

Electrochemical desorption of high-iron manganese ore

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ABSTRACT

In this thesis, the high-iron manganese ore is used to remove the chromium. After the adsorption is saturated, a certain magnetic field will be introduced, and the high-iron manganese ore will resume performance by the electrochemical desorption method. This thesis studies the reaction process and mechanism and investigates the influence rules of coexisting ions and electrochemical control conditions (electrode distance, electrolysis voltage, and desorption time) on the desorption effect. Chloride ions do not participate in the deposition process, but they affect the formation process of the passivation layer. The sulfate ions participate in the deposition process and affect the formation process of the passivation layer. The bicarbonate ions, calcium ions, and magnesium ions are involved in the deposition process and can promote the passivation of the high-iron manganese ore. After the electrochemical desorption, the regeneration time is about 109.53% and 120.96% of the initial use time under the condition that calcium ions and magnesium ions are mixed with bicarbonate ions at 1 mM/1 mM. At the same time, the service life of high-iron manganese ore also improves with the increase in electrolysis voltage and the extension of desorption time, and it increases first and then decreases with the increase in electrode distance. The optimal electrode distance is 9.0 cm, the optimal desorption time is 20 min, and the optimal electrolysis voltage is 100.0 V.

Keywords: High-iron manganese ore; Electrochemistry; Desorption

1. Introduction

The fillers' passivation that leads to the decline of long-term processing capacity is a key issue which affects the application of fillers [1,2]. Chen [3] and others have confirmed that the high-iron manganese ore can achieve the efficient removal of Cr(VI); however, as the reaction progresses, the active sites on the surface of the material are saturated because of the cover of precipitation [4,5]. The electron transfer process between Fe(II)/Fe(III) and Cr(VI)/Cr(III) becomes the rate-limiting step for the reaction, and the reaction rate constant decreases significantly [6,7]. In this case, the removal efficiency of Cr(VI) will be seriously affected, and the water cannot meet the relevant national standards [8,9]. At present, the control of the passivation problem is mainly based on two kinds of ideas, one is to

alleviate the production of mineral deposits, the other is to make the inactivated filler restore its activity with the treatment [10,11]. But the two ideas can only partially alleviate the phenomenon of inactivation with high cost and large workload, which means that the repair operability in situ is not strong [12]. Therefore, there is a need for a method with low cost, high efficiency, and easy operation or technique to solve the bottleneck problem that the handling capacity of high-iron manganese ore filler decreases due to the deactivation of high-iron manganese ore [1,13–16]. It is confirmed that the electrochemical method has been widely used in the actual operation of water treatment [17–20]; for example, the removal of metal pipe scale uses the electrochemical methods for cleaning [21–23]. In this thesis, a certain electric field is introduced into the desorption process after the high-iron manganese ore filler is inactivated, and this thesis proposes the electrochemical desorption method creatively, which provides a new solution for the bottleneck

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problem of high-iron manganese ore's popularization and application [24].

2. Materials and methods

2.1. Materials

The high-iron manganese ore used in this experiment which comes from Guangxi Guilin is screened by 60 mesh screens.

Reagents: potassium dichromate, sodium chloride, sodium sulfate, sodium bicarbonate, calcium chloride, magnesium chloride and so on. All the above reagents are of analytical grade.

Instruments: graphite electrode, TDL-5 centrifuge; SHZ-82 constant temperature oscillator; MAPADA UV-1100 spectrophotometer; Axios advanced X-ray fluorescence spectrometer; S-4800 scanning electron microscope (SEM).

2.2. Methods

2.2.1. Pretreatment of high-iron manganese ore

The experimental results and data show that the pickling pretreatment can increase the effective reaction specific surface area of high-iron manganese ore to a certain extent.

The high-iron manganese ore should be soaked in 0.5 mol/L hydrochloric acid for 4.0 h, washed with deionized water until neutral, dried at $103^{\circ}\text{C} \pm 2^{\circ}\text{C}$ until constant weight, and sealed for reserve.

2.2.3. Electrochemical desorption

Use a 500 mL beaker as the reactor for the test, and seal the upper end with a sealing film. Use 20.0000 ± 0.0001 g pretreatment high-iron manganese ore as a reaction medium at the bottom, and add 300 mL Cr(VI) standard reaction solution with mass concentration of 5.0 mg/L. When the concentration of Cr(VI) remains constant, filtrate and dry the high-iron manganese ore fillers in the control group and then place them in the reactor. Readd the newly prepared Cr(VI) standard reaction solution and repeat the earlier steps with the same other parameters. Dry the high-iron manganese ore fillers of experimental group at low temperature,

and add 300 mL sodium chloride electrolyte solution whose molar concentration is 0.1 mol/L, and plug the graphite electrode to carry out the electrochemical desorption operation. That is, under the conditions of 100.0 V electrolysis voltage and 9.0 cm electrode distance, carry out the electrolysis for 20 min. When the desorption is completed, filtrate and dry the high-iron manganese ore fillers in the control group and then place them in the reactor. Readd the newly prepared Cr(VI) standard reaction solution and repeat the earlier steps with the same other parameters.

The first 60 min removal process is the first cycle, and the second 60 min removal process is the second cycle. Remove 5 mL supernatant at the time of 5, 10, 15, 20, 30, 45, 60 min during every removal cycle, detect the Cr(VI)'s concentration in solution by Diphenylcarbazide Spectrophotometry, and compare the removal rules and results of the second cycle with the control group. Each test group's condition has three parallel samples.

It is worth noting that all electrolytic tests are carried out based on the results of the first-cycle removal rate of $70.0\% \pm 0.7\%$, and the high-iron manganese ore materials that are not in this range are discarded.

- Chemical conditions

Species and content of ions added in the Cr(VI) standard reaction solution are shown in Table 1.

- Operating conditions

The effects of different electrochemical desorption operating conditions on the experimental results were investigated, namely, introducing the desorption operation under different electrochemical conditions at the end of the first cycle. The specific values of the relevant parameters are shown in Table 2.

3. Results and discussion

3.1. Electrochemical desorption conditions

3.1.1. Chemical conditions

The initial removal rate of group Z0 is 92.80%, and its service life is about 4,300 min. The initial removal rate of

Table 1
Species and content of ions

Number	Chromium concentration (mg/L)	Explore ions	Control group	Add ingredients	Content
Z0	5.0	/	/	/	/
Z0'	5.0	Cl ⁻	/	NaCl	2 mM
Z1	5.0	Cl ⁻	Z0	NaCl	4 mM
Z2	5.0	SO ₄ ²⁻	Z0	Na ₂ SO ₄	2 mM
Z3	5.0	HCO ₃ ⁻	Z0	NaHCO ₃	2 mM
Z4	5.0	Ca ²⁺	Z1	CaCl ₂	2 mM
Z5	5.0	Mg ²⁺	Z1	MgCl ₂	2 mM
Z6	5.0	Ca ²⁺ /HCO ₃ ⁻	Z0'	CaCl ₂ /NaHCO ₃	1 mM/1 mM
Z7	5.0	Mg ²⁺ /HCO ₃ ⁻	Z0'	MgCl ₂ /NaHCO ₃	1 mM/1 mM

Table 2
Test parameters

Variables to be examined	Variable parameter values	Other parameters values
Electrode distance (cm)	4.7, 5.2, 5.9, 7.1, 9.0, 11.2, 13.8	100.0 V, 20 min
Electrolysis voltage (V)	10.0, 15.0, 20.0, 25.0, 50.0, 100.0, 150.0	20 min, 9.0 cm
Desorption time (min)	5, 10, 15, 20, 30, 45, 60	50.0 V, 9.0 cm 100.0 V, 9.0 cm 150.0 V, 9.0 cm

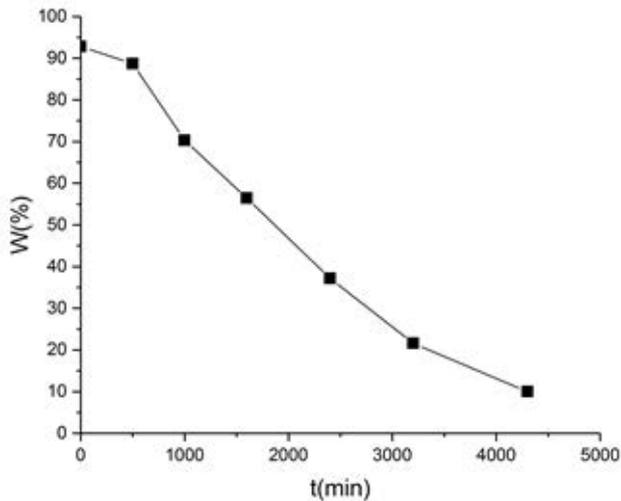


Fig. 1. The removal rate curve of group Z0.

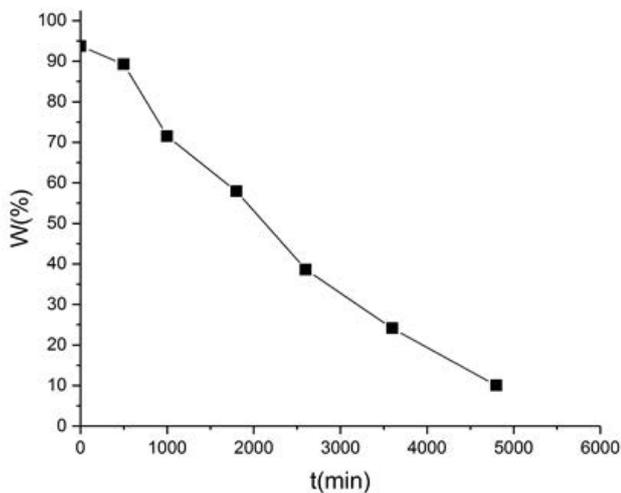


Fig. 2. The removal rate curve of group Z0'.

group Z0' is 93.70%, and its service life is about 4,800 min, as shown in Figs. 1 and 2.

- Effect of chloride ions

The initial removal rate of group Z1 is 97.32%, and its service life is about 6,600 min, as shown in Fig. 3.

Compared with the control group, the introduction of chloride ions makes the system's initial removal rate and service life increase a little.

After operating the electrochemical desorption, the initial removal rate of the system recovered to 98.26%, and the regenerative service life is about 87.12% of the initial service life, namely about 5,700 min.

- Effect of sulfate ions

The initial removal rate of group Z2 is 95.41%, and its service life is about 6,400 min, as shown in Fig. 4.

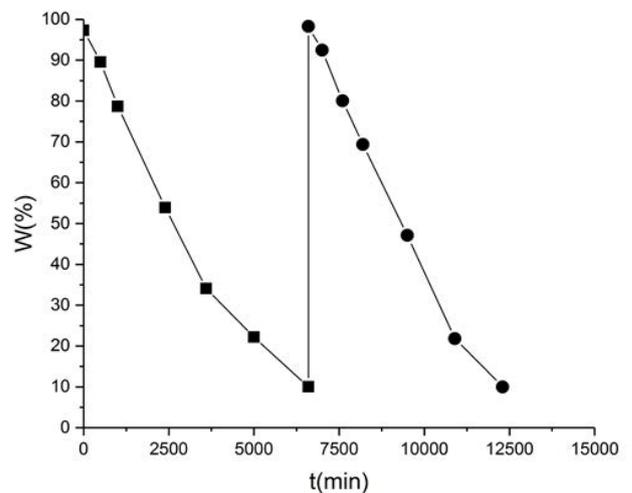


Fig. 3. Double cycle removal rate curve of group Z1.

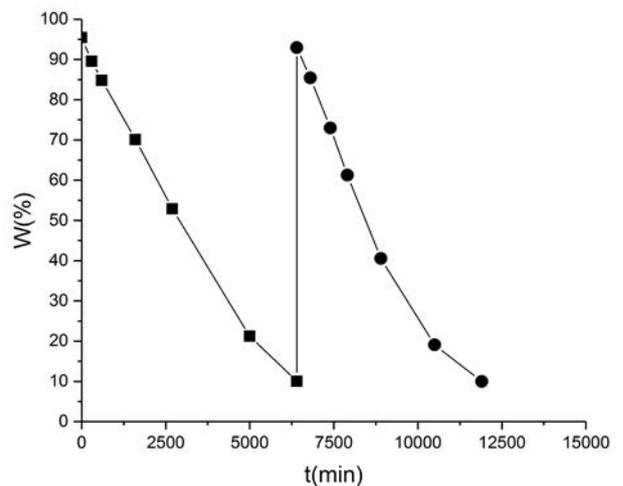


Fig. 4. Double cycle removal rate curve of group Z2.

Compared with the control group, the introduction of sulfate ions makes the system's initial removal rate and service life increase a little.

After operating the electrochemical desorption, the initial removal rate of the system recovered to 92.95%, and the regenerative service life is about 86.40% of the initial service life, namely about 5,500 min.

- Effect of bicarbonate ions

The initial removal rate of group Z3 is 96.24%, and its service life is about 3,700 min, as shown in Fig. 5.

Compared with the control group, the introduction of bicarbonate ions makes the system's initial removal rate increase a little. However, it makes the service life decrease a little.

After operating the electrochemical desorption, the initial removal rate of the system recovered to 93.76%, and the regenerative service life is about 69.03% of the initial service life, namely about 2,500 min.

- Effect of calcium ions

The initial removal rate of group Z4 is 97.30%, and its service life is about 2,800 min, as shown in Fig. 6.

Compared with the control group, the introduction of calcium ions makes the system's initial removal rate increase a little. However, it makes the service life decrease a lot.

After operating the electrochemical desorption, the initial removal rate of the system recovered to 98.62%, and the regenerative service life is about 57.33% of the initial service life, namely about 1,600 min.

- Effect of magnesium ions

The initial removal rate of group Z5 is 98.02%, and its service life is about 1,600 min, as shown in Fig. 7.

Compared with the control group, the introduction of magnesium ions makes the system's initial removal rate and

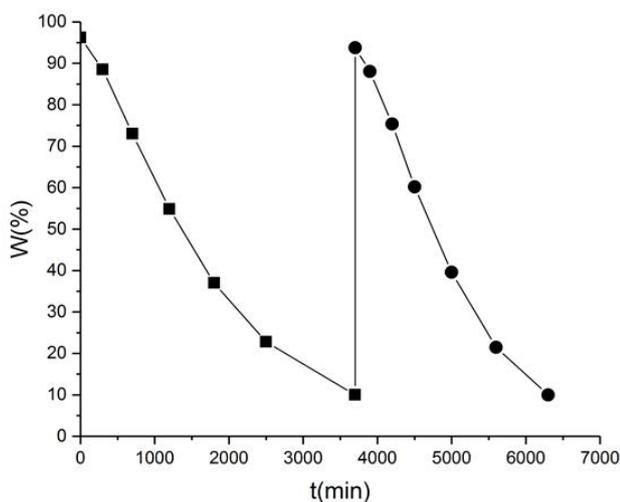


Fig. 5. Double cycle removal rate curve of group Z3.

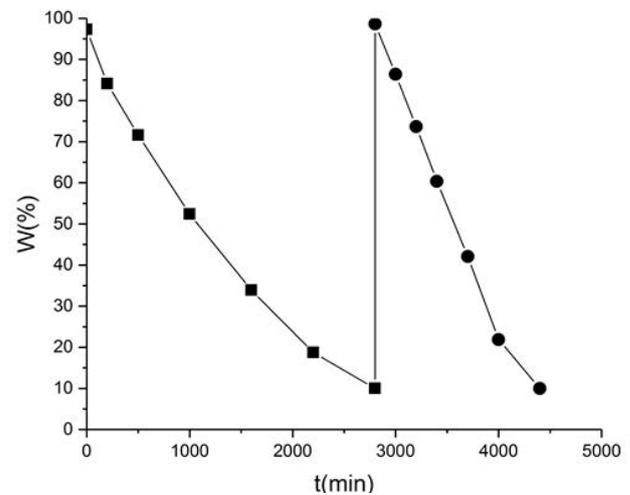


Fig. 6. Double cycle removal rate curve of group Z4.

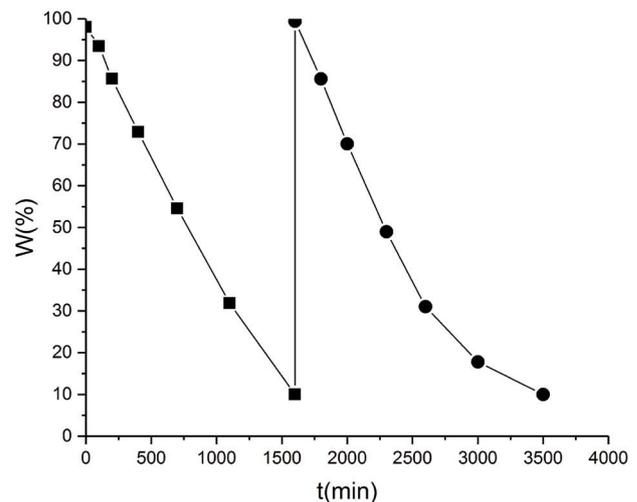


Fig. 7. Double cycle removal rate curve of group Z5.

service life increase a little. However, it makes the service life decrease a lot.

After operating the electrochemical desorption, the initial removal rate of the system recovered to 99.43%, and the regenerative service life is about 112.77% of the initial service life, namely about 1,900 min.

- Effect of calcium ions and bicarbonate ions mixture

The initial removal rate of group Z6 is 97.00%, and its service life is about 2,500 min, as shown in Fig. 8.

Compared with the control group, the introduction of calcium ions and bicarbonate ions does not change the system's initial removal rate. However, it makes the service life decrease a little.

After operating the electrochemical desorption, the initial removal rate of the system recovered to 99.52%, and the regenerative service life is about 109.53% of the initial service life, namely about 2,800 min.

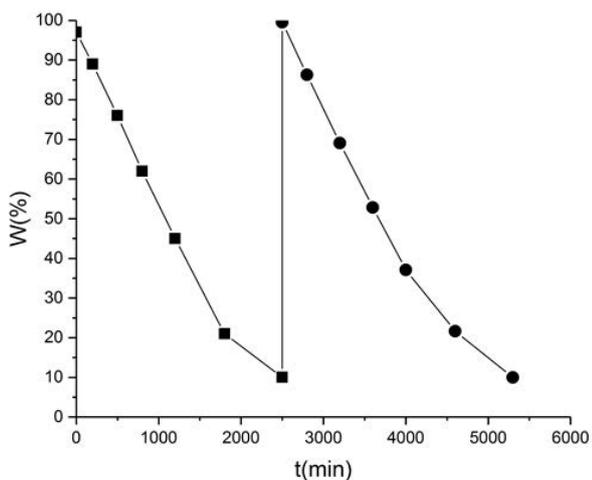


Fig. 8. Double cycle removal rate curve of group Z6.

- Effect of magnesium ions and bicarbonate ions mixture

The initial removal rate of group Z7 is 98.80%, and its service life is about 1,900 min, as shown in Fig. 9.

Compared with the control group, the introduction of magnesium ions and bicarbonate ions makes the system's initial removal rate and service life increase a little. However, it makes the service life decrease a lot. The service life of this group is the shortest in the whole groups.

After operating the electrochemical desorption, the initial removal rate of the system recovered to 98.80%, and the regenerative service life is about 120.96% of the initial service life, namely about 2,500 min.

3.3.2. Operating conditions

- Electrode distance

The research result of electrode distance's influence on desorption effect is shown in Fig. 10.

It can be seen that the effect of electrochemical desorption increases gradually and then weakens with the

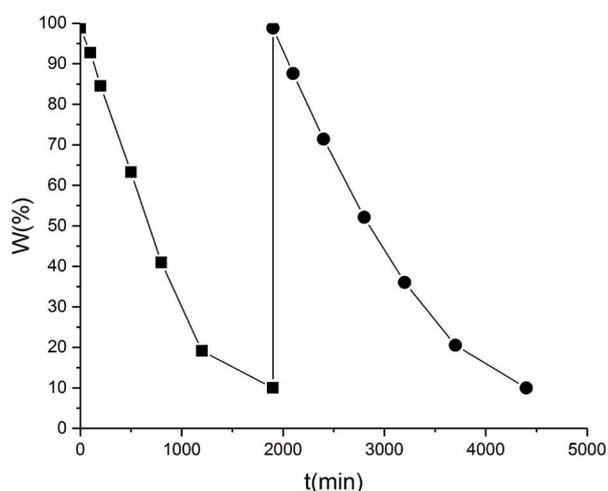


Fig. 9. Double cycle removal rate curve of group Z7.

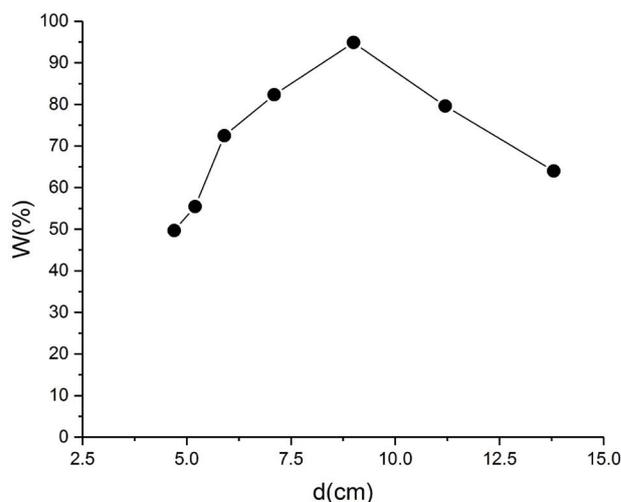


Fig. 10. Effect of electrode distance.

increasing electrode distance. The optimal electrode distance is 9.0 cm.

- Electrolysis voltage

The research result of electrolysis voltage's influence on desorption effect is shown in Fig. 11.

At the electrolysis voltage of 10.0 and 15.0 V, the removal efficiency of the second cycle is not significantly different, and the removal rates are 49.34% and 50.44%, respectively. In the range of 20.0–100.0 V electrolysis voltage, the removal rate increases with the increase in electrolysis voltage. However, with the further increase in electrolysis voltage, the removal rate of Cr(VI) decreases gradually at the end of the second cycle.

At the electrolysis voltage of 150.0 V, the removal rate is 82.08% at the end of the second cycle. In the electrolyte, Cr(VI) does not reduce, and no iron ions are detected. Therefore, the reason that the decrease in the removal rate after the high-voltage desorption operation may be that the

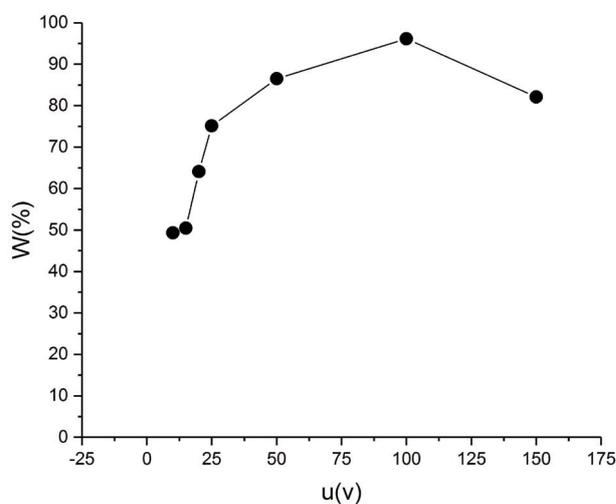


Fig. 11. Effect of electrolysis voltage.

dissolution of iron ions increases with the increase in electrolysis voltage, and the new precipitation generation reaction is converted into the dominance process of electrochemical desorption operation. In addition, long over-electrolysis will make high-iron manganese ore filler decrease rapidly, which is not conducive to the stable and sustainable operation of high-iron manganese ore filler.

- Desorption time

Desorption time is an important factor that affects the desorption effect. The experimental results show that the activity of high-iron manganese ore recovers effectively with the operation, and the removal rate of Cr(VI) is higher than that of the control group at the end of the second cycle.

Under the condition of 50.0 V electrolysis voltage, when the desorption time reaches 15 min, the removal rate of Cr(VI) is 64.21% at the end of the second cycle, and the removal rate of Cr(VI) increases with the prolongation of time after the desorption operation. When the desorption time reaches 45 min, the removal rate of the system reaches the highest value, 93.82%. However, when the electrolysis time is further extended to 60 min, the removal rate of Cr(VI) begins to decrease to 72.70%, as shown in Fig. 12(a).

When the electrolysis voltage is at 100.0 and 150.0 V, the same change rule appears. At the electrolysis voltage of 100.0 V, the optimal electrolysis time is 20 min, as shown in Fig. 12(b). At the electrolysis voltage of 150.0 V, the optimal electrolysis time is 10 min, as shown in Fig. 12(c).

3.2. Characterization analysis

3.2.1. X-ray fluorescence analysis

The ferrous ions and iron ions solution mentioned in this study are obtained by soaking natural high-iron manganese ore with acid, and the composition of natural high-iron manganese ore is complicated. Natural high-iron manganese ore contains Mn, Fe, Si, Al, Ca, Mg, Zn, and other elements, which is detected in the previous experiment by X-ray fluorescence (XRF) analysis technique. Therefore, the soaking solution with acid contains not only ferrous ions, iron ions, but also a variety of other elements. The analysis results are shown in Table 3.

In Table 3, the content of the various elements is represented by their oxide forms, but the element does not necessarily present in the form of an oxide in natural high-iron manganese ore. For example, iron is represented by Fe_2O_3 , but iron in the natural high-iron manganese ore may exist in the form of other kind of oxide or hydroxide; loss on ignition refers to the percentage of weight lost by burning the sample at $1,000^\circ\text{C}$ – $1,100^\circ\text{C}$, usually including moisture and carbon dioxide.

It can be seen in Table 3 that in natural high-iron manganese ore, in addition to iron and manganese oxide, only Al oxide content is more than 1%, while the content of the remaining elements is very small which can be ignored.

Characterization results show that natural high-iron manganese ore contains a lot of Fe element. When the high-iron manganese ore filler is inactivated, the electric field with a certain intensity is introduced. Then, the direction at which the electronic flow in the high-iron manganese ore filler is the

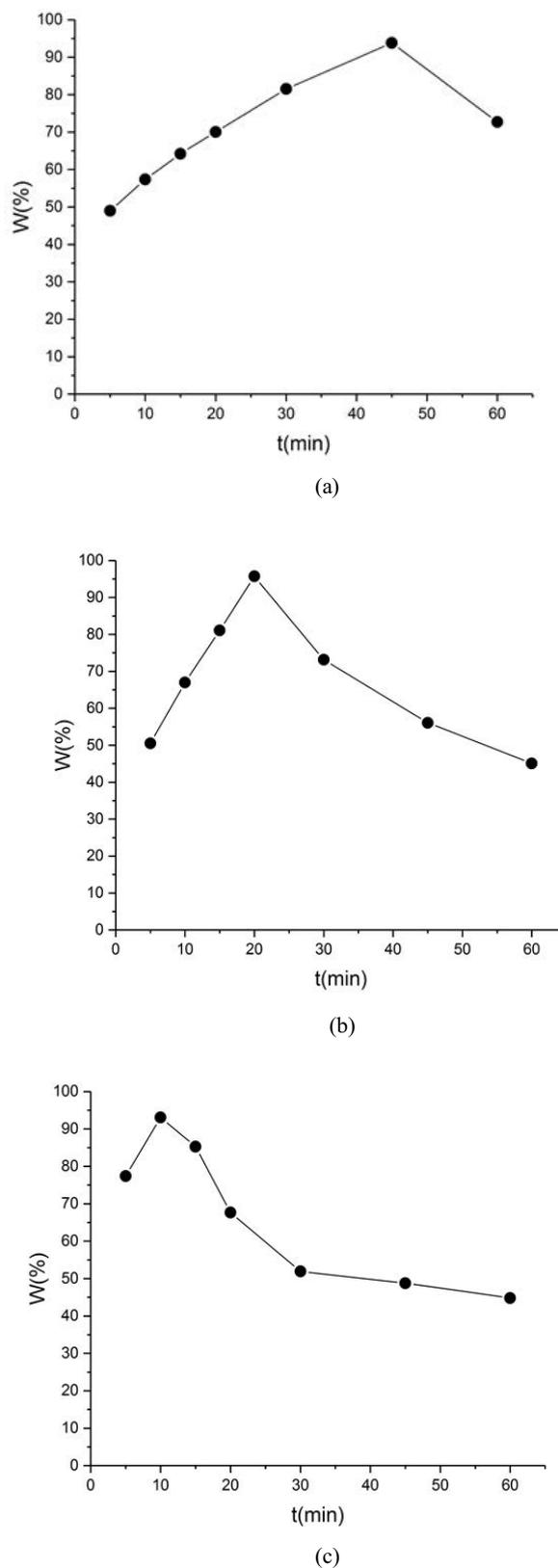


Fig. 12. Effect of desorption time. (a) Effect of desorption time under the condition of 50.0 V. (b) Effect of desorption time under the condition of 100.0 V. (c) Effect of desorption time under the condition of 150.0 V.

Table 3
Mass fraction of each element's oxides in natural high-iron manganese ore

Composition	Mass fraction (%)
Na ₂ O	0.42
Al ₂ O ₃	1.14
SiO ₂	0.10
P ₂ O ₅	0.16
SO ₃	0.89
CaO	0.29
MnO	15.36
Fe ₂ O ₃	76.13
ZnO	0.04
Loss on ignition	5.47

cathode, and the direction at which the electronic flow out the filler is the anode. The anode side dissolves a large amount of ferrous ions, which can react to remove the precipitation layer. The cathode side generates a lot of hydrogen, and the bubbles escape from the surface of the material, which peels off the sediment layer at the same time.

In the process of power, the acidity and alkalinity near the poles can also be changed through the inverted pole from time to time, destroying the precipitation conditions, decompose the precipitation layer.

3.2.2. SEM analysis

Figs. 13 and 14 show the true structure and pattern photograph of the natural high-iron manganese ore before and after its adsorption of Cr(VI) under SEM. The magnification is 500 times.

The results show that there is little gap between the solid spherical particles before desorption, and a large amount of chromium particles are adsorbed on the surface.

Solid spherical particles arrange loosely with good uniformity before desorption, so they have good effects on

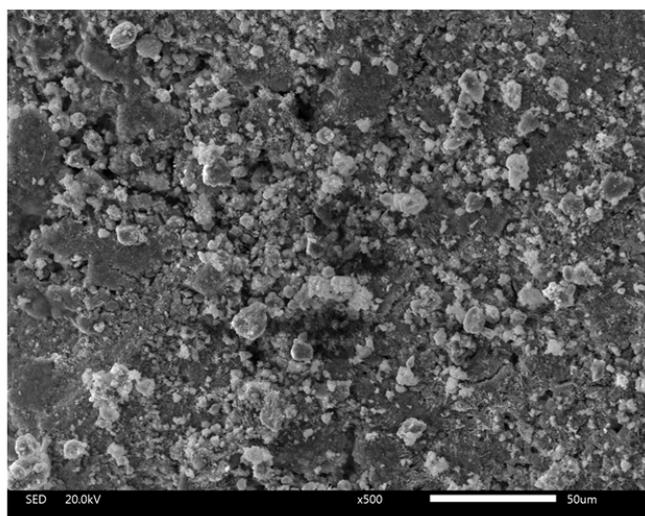


Fig. 13. SEM micrograph before desorption.

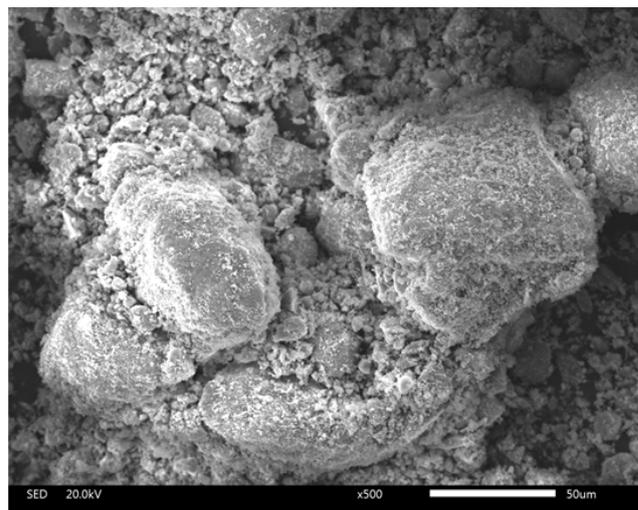


Fig. 14. SEM micrograph after desorption.

water particles at the aspects of adsorption, bridging and network capture. At the same time, the chromium in the water is easily absorbed in their voids, reducing pollution, which further explains that the electrochemical technology is an effective method to make the high-iron manganese ore filler restore activity and operate stably and sustainably.

4. Conclusions

- After the inactivation and deactivation of the high-iron manganese ore, the introduction of successive electrochemical desorption operations based on different electrolysis time makes the initial removal rate of the system restore and reuse effectively.
- Chloride ions do not participate in the deposition process, but they affect the formation process of the passivation layer. The sulfate ions participate in the deposition process and affect the formation process of the passivation layer. The bicarbonate ions, calcium ions, and magnesium ions are involved in the deposition process and can promote the passivation of the high-iron manganese ore. After the electrochemical desorption, the regeneration time is about 109.53% and 120.96% of the initial use time under the condition that calcium ions and magnesium ions are mixed with bicarbonate ions at 1 mM/1 mM.
- The influence mechanism of electrochemical control conditions and the experimental results show that Cr(VI) removal rate of high-iron manganese ore improves with the increase in electrolysis voltage and the extension of desorption time, and it increases first and then decreases with the increase in electrode distance. The optimal electrode distance is 9.0 cm, the optimal desorption time is 20 min, and the optimal electrolysis voltage is 100.0 V.

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