is, the richer the surface oxygen is, and the oxygen coordination...
around the manganese vacancy is unsaturated, resulting in the formation of a large number of hydroxyl groups on the surface of MnO₂, which is more conducive to the surface complexation reaction. The O/Mn ratios of δ₁-MnO₂ and δ₂-MnO₂ are 2.76 and 2.65, respectively, which indicate that the two kinds of δ-
MnO₂ have a high surface oxygen content and could form more hydroxyl functional groups on their surfaces, so they have the potential to become adsorbents with a high adsorption capacity.

It can be seen from Figure 11 that Mn and O in the products adsorbed by δ₁-MnO₂ are still the main two elements, and a large
number of Co\textsuperscript{2+} and Ni\textsuperscript{2+} are distributed, indicating that Co\textsuperscript{2+} and Ni\textsuperscript{2+} are adsorbed by MnO\textsubscript{2}. At the same time, it can be seen that there is still O element distribution in the area without Mn element. This part of oxygen may come from the crystal water formed by MnO\textsubscript{2} adsorbed water. According to the distribution of Co\textsuperscript{2+} and Ni\textsuperscript{2+} elements, it is speculated that it may also come from the oxides of Co and Ni. It can be seen from Table 1 that the O/Mn ratio of δ\textsubscript{1}-MnO\textsubscript{2} increased from 2.76 to 3.11 after adsorption. In the process of surface hydroxyl binding to metal ions, with the progress of complexation reaction, O element was increasing. According to $\equiv$SO\textsuperscript{−} + M\textsuperscript{2+} + H\textsubscript{2}O$\equiv$SOMnOH + H\textsuperscript{+}, surface hydroxyl $\equiv$SOH reacted with metal ions M to form $\equiv$SOMOH. The second sources of oxygen are crystal water produced during adsorption and manganese oxide in the SOMOH. The second sources of oxygen are crystal water distributed in the gap of MnO\textsubscript{2}.

In the adsorption process, the vibration peak near 1000 cm\textsuperscript{-1} is caused by the increase of O atoms so as to achieve an excellent adsorption effect.

The enhancement of the vibration peak near 1000 cm\textsuperscript{-1} is caused by the increase of adsorbed water on the surface of δ-MnO\textsubscript{2}, which is basically consistent with the EDS surface oxygen scanning analysis. The

![Figure 12. EDS surface scan diagram of δ-MnO\textsubscript{2} after adsorption.](image)

**Table 2. The Proportion of Each Element after the Adsorption of Two Kinds of δ-MnO\textsubscript{2}**

| δ-MnO\textsubscript{2} | element | Mn | O  | Ni | Co | K |
|------------------------|---------|----|----|----|----|---|
| δ1-MnO\textsubscript{2} | percentage by weight | 50.33 | 45.63 | 1.87 | 2.17 | 0 |
| | atomic percent ratio | 23.87 | 74.34 | 0.83 | 0.96 | 0 |
| δ2-MnO\textsubscript{2} | percentage by weight | 51.66 | 43.67 | 1.67 | 2.40 | 0.59 |
| | atomic percent ratio | 25.05 | 72.71 | 0.76 | 1.09 | 0.40 |

**2.2.3. Surface Hydroxyl and Other Groups.** The infrared spectral characteristics of manganese dioxide before and after Co and Ni adsorption are shown in Figure 13.

In the δ\textsubscript{1}-MnO\textsubscript{2} and δ\textsubscript{2}-MnO\textsubscript{2} before adsorption, there are surface hydroxyl stretching vibration peak near 3400 cm\textsuperscript{-1}, surface hydroxyl bending vibration peak near 1600 and 1100 cm\textsuperscript{-1}, and Mn−O lattice vibration peak near 500−600 cm\textsuperscript{-1}. In addition, there are acetate ion C−O and C−H vibration peaks near 1400 cm\textsuperscript{-1} in δ\textsubscript{1}-MnO\textsubscript{2} prepared by manganese acetate. δ\textsubscript{1}-MnO\textsubscript{2} and δ\textsubscript{2}-MnO\textsubscript{2} have broad and strong hydroxyl vibration peaks. So they are rich in surface hydroxyl, which is more conducive to surface complexation reaction with heavy metal ions so as to achieve an excellent adsorption effect.

In the δ\textsubscript{1}-MnO\textsubscript{2} and δ\textsubscript{2}-MnO\textsubscript{2} after adsorption, the vibration hydroxyl stretching vibration peaks near 3400 and 1600 cm\textsuperscript{-1} are obviously weakened, indicating that a large number of hydroxyls are bound to metal ions, and the utilization rate of hydroxyls is greatly increased. There are new vibration peaks that appeared near 2600 and 2000 cm\textsuperscript{-1}, which are likely to be $\equiv$SOCoOH and $\equiv$SONiOH formed by the complexation of Co\textsuperscript{2+}, Ni\textsuperscript{2+}, and hydroxyl groups on the surface of δ-MnO\textsubscript{2}. The enhancement of the vibration peak near 1000 cm\textsuperscript{-1} is caused by the increase of adsorbed water on the surface of δ-MnO\textsubscript{2}, which is basically consistent with the EDS surface oxygen scanning analysis. The
vibration peaks of the Mn-O lattice near 500–600 cm\(^{-1}\) moved and were enhanced, which are caused by Mn\(^{3+}\) adsorption on the \(\delta\)-MnO\(_2\) surface or MnO\(_2\) and MnOOH generated from Mn\(^{2+}\).  

2.2.4. Atomic Valence State. The XPS spectra of manganese dioxide before and after Co and Ni adsorption are shown in Figure 14.

From Figure 14a, it could be found that the K\(^{+}\) peak initially disappeared in \(\delta\)-MnO\(_2\) and \(\delta\)-MnO\(_2\) after adsorption. It indicates that the interlayer K\(^{+}\) was replaced by metal cations in the solution. Figure 14b shows that the structure oxygen of \(\delta\)-MnO\(_2\) has no obvious change after adsorption, but the proportion of adsorbed oxygen increases greatly. This indicates that in the adsorption process of surface hydroxyl, the surface hydroxyl groups reacted with metal ions (M) to form \(\equiv\text{SOMOH}\). The oxygen in \(\equiv\text{SOMOH}\) causes the increase of adsorbed oxygen on the surface of \(\delta\)-MnO\(_2\). Therefore, the adsorbed oxygen content increases with the adsorption. It could be seen from Figure 14c that the peak bond energy of Mn2p decreased after adsorption, indicating that the proportion of low-valent Mn increased, which was related to Mn\(^{3+}\) adsorbed by MnO\(_2\) and the Mn\(_3\)O\(_4\) and MnOOH generated during the adsorption process. Figure 14d,e could also verify that Co\(^{3+}\) and Ni\(^{2+}\) were adsorbed by MnO\(_2\), but the adsorption amounts of Co\(^{3+}\) and Ni\(^{2+}\) were relatively small compared with the adsorbent body, so the 2p peak was not obvious. It could be speculated that the combined valence of Co and Ni was bivalent according to the binding energy.

2.2.5. Adsorption Mechanism. According to the above research, the mechanism of manganese dioxide adsorbing Co and Ni ions is as follows. The protonation and deprotonation of surface hydroxyl (\(\equiv\text{SOH}\)) occurred first when MnO\(_2\) was in contact with solution.\(^{55,58}\) The reaction formulas are shown in formula 1 and formula 2.

\[
\equiv\text{SOH} + \text{H}^+ \rightleftharpoons \equiv\text{SOH}^2+ \quad (1)
\]

\[
\equiv\text{SOH} + (\text{OH}^-) \rightleftharpoons \equiv\text{SO}^- + \text{H}_2\text{O} \quad (2)
\]

The hydroxyl group underwent deprotonation reaction to form \(\equiv\text{SO}^-\) and then complexed with Co\(^{3+}\) and Ni\(^{2+}\) in the solution. The reaction formulas are shown in formula 4 and formula 5.

\[
\equiv\text{SOH} + \text{Co}^{3+} \rightleftharpoons \equiv\text{SOCo}^+ + \text{H}^+ \quad (3)
\]

\[
\equiv\text{SOH} + \text{Ni}^{2+} \rightleftharpoons \equiv\text{SONi}^+ + \text{H}^+ \quad (4)
\]

Due to the difference in the complexing ability of hydroxyl groups on the surface of MnO\(_2\) to different cations, there would be an ion exchange reaction on the surface of \(\delta\)-MnO\(_2\). For example, the K\(^{+}\) supporting the layered structure was replaced by metal ions, and a large number of Mn\(^{2+}\), Co\(^{3+}\), and Ni\(^{2+}\) entered the macropore structure of MnO\(_2\), resulting in the change of its microstructure. The complex reaction produced \(\equiv\text{SOCO}^+\) and \(\equiv\text{SONi}^+\), so Co and Ni appeared on the surface element distribution of \(\delta\)-MnO\(_2\) after adsorption. A large number of surface hydroxyl groups of MnO\(_2\) combined with metal ions, and the utilization rate of hydroxyl groups increased, resulting in the weakening of hydroxyl vibration peak. The surface hydroxyl group reacted with metal ions (M) to form \(\equiv\text{SOMOH}\). The oxygen in \(\equiv\text{SOMOH}\) still only existed on the surface of MnO\(_2\) in the form of adsorbed oxygen. Therefore, the adsorbed oxygen content increased with the adsorption. After the complexation reaction, Co\(^{3+}\) and Ni\(^{2+}\) appeared on the surface of MnO\(_2\), Mn\(^{3+}\) was also adsorbed by MnO\(_2\), and MnO\(_2\) and MnOOH were produced during the adsorption process, which would increase the proportion of low-valence Mn.

3. EXPERIMENTS

3.1. Experimental Materials and Equipment. Sulfuric acid, ammonia, potassium permanganate, manganese acetate, manganese sulfate monohydrate, nickel sulfate hexahydrate, and cobalt sulfate heptahydrate used in the experiment were all analytically pure reagents and produced by Tianjin Comitry Co., Ltd. The experimental equipment used was as follows: the PHS-25 digital pH meter was produced by Shanghai Yidan Scientific Instruments Co., Ltd.; the HH-3 constant-temperature water bath boiler was produced by Shanghai Scientific Analysis Experimental Instruments Co., Ltd.; the DHG-905A constant-temperature drying box was produced by Beijing Yongguangming Medical Instruments Co., Ltd.; the P4Z vacuum pump was produced by Beijing Jinghui Kaiye Co., Ltd.; the PL2002 electronic analysis balance was produced by Mettler-Toledo Instruments (Shanghai) Co., Ltd.; the JJ-1 precision booster electric stirrer was produced by Changzhou Aohua Instruments Co., Ltd.; the SHA-C constant-temperature water bath shaker...
Figure 14. XPS spectra of δ-MnO₂ before and after adsorption: (a) full spectrum, (b) O1s spectrum, (c) Mn2p spectrum, (d) Ni2p spectrum, and (e) Co2p spectrum.
A recirculating oscillator was produced by Changzhou Guohua Electric Co., Ltd.; the SX-4-10 box resistance furnace was produced by Tianjin Tate Scientific Instruments Co., Ltd.; the HY-SB rotary oscillator was produced by Changzhou Langyue Instruments Manufacturing Co., Ltd.; and the A3AFG-13 flame atomic absorption spectrometer was produced by Beijing Pusan General Instrument Co., Ltd.

3.2. Experimental Process. The synthesis steps of $\delta$-MnO$_2$ are as follows: 0.1 mol/L potassium permanganate solution 300 mL and 0.15 mol/L manganese acetate solution 150 mL were prepared with deionized water, respectively. The potassium permanganate solution was first stirred by magnetic force for 30 min, and then the prepared concentration of manganese acetate solution was added. The stirring reaction was carried out at 80 °C for 6 h. After the solution was cooled to room temperature, the black precipitate was obtained. The product was washed with deionized water many times, and the impurity ions were removed. The product was dried at 100 °C for 5 h.

The steps of synthesizing $\delta$-MnO$_2$ are as follows: 0.1 mol/L potassium permanganate solution 300 mL and 0.15 mol/L manganese sulfate solution 150 mL were prepared with deionized water, respectively. The potassium permanganate solution was first stirred by magnetic force for 30 min, and then the prepared concentration of manganese sulfate solution was added. The magnetic stirring reaction was carried out at 80 °C for 6 h. After the solution was cooled to room temperature, the brown and black precipitate was obtained. The product was washed with deionized water many times, and the impurity ions were removed. The product was dried at 100 °C for 5 h.

A mixed solution of Mn$_2$O$_3$, Ni$_2$O$_3$, and Co$_2$O$_4$ was prepared with manganese sulfate monohydrate, nickel sulfate hexahydrate, cobalt sulfate heptahydrate, and deionized water. The pH of the solution was adjusted with 10% ammonia, and a certain amount of prepared $\delta$-MnO$_2$ was added. The solution was continuously stirred in a constant-temperature water bath at a certain temperature. Due to the influence of the pH of MnO$_2$ equi-acidity point, the pH of the solution would decrease to a certain value. The pH of the solution was adjusted to 7 by dropping ammonia. With the progress of the reaction, the pH of the solution decreased again and continued to be adjusted until the pH did not decrease. The adsorption experiments were carried out by controlling the reaction time, reaction temperature, reaction pH, MnO$_2$ addition, Mn$^{2+}$ concentration, Co$^{2+}$ concentration, and Ni$^{2+}$ concentration. After the adsorption, the solution was quickly filtered. The concentrations of Ni$^{2+}$ and Co$^{2+}$ in the filtrate were determined by an A3AFG-13 flame atomic absorption spectrometer, and the filter residue was further characterized and analyzed after drying.

3.3. Characterization Methods. The adsorption rate formula is shown in formula 5:

$$Q = \frac{c_0 - c}{c_0} \times 100\%$$  \hspace{1cm} (5)

$c_0$ is the initial concentration of impurity ions before adsorption, and $c$ is the concentration of impurity ions after adsorption.

In the experiment, the phase identification was done by a Bruker D8 ADVANCE diffraction analyzer from Bruker, Germany. The microstructure and energy spectrum were analyzed by an SU8020 scanning electron microscope from Hitachi, Japan. The FT-IR analysis was collected on a Nicolet is10 infrared spectrometer produced by Nigaoji, USA. The XPS data were collected on a Thermo ESCALAB 250Xi electronic energy spectrometer produced by ThermoFisher Scientific, USA.

4. CONCLUSIONS

Two kinds of $\delta$-MnO$_2$ were prepared under controlled conditions. With $\delta$-MnO$_2$ addition amount of 10 g/L, Co$^{2+}$ and Ni$^{2+}$ in the manganese sulfate solution with Mn$^{2+}$ concentration of 20 g/L were adsorbed and removed, and better adsorption conditions were obtained. They were as follows: When Co$^{2+}$ concentration was 80 mg/L, Ni$^{2+}$ concentration was 80 mg/L, reaction time was 60 min, reaction temperature was 80 °C, and pH value was 7, the adsorption rate of Co$^{2+}$ and Ni$^{2+}$ by the two kinds of $\delta$-MnO$_2$ reached more than 80%. The phase, microstructure, surface hydroxyl, surface element content, and surface oxygen of the $\delta$-MnO$_2$ were analyzed after adsorption. MnOOH phase was found in both kinds of $\delta$-MnO$_2$ after adsorption. $\delta_1$-MnO$_2$ and $\delta_2$-MnO$_2$ showed dense rod-like structures with different lengths and flake-like structures of fine particles. Co and Ni were distributed on the surface and gap of MnO$_2$ particles after adsorption, the atomic percentage of Co was slightly higher than that of Ni, and the oxygen content would increase after adsorption. After adsorption, the surface hydroxyl vibration peaks of $\delta$-MnO$_2$ decreased, and new vibration peaks appeared near 2668.32, 1401.00, and 2052.19 cm$^{-1}$, indicating that cations such as Co$^{2+}$ and Ni$^{2+}$ complexed with hydroxyl and new vibration peaks were formed on the surface of $\delta$-MnO$_2$. After adsorption, partial Co$^{2+}$ and Ni$^{2+}$ appeared on the surface of $\delta$-MnO$_2$ and the surface oxygen increased. The adsorption mechanism of manganese dioxide is revealed, as follows: $\delta$-MnO$_2$ reacted with metal ions (M) to form $\text{M\text{=SOMOH}}$ through surface hydroxyl groups so as to realize the adsorption and removal of Co$^{2+}$ and Ni$^{2+}$ in the manganese sulfate solution.

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Notes
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**REFERENCES**

(1) Liu, Y.; Ming, X. Q.; Huang, B. H.; Liu, H. H.; Yuan, M. L. Control of Fluorine Content in High Purity Manganese Sulfate Prepared By Fluorination. Min. Metall. Eng. 2021, 41, 98–102.

(2) He, Y. H.; Zhang, H. J.; Xiong, S. MnSO₄ solution and preparation of battery grade high purity manganese sulfate. Hydrometallurgy 2019, 38, 380–384.

(3) Zhao, Y. H.; Wu, R. L.; Hu, P. Study on impurity characteristics and purification process of high purity manganese sulfate. World Nonferrous Metals 2020, 1, 186–190.

(4) Chen, Z. H.; Feng, H. C.; Luo, Y. Y.; Lei, J.; Huang, X. Determination of silicon content in manganese sulfate for battery and battery materials. Shanxi Chemical Industry 2021, 41, 35–36.

(5) He, B. H. Experimental study on removal of heavy metals from industrial manganese sulfate. China Manganese Industry 2021, 39, 56–60.

(6) Wang, Y.; Huang, P.; Li, C. Flexible and self-supported manganese dioxide/S composite cathode for high electrochemical performance. Ionics 2021, 27, S037–S047.

(7) Parveen, N.; Ansari, S. A.; Al-Arjan, W. S.; Ansari, M. O. Manganese dioxide coupled with hollow carbon nanofiber toward high-performance electrochemical supercapacitive electrode materials. J. Sci.: Adv. Mater. Devices 2021, 6, 472–482.

(8) Mahdi, F.; Javanbakht, M.; Shahrokhhian, S. Anodic pulse electrodeposition of mesoporous manganese dioxide nanostructures for high performance supercapacitors. J. Alloys Compd. 2021, 887, 161376.

(9) Ahmad, S.; Ahmad, Z.; Kumar, A.; Rafiq, M.; Vashistha, V. K.; Aishiq, M. N.; Kumar, A. Effective removal of methylene blue using nanoscale manganese oxide rods and sphere derived from different precursors of manganese. J. Phys. Chem. Solids 2021, 155, 110121.

(10) Fu, D. J.; Wang, H. F.; Gou, B. B.; Li, M. D.; Wang, J. W. Preparation of Octahedral Mn₃O₄ by Liquid Phase Method. J. Phys.: Cond. Ser. 2022, 2166, No. 012067.

(11) Zhang, H. J.; Song, D. J.; Zhang, Q. J.; Huang, X. P. Evaporation-Cooling Coupling Method to Remove the Calcium and Magnesium Impurities in Leaching Solution of Manganese Ore. IOP Conference Series: Earth and Environmental Science 2021, 651, No. 042055.

(12) Wang, Y. J.; Wang, W. N.; Liu, Y. L.; Liu, F.; Chen, X. Y. Removal of Heavy Metals from Manganese Sulfate Solution and Preparation Battery-level Manganese Sulfate. Nonferrous Metals (Extractive Metallurgy) 2020, 41, 79–84.

(13) Tian, J. Y.; Wang, H. F.; Kuang, S. D.; Yang, Q. K.; Hu, P.; Wang, J. W. Study on Removal of Heavy Metals from Manganese Sulfate Solution by Sulfide. Nonferrous Metals (Extractive Metallurgy) 2019, 12, 6–10.

(14) Lin, D. Z. Experimental Study on Purification of Cadmium from Manganese Sulfate Solution by Manganese Sulfide. China Steel Focus 2020, 11, 39–40.

(15) Lin, Q. Q.; Gu, G. H.; Wang, H. Separation of Manganese from calcium and magnesium in sulfate solutions via carbonate precipitation. Trans. Nonferrous Met. Soc. China 2016, 26, 1118–1125.

(16) Yan, S.; Qiu, Y. R. Preparation of electronic grade Manganese sulfate from leaching solution of ferromanganese slag. Trans. Nonferrous Met. Soc. China 2014, 24, 3716–3721.

(17) He, G. X.; He, L. H.; Zhao, Z. W. Thermodynamic study on phosphorus removal from tungstate solution via magnesium salt precipitation method. Trans. Nonferrous Met. Soc. China 2013, 23, 3440–3447.

(18) Chen, X. L.; Wang, H. F.; Wang, J. W.; Zhao, P. Y. Removal of Cobalt and Nickel from Manganese Sulfate Leachate by Carbonization. Conservation and Utilization of Mineral Resources 2020, 40, 103–107.

(19) Chen, X. L.; Wang, H. F.; Wang, J. W. Removal of Calcium and Magnesium from Manganese Sulfate Leaching Solution via a Reverse Precipitation by Carbonation. Kuangye Gongcheng (Changsha, China) 2020, 40, 82–85+93.

(20) Jantunen, N.; Kauppinen, T.; Salminen, J.; Virolainen, S.; Lassi, U.; Sainio, T. Separation of zinc and iron from secondary manganese sulfate leachate by solvent extraction. Miner. Eng. 2021, 173, 107200.

(21) Chen, H. Y.; Wang, K. T.; Ming, X. Q.; Zhan, F.; Muhammad, Y.; Zhan, Y. Z.; Wei, W. J.; Li, H. Q. The Efficient Removal of Calcium and Magnesium Ions from Industrial Manganese Sulfate Solution through the Integrated Application of Concentrated Sulfuric Acid and Ethanol. Metals 2021, 11, 1339.

(22) Wang, H. F.; You, X. Y.; Tian, J. Y.; Chen, X. L.; Wang, J. W. Solubility and crystallinity of manganese, magnesium and ammonium double salt systems. Mater. Express 2021, 11, 540–550.

(23) Wang, H. F.; You, X. Y.; Tian, J. Y.; Chen, X. L.; Wang, J. W. Removal of Calcium and Magnesium from Manganese Sulfate Leaching Solution via a Reverse Precipitation by Carbonation. Kuangye Gongcheng (Changsha, China) 2020, 40, 82–85+93.

(24) Wang, H. F.; You, X. Y.; Tian, J. Y.; Chen, X. L.; Wang, J. W. Removal of Calcium and Magnesium from Manganese Sulfate Leaching Solution via a Reverse Precipitation by Carbonation. Kuangye Gongcheng (Changsha, China) 2020, 40, 82–85+93.

(25) Ihsanullah, I. Applications of MOFs as adsorbents in water purification: Progress, challenges and outlook. Current Opinion in Environmental Science & Health 2022, 26, 100335.

(26) Thakur, A. K.; Singh, R.; Teja, P. R.; Pundir, V. Green adsorbents for the removal of heavy metals from Wastewater: A review. Mater. Today: Proc. 2022, 57, 1468–1472.

(27) Zhang, H. S.; Xu, X. L.; Li, F. X.; Zhang, Y. X.; Xu, H. X.; Sun, Y. Y.; Xu, Y. X.; Gu, C. L.; Luo, J.; Gao, B. MIL. series of metal organic frameworks (MOFs) as novel adsorbents for heavy metals in water: A review. J. Hazard. Mater. 2022, 429, 128271.

(28) Zhao, P.; Huang, Z. B.; Ma, Q.; Zhang, B. L.; Wang, P. Artificial humic acid synthesized from food wastes: An efficient and recyclable adsorbent of Pb (II) and Cd (II) from aqueous solution. Environ. Technol. Innovation 2022, 27, 102399.

(29) Ihsanullah, I. Applications of MOFs as adsorbents in water purification: Progress, challenges and outlook. Current Opinion in Environmental Science & Health 2022, 26, 100335.

(30) Egorova, A. A.; Bushkova, T. M.; Kolesnik, I. V.; Yapryntsev, A. V.; Egorov, A. V. Purification of Water by Efficient Adsorbents. Russ. J. Inorg. Chem. 2021, 66, 146–152.

(31) Ma, J. P.; Zhao, Q. Y.; Wang, C. Removal of heavy metal ions by manganese dioxide-based nanomaterials and mechanism research: A review. Environ. Chem. 2020, 39, 687–703.

(32) Zou, Z. H.; He, S. F.; Han, C. Y.; Zhang, L. Y.; Luo, Y. M. Progress of Research on Treatment of Heavy Metal Wastewater by Adsorption. Environ. Prot. Sci. 2010, 36, 22–24.
(31) Meng, K. Y.; Wu, X. W.; Zhang, X. Y.; Su, S. M.; Huang, Z. H.; Min, X.; Liu, Y. G.; Fang, M. H. Efficient Adsorption of the Cd(II) and As(V) Using Novel Adsorbent Ferrihydrite/Manganese Dioxide Composites. ACS Omega 2019, 4, 18627−18636.

(32) Maneekchar, P.; Mongkolertlop, S. Investigation on adsorption behaviors of heavy metal ions (Cd$^{2+}$, Cr$^{6+}$, Hg$^{2+}$ and Pb$^{2+}$) through low-cost/active manganese dioxide-modified magnetic biochar derived from palm kernel cake residue. J. Environ. Chem. Eng. 2020, 8, 104467.

(33) Tao, W. Q.; Lv, R. W.; Tao, Q. Q. Facile Preparation of Novel Manganese Dioxide Modified Nanofiber and Its Uranium Adsorption Performance. J. Appl. Math. Phys. 2021, 09, 1837−1852.

(34) Cheng, M. M.; Yao, C. X.; Su, Y.; Liu, J. L.; Xu, L. J.; Hou, S. F. Synthesis of membrane-type graphene oxide immobilized manganese dioxide adsorbent and its adsorption behavior for lithium ion. Ceramics 2021, 279, 130487.

(35) Zhang, H. P.; Xu, F. F.; Xue, J. Y.; Chen, S. Y.; Wang, J. J.; Yang, Y. J. Enhanced removal of heavy metal ions from aqueous solution using manganese dioxide-loaded biochar: Behavior and mechanism. Sci. Rep. 2020, 10, 6067.

(36) Yang, R. J.; Fan, Y. Y.; Ye, R. Q.; Tang, Y. X.; Cao, X. H.; Yin, Z. Y.; Zeng, Z. Y. MnO$_2$-Based Materials for Environmental Applications. Adv. Mater. 2021, 33, 2004862.

(37) Shi, W. H.; Liu, X. Y.; Deng, T. Q.; Huang, S. Z.; Ding, M.; Miao, X. H.; Zhu, C. Z.; Zhu, Y. H.; Liu, W. X.; Wu, F. F.; Gao, C. J.; Yang, S. W.; Yang, H. Y.; Shen, J. N.; Cao, X. H. Enabling Superior Sodium Capture for Efficient Water Desalination by a Tubular Polyaniline Decorated with Prussian Blue Nanocrystals. Adv. Mater. 2021, 32, 1907404.

(38) Wang, X. H. Study on adsorption effects of different crystalline MnO$_2$ adsorbents on thallium and antimony in water. Xi’an Polytechnic University 2018.

(39) Kong, L. G.; Zhu, Z. L. Adsorption of several heavy metal ions in micro-polluted water by δ-MnO$_2$, China Sustainable Development Forum 2006[C]. 2006. in Chinese

(40) Kanungo, S. B.; Tripathy, S. S.; Mishra, S.; et al. Adsorption of Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ onto amorphous hydrous manganese dioxide from simple (1-1) electrolyte solutions. J. Colloid Interface Sci. 2004, 269, 11−21.

(41) Oscarson, D. W.; Huang, P. M.; et al. Kinetics of oxidation of arsenite by various manganeseoxides. Soil Sci. Soc. Am. J. 1983, 47, 644−648.

(42) Chen, H.; Ye, Z. J. The study on adsorption of As(III) from wastewater by different types of MnO$_2$. China Environ. Sci. 1998, 2, 126−130.

(43) Li, S. Research on Adsorption Efficiency of Nickel Ion by Synthetic Manganese Oxides; Chongqing University, 2015. in Chinese

(44) Yao, L. N. Arsenic Adsorption Performance of Manganese Oxide Nanoparticles. Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, 2018. in Chinese

(45) Xia, W. T.; Zhao, Z. W.; Ren, Z. D. A Exploratory Research on Deep Removal Trace Molybdenum from Manganese Sulfate Solution with Powder Electrolytic Manganese Dioxide. China’s Manganese Industry 2008, 04, 30−33.

(46) Xia, W. T.; Zhao, Z. W.; Chen, A. L. Research on chemical manganese dioxide adsorbent for removing molybdenum from manganese sulfate solution. Chin. Battery Ind. 2008, 13, 363−366.

(47) Chen, X. L.; Wang, H. F.; Wang, J. W. Experimental Study on the Removal of Molybdenum from Manganese Sulfate Solution with Electrolytic Manganese Anode Slag. Metal Mine 2021, 05, 125−129.

(48) Wang, H. F.; Chen, X. L.; Zhao, P. Y.; Gao, Z. W.; You, X. Y.; Tian, J. Y.; Wang, J. W. Preparation of New Nano-MnO$_2$ and Its Molybdenum Adsorption in Manganese Sulfate Solution. Nanosci. Nanotechnol. Lett. 2020, 12, 1070−1079.

(49) Xue, W. L.; Yi, H.; Lu, Y. L.; Xia, L.; Meng, D. L.; Song, S. X.; Li, Y. T.; Wu, L.; Farias, M. E. Combined electrosorption and chemisorption of As(III) in aqueous solutions with manganese dioxide as the electrode. Environ. Technol. Innovation 2021, 24, 101832.

(50) Chen, J. W.; Chen, W.; Huang, M.; Tang, H. Y.; Zhang, J.; Wang, G.; Wang, R. L. Metal organic frameworks derived manganese dioxide catalyst with abundant chemisorbed oxygen and defects for the efficient removal of gaseous formaldehyde at room temperature. Appl. Surf. Sci. 2021, 565, 150445.