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Preparation of Micro-Electrolytic Iron-Carbon Filler for Sewage by Recycling Metallurgical Dust

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Abstract: In this paper, a new iron-carbon micro-electrolytic filler for wastewater treatment was prepared using the blast furnace dust. The effects of preparation conditions on the performance of the filler during the wastewater treatment were investigated. The optimal preparation conditions of the filler were obtained, which provided an experimental theoretical basis for the use of metallurgical dust sludge in the preparation of micro-electrolytic fillers. From the results of treating methyl orange-simulated wastewater with fillers of different preparation conditions, it could be obtained that the improvement of the filler processing performance requires a suitable iron to carbon ratio, sintering time, and sintering temperature. The optimum preparation conditions were a 1:2 iron-carbon ratio, 30 min sintering time, and 1100 °C sintering temperature. The effect of treatment conditions on the performance of the iron-carbon micro-electrolytic filler was also investigated. The results showed that increasing the filler addition, increasing the treatment temperature, and decreasing the initial pH could effectively improve the treatment efficiency of the filler for methyl orange-simulated wastewater. More than 99% of the methyl orange could be removed in the wastewater under the conditions of 5 g of filler, 40 °C, and pH = 3.

Keywords: metallurgical dust; iron-carbon micro-electrolytic filler; wastewater treatment; preparation parameters

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1. Introduction

The metallurgical dust produced by Chinese iron and steel enterprises accounts for about 10% of the crude steel output. In 2021, the production of metallurgical dust was about 103.3 million tons, which is a very large amount. The accumulation of metallurgical dust not only occupies a large number of land resources but also easily pollutes the soil and air [1,2]. Therefore, the resourceful utilization of metallurgical dust has always been an issue of great concern to the government, steel enterprises, and research institutions [3–7]. As a waste from steel plants, the metallurgical dust is rich in a large number of valuable elements, but with low content. The traditional recycling method is mixing with iron ore powder for sintering or injection into a blast furnace [8–11]. However, the alkali metals in the dust will be enriched in the ironmaking process and then will destroy the smooth operation of the sinter machine and blast furnace [12–14]. Therefore, it is of great practical importance to explore a new method for resourceful utilization of metallurgical dust.

The iron-carbon micro-electrolysis technology is based on the principle of electrochemical corrosion of metals and uses the micro-primary battery generated between iron and carbon to treat wastewater [15]. The schematic diagram of iron-carbon micro-electrolysis is shown in Figure 1. Iron-carbon micro-electrolysis technology involves complex reactions

such as redox, colloidal flocculation, and adsorption in the treatment process, with the following primary cell reaction equations [16–21]:

$$\text{Anode: } Fe - 2e^- \rightarrow Fe^{2+} \quad E^\theta\ (Fe/Fe^{2+}) = -0.44\ V \tag{1}$$

$$\text{Cathode: } 2H^+ + 2e^- \rightarrow 2[H] \rightarrow H_2 \quad E^\theta\ (H^+/H_2) = 0\ V \tag{2}$$

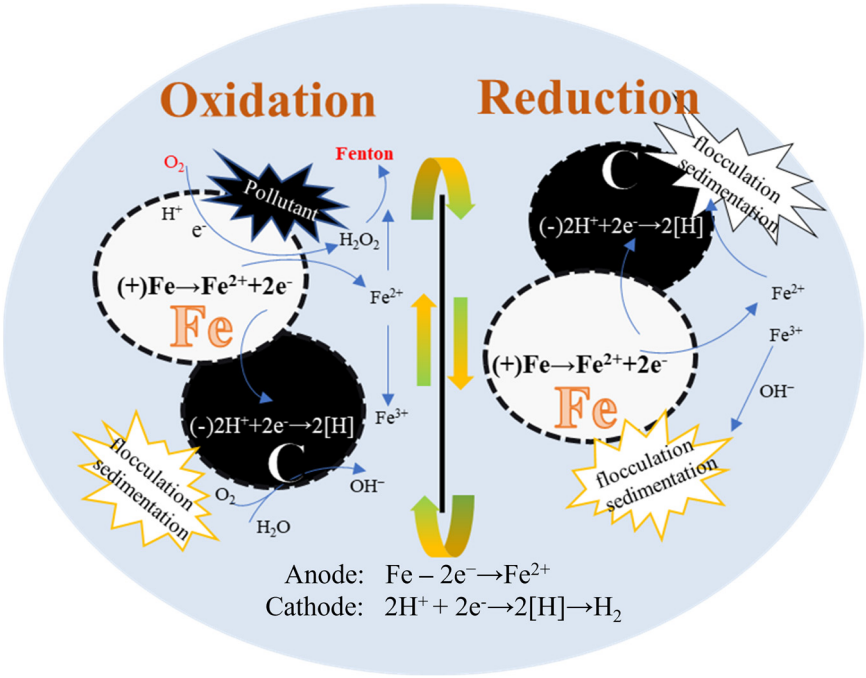

Figure 1. Schematic diagram of the iron-carbon micro-electrolysis principle.

In the presence of oxygen, the cathodic reaction is as follows:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^\theta\ (O_2) = +1.23\ V \tag{3}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E^\theta\ (O_2/OH^-) = +0.41\ V \tag{4}$$

$$O_2 + 2H^+ + 2e^- \rightarrow 2H_2O_2 \quad E^\theta\ (O_2/H_2O_2) = +0.68\ V \tag{5}$$

Due to the excellent effect of this process in the treatment of wastewater rich in organic, toxic, and refractory substances, abundant raw material sources, simple technical operation, and low energy consumption, it has been widely used in the treatment of domestic wastewater [22–26]. Sun et al. [27] prepared a new Fe-Cu-C ternary micro-electrolytic filler using iron powder, activated carbon, bentonite, and copper powder. The degradation rate can reach 93.41% with excellent degradation ability when used to treat simulated printing and dyeing wastewater. The key aspect of iron-carbon micro-electrolysis technology lies in the iron-carbon filler itself, which is mainly prepared from reduced iron powder, activated carbon, and additional non-ferrous metals, the raw materials of which are more expensive, and the production cost is higher. Metallurgical dust is a kind of ideal raw material source for iron-carbon fillers with wide sources and huge output, and containing zinc, alkali metals, and alkaline earth metals, which are harmful to the blast furnace, such as blast furnace dust, basic oxygen furnace dust, electric arc furnace dust, etc. If it can be applied to the preparation of iron-carbon micro-electrolytic filler, it can not only absorb a large amount of metallurgical dust in the iron and steel industry, but can also treat a lot of industrial wastewaters, which has important significance for the green development of the steel industry.

In this paper, the metallurgical dust, iron ore powder, and coal tar pitch, which were cheap materials, were used as the raw materials for the micro-electrolytic filler preparation. The micro-electrolytic filler with an integrated iron-carbon structure was prepared by high-temperature sintering and then used to treat methyl orange-simulated wastewater to explore the optimal preparation and treatment process so as to broaden the resource utilization of metallurgical dust sludge.

2. Materials and Methods

2.1. Materials

The raw materials for the preparation of micro-electrolysis fillers were blast furnace dust, iron ore powder, and coal tar pitch.

(1) Blast furnace dust

For the determination of the elemental composition of blast furnace dust ash by chemical analysis, the results are shown in Table 1. As can be seen from Table 1, the main components of dust removal ash are C and Fe, with 45.7% and 23.27% by mass, respectively. Therefore, this blast furnace dust is suitable for the preparation of the micro-electrolytic iron-carbon filler, which can be used as the source material for the carbon and iron.

Table 1. Blast furnace dust composition (wt%).

Element	C	TFe	Zn	Pb	K_2O	Na_2O
Content	45.70	23.27	0.46	0.05	0.52	0.50

Note: Fe^{2+} = 3.45%, Fe^{3+} = 19.82%, TFe = Fe^{2+} + Fe^{3+} = 23.27%.

(2) Iron ore powder

Iron ore powder can be used as a raw material for the micro-electrolysis iron-carbon filler, and its chemical composition is shown in Table 2. It can be seen from the table that the iron element content of the iron ore powder is relatively high, which is 55.15 wt%.

Table 2. Chemical composition of iron ore powder (wt%).

Element	TFe	FeO	SiO_2	CaO	Al_2O_3	MgO	P	S
Content	55.15	0.82	11.59	0.19	4.55	0.34	0.134	0.022

(3) Coal tar pitch

The results of proximate and ultimate analyses of the coal tar pitch are shown in Table 3. The fixed carbon content of coal tar pitch is as high as 51.64 wt%, which can be used as a source material of carbon for the preparation of iron-carbon micro-electrolytic fillers.

Table 3. Proximate and ultimate analyses of coal tar pitch (wt%).

Samples	Proximate Analysis				Ultimate Analysis				
Coal tar pitch	FCad	Vad	Mad	Aad	C	H	O	N	S
Samples	51.64	37.46	2.63	8.27	91.81	3.82	2.72	0.73	0.68

2.2. Micro-Electrolytic Packing Preparation Method

Before preparing the micro-electrolyzed iron-carbon filler, the raw materials blast furnace dust, coal tar pitch, and iron ore powder were put into a drying box and dried at a temperature of 80 °C for 5 h. A crusher was used to crush the iron ore, and then the iron ore powder that had passed through a 50-mesh (0.27 mm) sieve was collected for use. According to the different iron-carbon ratios (molar ratios) in the ingredients in Table 4, a certain amount of blast furnace dust, iron ore powder, and coal tar pitch

(20 wt%) was weighed, and then the three raw materials were evenly mixed and stirred. Then, 16 g of the mixture was packed into a cylindrical graphite crucible (20 mm inner diameter, 60 mm height) and compacted with a stainless-steel post (20 mm diameter). Five small cylindrical graphite crucibles were placed in a large crucible and then heated in a high-temperature furnace.

Table 4. Micro-electrolytic filler ingredients table.

Samples	Fe:C 1:1	Fe:C 1:1.5	Fe:C 1:2	Fe:C 1:2.5	Fe:C 1:3
Blast furnace dust/%	9.2	16.3	22.7	28.4	39
Iron ore powder/%	70.8	63.7	57.3	51.6	41
Coal tar pitch/%	20	20	20	20	20

Figure 2 show the preparation process of the micro-electrolytic packing. Figure 3 shows the high-temperature tubular furnace used to prepare the experimental product. The temperature, atmosphere, flow rate, and other parameters of the high-temperature furnace can be controlled by the computer. The heating regime for the experiments in this study was as follows: Firstly, it rose from room temperature to the set temperature (950 °C, 1000 °C, 1050 °C, 1100 °C, 1150 °C) at a heating rate of 10 °C/min, and then the final temperature was retained for a certain time (10 min, 20 min, 30 min, 40 min, 50 min), and the furnace tube automatically rose out of the furnace chamber after the sintering finished, and then cooled down at room temperature. N_2 at 1 L/min was passed throughout the experiment as a protective atmosphere. The cooled micro-electrolytic filler was removed from the crucible, ground with a mortar, and sieved with a 50-mesh (0.27 mm) sieve, and the resulting filler powder was placed in a sealed bag.

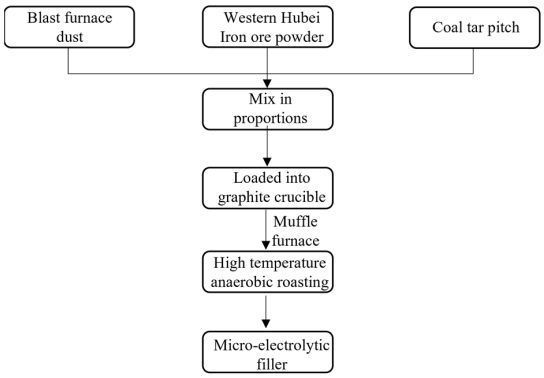

Figure 2. Flow chart of the preparation of micro-electrolytic fillers.

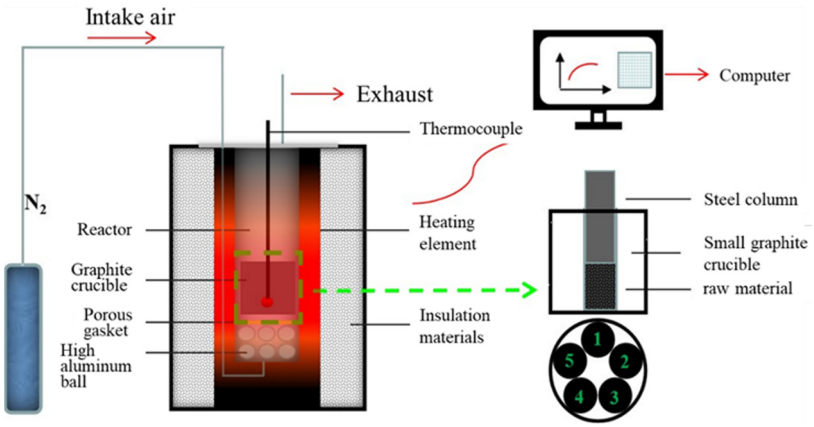

Figure 3. Schematic diagram of the high-temperature furnace.

2.3. Treatment of Simulated Wastewater

Methyl orange wastewater is a common printing and dyeing wastewater, with a high organic content, bright color, certain toxicity, and poor biochemical properties, and it is a suitable wastewater treatment choice due to it containing more refractory organic matter, which is necessary to pretreat it in order to obtain a better treatment effect.

Here, 500 mL of simulated wastewater with a concentration of 100 mg/L of methyl orange was poured into the beaker, and the acid–base solution was used to adjust its initial pH value. Then, the beaker was placed in a water bath to adjust the treatment temperature of the solution, and the mechanical stirrer was turned on to stir the solution at a speed of 500 r/min. Next, 3 g (2 g, 4 g, 5 g, 6 g, 7 g) of the prepared micro-electrolytic filler was weighed and add into the solution for the reaction. About 6 mL of simulated wastewater was drawn using a syringe at the reaction times of 2 min, 4 min, 6 min, 8 min, 10 min, and 12 min, the extracted samples were filtered through a 0.45 μm aqueous filter head, and then the filtered solutions were collected in 10 mL glass sample bottles.

The concentration of methyl orange solution was measured using a UV spectrophotometer. The absorbance of the solution was measured at a wavelength of 464 nm, and then the absorbance of the solution was converted to the corresponding concentration value by the equation of the drawn standard curve. The standard curve of methyl orange solution needed to be plotted before the experiment and is shown in Figure 4.

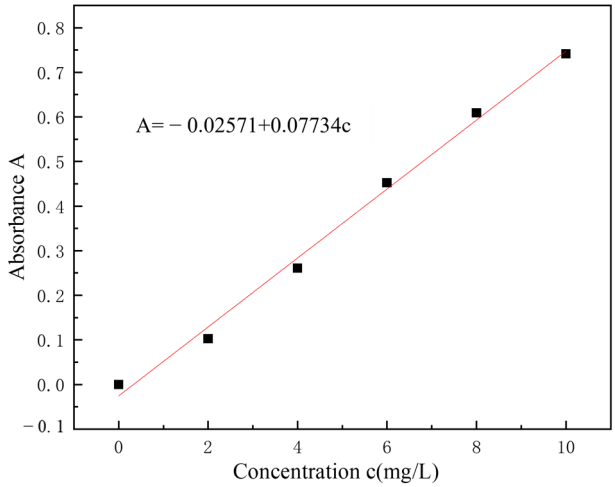

Figure 4. Standard curve of methyl orange solution.

Methyl orange standard curve: A = −0.02571 + 0.07734c, where A is the absorbance and c is the concentration of the solution.

2.4. Analysis of Physical and Chemical Properties

A Rigaku D/MAX 2500PC X-ray diffractometer, Cu target radiation, voltage of 40 kV, current of 150 mA, scanning angle of 10~90°, scanning rate of 4 (°)/min, sampling interval of 0.02°, and a sample particle size of less than 0.074 mm were used to analyze the microcrystalline structure of the micro-electrolytic fillers. The microscopic morphology of the micro-electrolytic filler was observed using an FEI Quanta 250 electron scanning microscope.

3. Results and Discussion

The main factors affecting the treatment effect of micro-electrolytic fillers in treating wastewater are the iron-carbon ratio, sintering temperature, sintering time, filler dosage, treatment temperature, and the initial pH of the simulated wastewater. In this study, the effect of various factors on the removal of methyl orange was investigated through optimization experiments using the single-factor method, so as to obtain the optimal preparation process of micro-electrolysis and the optimal treatment conditions for methyl orange

wastewater. In addition, by characterizing the phase and microstructure of the prepared micro-electrolysis filler, the influence mechanism of various factors on the performance of the filler was explored.

3.1. Study on the Effect of Preparation Conditions on the Performance of Fillers

3.1.1. The Effect of Iron-Carbon Ratio on the Properties of Filler

When the sintering temperature was 1100 °C, the sintering time was 30 min, the initial pH of the simulated wastewater was 7, and the amount of filler was 5 g, the removal effect of the micro-electrolytic fillers prepared under the conditions of the iron-carbon ratios of 1:1, 1:1.5, 1:2, 1:2.5, and 1:3 on the methyl orange in wastewater was investigated. The experimental results are shown in Figure 5.

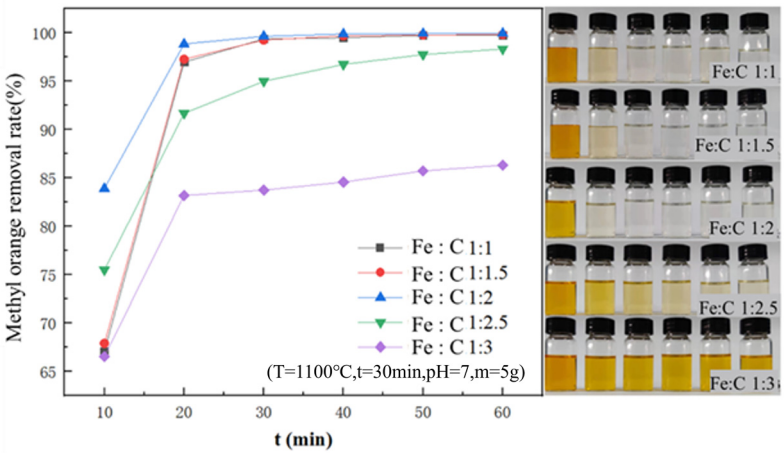

Figure 5. The effect of the iron-carbon ratio on the removal of the filler methyl orange.

From Figure 5, it can be seen that the iron-carbon ratio of the micro-electrolytic filler has a certain influence on the simulated wastewater treatment performance of the filler. When the iron-carbon ratio was 1:1 and the treatment time was 20 min, the removal rate of methyl orange reached more than 95%. When the treatment time was 30 min, the removal rate of methyl orange reached more than 99%. The treatment effect of an iron-carbon ratio of 1:1 was relatively good. The treatment effect of an iron-carbon ratio of 1:1.5 was similar to that of an iron-carbon ratio of 1:1, but the iron-carbon ratio of 1:1.5 was slightly better. When the iron-carbon ratio of the filler was reduced to 1:2, the removal rate of methyl orange reached 98.8% at 20 min, 99% at 30 min, and 99.9% at 40 min. It can be seen that its effect of removing methyl orange was excellent and significantly better than other fillers. Further reducing the iron-carbon ratio to 1:2.5 and 1:3, the methyl orange removal rate was 91.7% and 83.2% at the treatment time of 20 min, respectively. The treatment effect was worse than the filler with a 1:2 iron-carbon ratio. From the above results, it can be concluded that with the decrease in the iron-carbon ratio, the removal effect of methyl orange-simulated wastewater of fillers first became better and then worse, and the micro-electrolysis filler with an iron-carbon ratio of 1:2 had the best effect on methyl orange wastewater treatment.

Understanding the mineral phase of the iron-carbon micro-electrolytic filler is of great significance for studying its mechanism of treating simulated wastewater. The prepared micro-electrolysis filler was analyzed by XRD to further reveal its influence mechanism. The micro-electrolytic fillers prepared under five conditions of iron-carbon ratios of 1:1, 1:1.5, 1:2, 1:2.5, and 1:3 were characterized. The obtained XRD patterns are shown in Figure 6.

It can be seen from the figure that the fillers with different ratios all generated the diffraction peaks of zero-valent iron at 44.52°, 65.14°, and 82.32°, and the diffraction peak of SiO_2 at 26.61°, and there were no other obvious impurity peaks. It can be seen that the iron ore powder in the filler has been basically reduced to metallic iron, and Zn and Pb were removed by evaporation during roasting. When the iron-carbon ratio was reduced to 1:2.5 and 1:3, there was an obvious 002-wide peak on the XRD curve, which corresponded

to the graphite peak of coal tar. The reason for the poor treatment efficiency may be due to the high carbon content of the filler, and the number of primary cells generated decreased, thus reducing the efficiency of wastewater treatment.

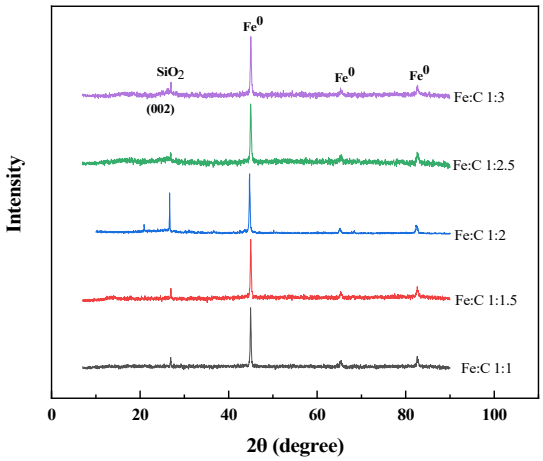

Figure 6. XRD patterns of fillers with different ratios.

SEM images of iron-carbon micro-electrolytic fillers with different ratios are shown in Figure 7. Many pores can be observed on the surface of the filler, and the boundary between iron and carbon is also very clear. After sintering, the metal iron particles produced by reduction had an oolitic structure. The filler with an iron-carbon ratio of 1:1 had a larger particle size of iron particles, but its carbon content was the lowest among all fillers. The low carbon content will affect the reduction of iron ore. Therefore, it can be seen from the figure that the number of iron particles on the surface was obviously small, and there were many iron minerals that have not been reduced. It can be seen from the electron microscope image of the filler with the iron-carbon ratio of 1:2 that it had more iron particles that have been reduced, and the iron particles and the carbon matrix were evenly distributed, and the reduction degree was relatively high. The reaction chemical formula is as follows:

$$Fe_2O_3 + 3C == 3CO\uparrow + 2Fe \quad (6)$$

$$3Fe_2O_3 + CO == 2CO_2\uparrow + 2Fe_3O_4 \quad (7)$$

$$2Fe_3O_4 + 2CO == 2CO_2\uparrow + 6FeO \quad (8)$$

$$FeO + CO == CO_2\uparrow + Fe \quad (9)$$

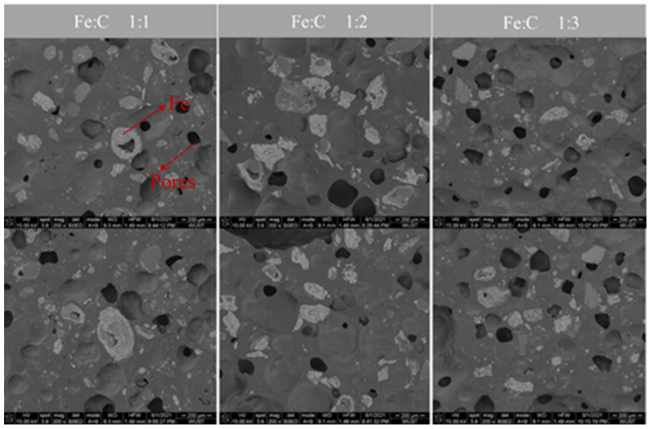

Figure 7. SEM images of iron-carbon micro-electrolytic fillers with different ratios.

Therefore, in the process of treating wastewater, the filler with an iron-carbon ratio of 1:2 had a better treatment effect.

3.1.2. Effect of Sintering Time on Filler Performance

At a sintering temperature of 1100 °C, an iron to carbon ratio of 1:2, an initial pH of 7, and a filler dosage of 5 g, the effect of micro-electrolytic fillers prepared under five conditions of the sintering times of 10 min, 20 min, 30 min, 40 min, and 50 min on the removal of methyl orange from wastewater was investigated. The experimental results are shown in Figure 8.

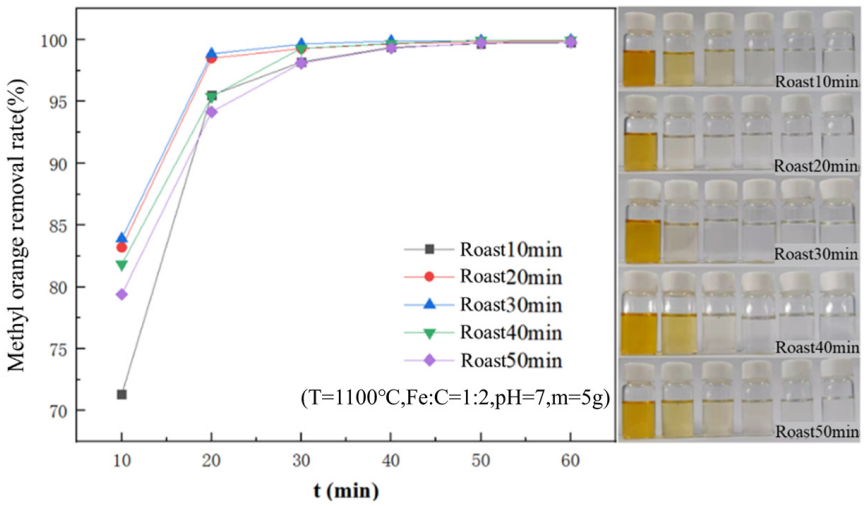

Figure 8. Effect of sintering time on removal of the filler methyl orange.

From Figure 8, it can be seen that the sintering time had a significant effect on the treatment performance of the micro-electrolytic filler and had a clear regularity. When the sintering time was increased from 10 min to 20 min and 30 min, the removal rate of methyl orange in the simulated wastewater with fillers increased from 95.5% to 98.5% and 98.8%, respectively. When the sintering time was further increased to 40 min and 50 min, the methyl orange removal rate of the wastewater decreased to 95.4% and 94.2%, respectively. Therefore, it can be concluded that the performance of the micro-electrolytic filler in removing methyl orange from simulated wastewater improved and then decreased with the increasing sintering time, and neither too long nor too short sintering time is conducive to improving the wastewater treatment performance of the micro-electrolytic filler. The sintering time of 30 min was the best preparation condition.

The micro-electrolytic fillers prepared under five conditions of the sintering times of 10 min, 20 min, 30 min, 40 min, and 50 min were characterized by XRD, as shown in Figure 9.

It can be seen that the fillers prepared with different sintering times all contained reduced zero-valent iron, and the diffraction peaks of zero-valent iron were generated at 44.52°, 65.14°, and 82.32°. However, under the conditions of sintering times of 10 min and 20 min, the reduction of iron minerals was not high, and some small diffraction peaks of iron oxides were generated at about 30°, and graphite diffraction 002 peaks appeared. Therefore, the content of zero-valent iron in the fillers sintered for 10 min and 20 min was less, and the number of galvanic cells that can be generated was reduced, so the treatment effect was not good. The XRD curve of the filler with a sintering time of 30 min was smoother, with less spurious peaks and a high degree of zero-valent iron reduction, and increasing the sintering time did not significantly change the content of zero-valent iron, so the filler with a sintering time of 30 min had the best treatment effect.

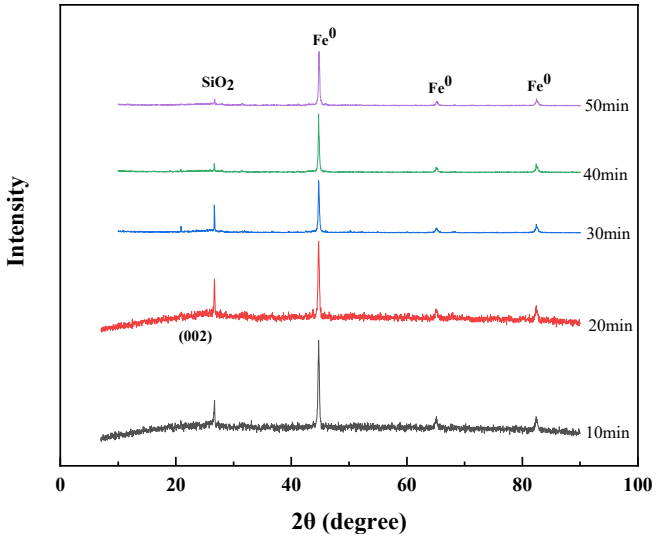

Figure 9. XRD patterns of fillers with different sintering times.

Figure 10 shows that SEM images of iron-carbon micro-electrolytic packing at different sintering times. From the figure, it can be seen that the surface of the filler with a sintering time of 10 min had more incompletely reduced metal iron particles wrapped by iron minerals, which may be the reason for the short sintering time and its lower reduction degree. The sintering time of 50 min had fewer iron particles on the surface of the filler, and the distribution of the reduced metallic iron was more concentrated. The surface of the filler with a sintering time of 30 min had relatively more metallic iron and a high degree of reduction, and obvious silver-white iron particles could be seen. Therefore, the iron-carbon micro-electrolytic filler with a sintering time of 30 min had the best treatment effect.

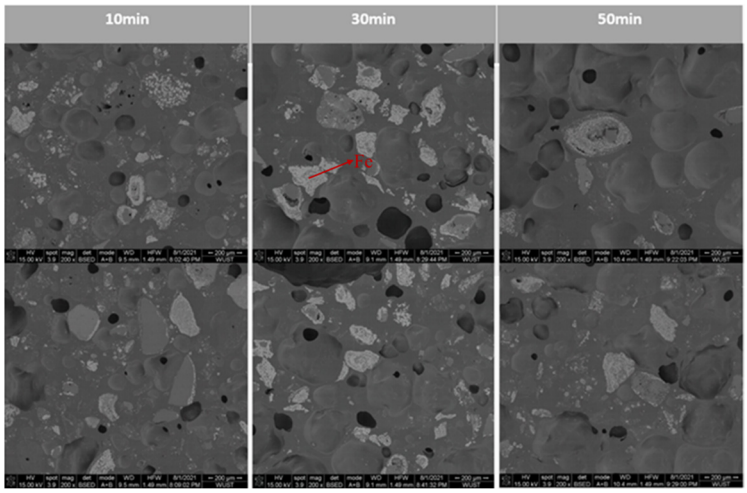

Figure 10. SEM images of iron-carbon micro-electrolytic fillers with different sintering times.

3.1.3. Effect of Sintering Temperature on Filler Performance

At an iron-carbon ratio of 1:2, a sintering time of 30 min, an initial pH = 7 of the simulated wastewater, and a filler dosage of 5 g, the effectiveness of micro-electrolytic fillers prepared at five conditions of sintering temperatures of 950 °C, 1000 °C, 1050 °C, 1100 °C, and 1150 °C on the removal of methyl orange from wastewater was investigated. The experimental results are shown in Figure 11.

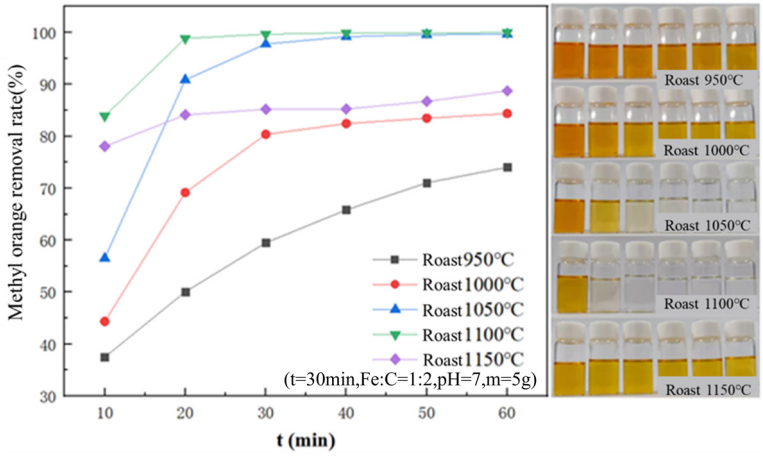

Figure 11. The effect of sintering temperature on the removal of the filler methyl orange.

From Figure 11, it can be seen that the sintering temperature had a large and regular effect on the treatment performance of the micro-electrolytic filler. With the increase of the sintering temperature from 950 °C to 1000 °C, 1050 °C, and 1100 °C, the methyl orange removal rate of the wastewater increased from 74.1% to 84.4%, 99.6%, and 99.9% at 60 min of treatment. However, when the sintering temperature was increased from 1100 °C to 1150 °C, the methyl orange removal rate of the wastewater decreased to 88.7% at 60 min of treatment. It can be seen that either too low or too high sintering temperature was not conducive to improving the wastewater treatment performance of the micro-electrolytic packing: with the increase of the sintering temperature, the wastewater treatment performance of the micro-electrolytic filler first improved and then decreased, reaching the best at 1100 °C.

Under the condition that the iron-carbon ratio was 1:2 and the sintering time was 30 min (protective gas was N_2), the micro-electrolytic fillers were prepared under five conditions of sintering temperature: 950 °C, 1000 °C, 1050 °C, 1100 °C, and 1150 °C. The obtained XRD spectrum is shown in Figure 12. It can be seen from the diagram that the micro-electrolysis fillers prepared at each sintering temperature had the diffraction peaks of zero-valent iron and the XRD curve was relatively smooth, without other complex diffraction peaks.

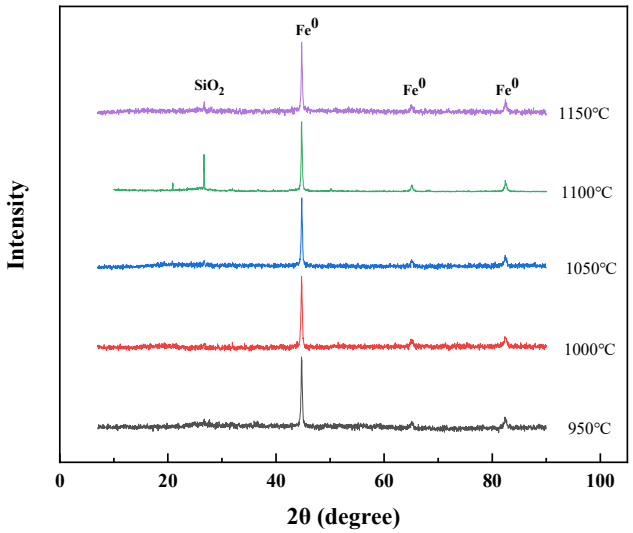

Figure 12. XRD patterns of fillers at different sintering temperatures.

Figure 13 shows the SEM electron micrographs obtained after making powders of iron-carbon micro-electrolytic fillers with different sintering temperatures. It can be seen that the reduced silver-white metallic iron on the surface of the filler with a sintering

temperature of 950 °C and a sintering temperature of 1150 °C was less than that of the filler with a sintering temperature of 1100 °C. The filler with a calcination temperature of 950 °C contained more iron particles wrapped by iron minerals and gangue, with a lower reduction degree. On the surface of the filler calcined at 1150 °C, the reduced iron particles were merged and aggregated, and the metal iron particles were large and unevenly distributed. These factors are not conducive to the treatment of wastewater by micro-electrolysis fillers, so the sintering time of 1100 °C with a high metal iron content and a high reduction degree was the best for the treatment of fillers.

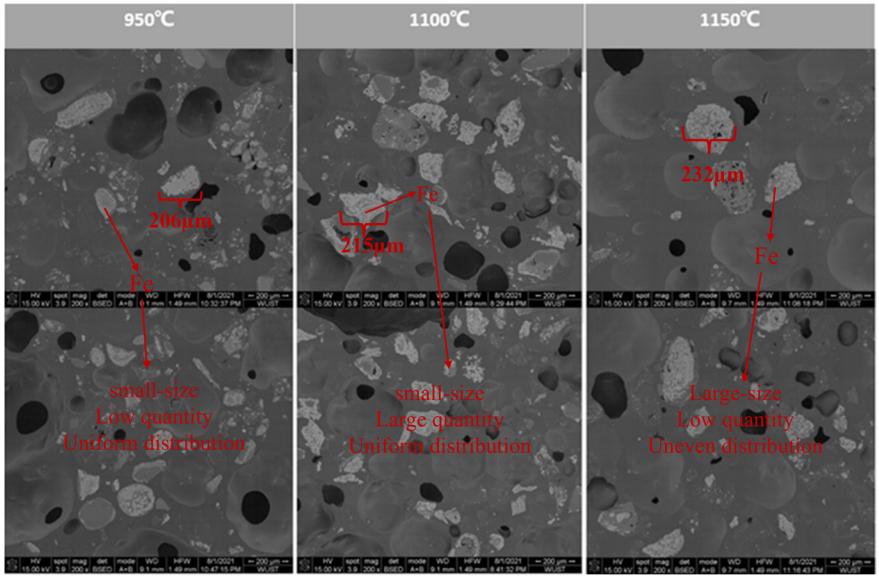

Figure 13. SEM images of iron-carbon micro-electrolytic fillers at different sintering temperatures.

In summary, the best preparation conditions of the micro-electrolytic filler were a 1:2 iron-carbon ratio, a 30 min sintering time, and a 1100 °C sintering temperature. Under these conditions, the removal rate of methyl orange can reach more than 99% in 30 min and 99.9% in 50 min when the filler is used to treat wastewater.

3.2. Study of the Effect of Treatment Conditions on the Wastewater Treatment

In order to further investigate the treatment effect of the micro-electrolytic fillers obtained under the optimal preparation conditions on the simulated wastewater and the effect of different treatment conditions on the treatment effect of the micro-electrolytic fillers, the fillers obtained under the optimal preparation conditions were used to treat the simulated wastewater of methyl orange under different conditions.

3.2.1. Amount of Filler Addition

At a treatment temperature of 30 °C and an initial pH of 7 for the methyl orange solution, the removal effect of the micro-electrolysis filler on the simulated wastewater methyl orange was investigated under the four conditions of 2 g, 3 g, 4 g, and 5 g of filler added in 500 mL of simulated wastewater. The experimental results are shown in Figure 14.

From Figure 14, it can be seen that the larger the amount of filler added, the better the effect of the wastewater treatment. The removal of methyl orange from the simulated wastewater with the addition of 2 g, 3 g, 4 g, and 5 g of fillers reached 65.21%, 79.06%, 97.83%, and 98.52% at 6 min of treatment, respectively. The simulated wastewater with the filler addition of 5 g had a fast removal rate of methyl orange in the early stage of treatment, and the removal rate of methyl orange reached 90% by 4 min of treatment, but the rate began to slow down at the later stage of treatment, and the removal rates were 94.11%, 97.18%, and 98.52% at 5 min, 6 min, and 7 min, respectively, which were very close to the removal rate of the experimental group with 5 g of filler addition. Therefore, when the

amount of filler reached a certain value, increasing the amount of filler did not significantly improve the treatment effect of wastewater, and it also increased the consumption of filler and treatment cost. The filler dosage of 5 g was the best filler addition in this study.

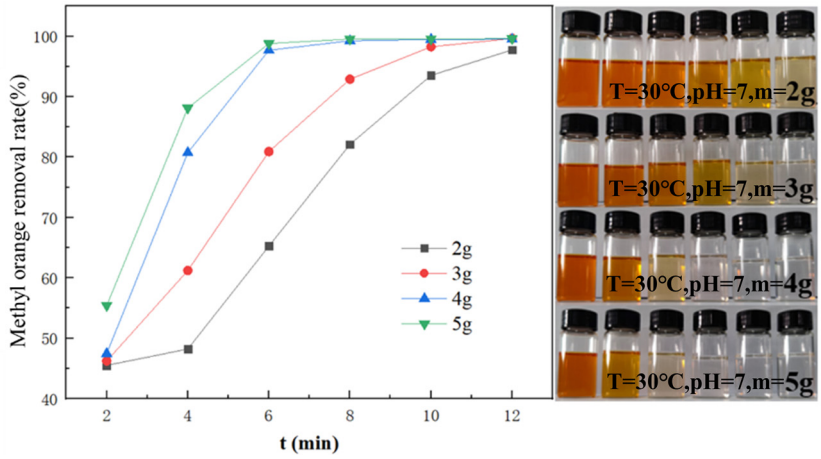

Figure 14. Effect of filler addition on methyl orange removal.

3.2.2. Treatment Temperature

When the amount of filler added was 5 g and the initial pH of methyl orange solution was 7, the removal effect of the micro-electrolytic filler on the simulated wastewater methyl orange was investigated under four conditions of 500 mL of simulated wastewater treatment temperatures of 25 °C, 30 °C, 35 °C, and 40 °C. The experimental results are shown in Figure 15.

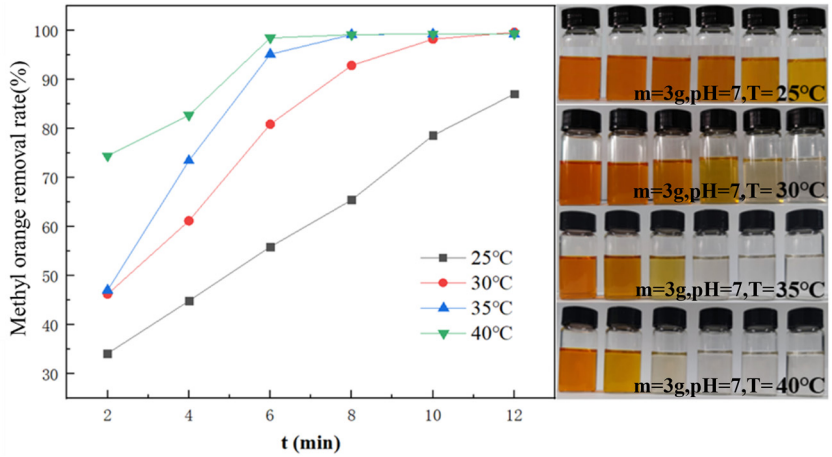

Figure 15. Influence of treatment temperature on the removal of methyl orange.

It can be seen from Figure 15 that the solution treatment temperature had a greater influence on the methyl orange removal effect, and the methyl orange removal effect of the simulated wastewater gradually became better as the solution treatment temperature increased. At the treatment time of 6 min, the removal rate of methyl orange in the experimental group with a temperature of 40 °C reached 98.5%. In contrast, the removal of methyl orange in the experimental groups with treatment temperatures of 35 °C, 30 °C, and 25 °C only reached 95.17%, 80.9%, and 55.87%, respectively. At the treatment time of 12 min, the removal rate of methyl orange was above 99% for the experimental groups with treatment temperatures of 30 °C, 35 °C, and 40 °C. The experimental group with a treatment temperature of 25 °C also achieved 87% removal of methyl orange. Therefore, increasing the solution processing temperature can effectively improve the removal efficiency of methyl orange.

3.2.3. Initial pH

When the amount of filler added was 5 g and the solution treatment temperature was 30 °C, the removal effect of the micro-electrolysis filler on wastewater methyl orange was investigated under the conditions of initial pH = 3, pH = 5, pH = 7, and pH = 9 in simulated wastewater. The experimental results are shown in Figure 16.

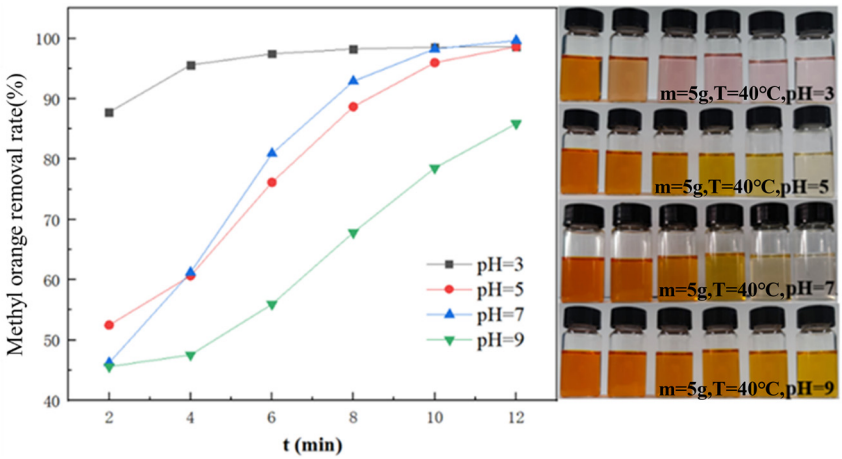

Figure 16. Effect of initial pH on the removal of methyl orange.

As shown in Figure 16, the initial pH of the simulated wastewater had a large effect on the removal efficiency of methyl orange. The methyl orange removal effect of the simulated wastewater was relatively poor when the initial pH $\geq$ 9, and the methyl orange removal efficiency of the simulated wastewater gradually improved as the initial pH decreased. When the removal rate of simulated wastewater reached more than 98%, the experimental group with pH = 9 could not reach this removal rate, and it took 12 min for the experimental group with pH = 7, 11 min for the experimental group with pH = 5, and 11 min for the experimental group with pH = 3. It can be seen that reducing the initial pH of the simulated wastewater can improve the removal efficiency of methyl orange very effectively, i.e., the acidic conditions are more favorable for the treatment of methyl orange wastewater with micro-electrolytic fillers.

3.3. Mechanism of Treating Methyl Orange with Micro-Electrolytic Filler

Methyl orange is a very common strong acid–base indicator, which is the diazo salt of p-aminobenzenesulfonic acid obtained by diazotization of p-aminobenzenesulfonic acid and N, then coupled with N-dimethylaniline in a weakly acidic medium. The molecular structure of methyl orange is shown in Figure 17.

When the simulated wastewater of methyl orange was treated by micro-electrolysis filler prepared from blast furnace dust, methyl orange molecules adsorbed on the surface of zero-valent iron, which is caused by the π-π interaction between methyl orange molecules and the carbon surface, the large specific surface area, and the abundant porosity of methyl orange molecules. Zero-valent iron is essential for the degradation of methyl orange, which can decompose the azo bond (-N=N-) of the methyl orange molecule to achieve the purpose of degrading it.

The mechanism of treating methyl orange wastewater with iron-carbon micro-electrolytic filler is shown in Figure 18. The zero-valent iron in the filler acts as an anode, is oxidized to Fe^{2+}, and provides electrons. The carbon in the filler acts as a cathode to adsorb methyl orange molecules for reduction and decomposition. Figure 19 shows the degradation of the methyl orange molecule by zero-valent iron. The process was divided into two steps: First, the methyl orange molecule obtained the electrons provided by zero-valent iron and combined with H^+ to form an intermediate. The intermediate is unstable and can react to return to the raw material methyl orange molecule, so the first step is a reversible reaction.

Second, methyl orange and zero-valent iron continued to react and further consumed H^+, and finally decomposed to form sulfonic acid and aromatic amine, and the solution also faded [23].

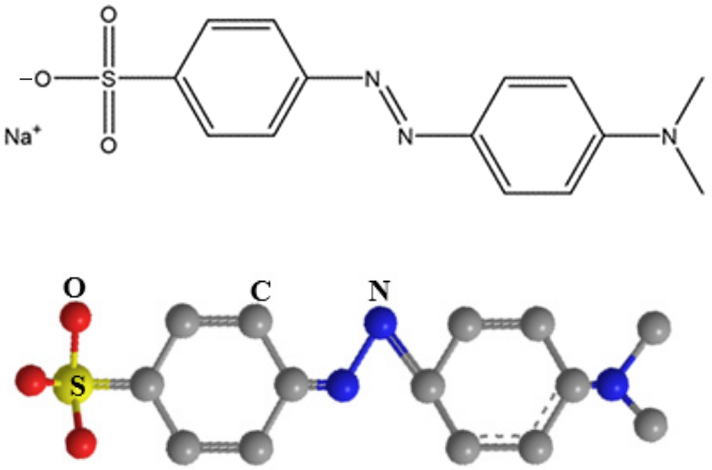

Figure 17. Molecular structure formula of methyl orange.

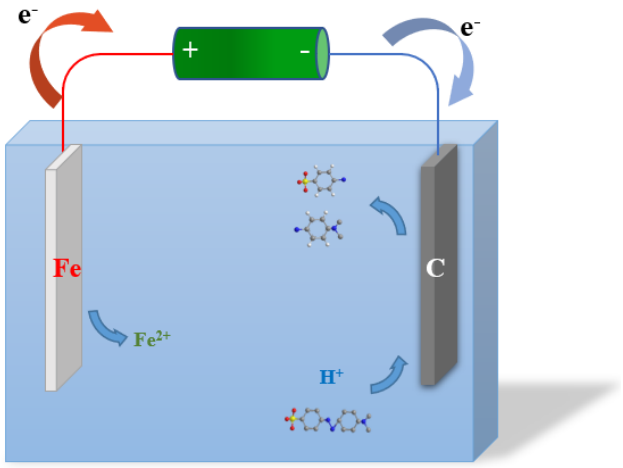

Figure 18. Mechanisms of the filler treatment of methyl orange wastewater.

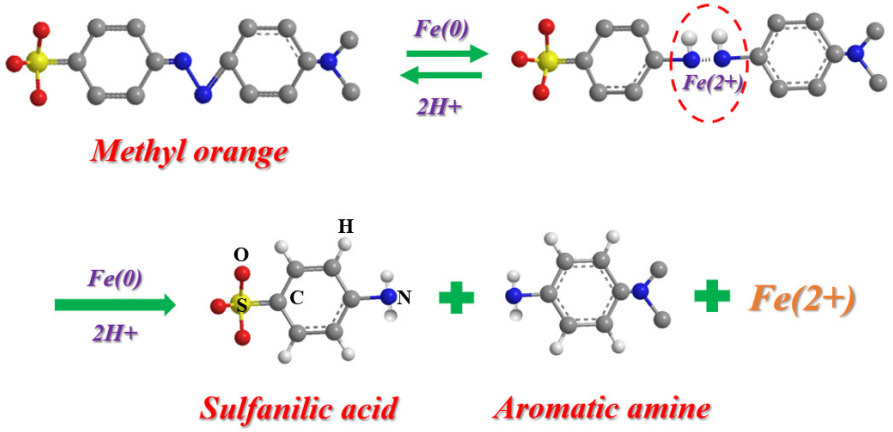

Figure 19. Zero-valent iron degradation process of methyl orange.

4. Conclusions

In this paper, single-factor experiments were used to simulate wastewater treatment experiments with a micro-electrolytic iron-carbon filler under different preparation condi-

tions, and comparative analysis of the mineral composition and microscopic morphology of the micro-electrolytic iron-carbon filler were conducted, and the following conclusions were drawn:

(1) The optimal ratio of micro-electrolytic packing is an iron-carbon ratio of 1:2. A high iron–C ratio will reduce the reduction of iron minerals in the raw material, while a low iron–C ratio will reduce the zero-valent iron content of the prepared micro-electrolytic filler.
(2) The optimal sintering time of the micro-electrolytic filler was 30 min. Too short a sintering time will decrease the reduced zero-valent iron, and too long a sintering time will increase the graphitization of C in the filler, both of which are not conducive to improving the treatment effect of wastewater.
(3) The best sintering temperature of the micro-electrolysis filler was 1100 °C. If the sintering temperature is too low, the reduction degree of iron minerals in the filler will be low. If the sintering temperature is too high, the graphitization degree of carbon in the filler increases, and its activity decreases, which is not conducive to the treatment of wastewater.
(4) Increasing the filler addition, raising the treatment temperature, and lowering the pH of the simulated wastewater can effectively improve the treatment efficiency of methyl orange wastewater. When the filler addition amount was 5 g, the treatment temperature was 40 °C, and the initial pH of methyl orange was 3, the removal rate of methyl orange-simulated wastewater reached a maximum of more than 99%.

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