

## Article

# Experimental Study on the Treatment of Printing and Dyeing Wastewater by Iron–Carbon Micro-Electrolysis and Combined Processes

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## Abstract

Iron–carbon micro-electrolysis and combined processes were used to treat simulated dyeing wastewater containing direct Big Red 4BE dye (concentration of 1500 mg/L, chromaticity of 80,000 times, and salt content of 20 g/L). Through single-factor experiments, the optimal reaction conditions were determined as follows: reaction time of 110 min, initial pH of 5, and iron and carbon mass ratio of 1:2. Under the optimal conditions, the concentration was reduced to 14.51 mg/L, the chromaticity was reduced to 3000 times, and the decolorization rate reached 99.03%. In order to further decrease the wastewater chromaticity, coagulation and Fenton oxidation were respectively employed for in-depth treatment after iron–carbon micro-electrolysis. The total decolorization rate of the dye wastewater exceeded 99.7%, with the treated effluent meeting the specified chromaticity discharge standard (80-fold). The integrated processes of iron–carbon micro-electrolysis combined with either coagulation sedimentation or Fenton oxidation demonstrated superior performance in treating direct Big Red 4BE dye wastewater.

**Keywords:** iron–carbon micro-electrolysis; printing and dyeing wastewater; decolorization rate; coagulation; Fenton oxidation



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## 1. Introduction

The printing and dyeing industry is a major source of industrial wastewater discharge. Statistically, China's printing and dyeing industry discharges more than 4 million tons of wastewater daily. Printing and dyeing wastewater is characterized by its diversity, high chromaticity, poor biochemistry, abundance of toxic and hazardous substances, and high salinity. Improper treatment of such wastewater can lead to severe environmental pollution and pose risks to human health [1].

Printing and dyeing wastewater treatment technologies primarily include adsorption, coagulation, membrane separation, chemical oxidation, photocatalytic oxidation, electrochemical methods, and biological treatment. Traditional treatment methods, such as adsorption [2–4], coagulation, and precipitation [5,6], etc., are mainly used for low-concentration printing and dyeing wastewater or as a pretreatment process for biological treatment to improve the biochemistry of the printing and dyeing wastewater. However,

it remains challenging to enable high-concentration printing and dyeing wastewater to meet the discharge standards. Chemical oxidation [7–9] necessitates constant addition of oxidants, membrane separation technology [10,11] suffers from high power consumption and operational costs, while photocatalytic oxidation technology [12] imposes strict requirements on photocatalyst preparation. Printing and dyeing wastewater features poor biodegradability and abundant toxic/hazardous substances, while its high salinity inhibits microbial growth. Therefore, biological methods are often combined with other techniques for treating such wastewater [13]. Under the condition of high salinity, the wastewater has high electrical conductivity. This characteristic considerably facilitates the application of electrochemical methods in the treatment of high salinity printing and dyeing wastewater.

Iron–carbon micro-electrolysis follows the principle of electrochemical corrosion of metals. In the filler, Fe with a low potential and C with a high potential jointly generate a potential difference in wastewater with certain electrical conductivity, forming countless tiny primary batteries. The wastewater is treated through the electrode reaction, coupled with a series of synergistic effects, such as coagulation, sedimentation, and air flotation [14], frequently used to treat printing and dyeing wastewater [15–17]. He Wei et al. [18] pretreated methyl orange simulated printing and dyeing wastewater using micro-electrolytic materials with a wide range of pH adaptability. The optimal process parameters were determined, and the BOD/COD value of the effluent was increased by approximately five times after pretreatment. Jia Yanping et al. [19] treated the rinsing workshop wastewater of a woolen mill in Jilin City via iron–carbon micro-electrolysis. The highest colorimetric removal rate was 75.34%. The iron–carbon micro-electrolysis process could efficiently decompose pollutants, such as esters and alcohols, and convert them into small-molecule organic pollutants that were readily biodegradable. The biochemistry of the wastewater was improved. She Shuaiqi et al. [20] studied the action mechanism of iron–carbon micro-electrolysis for the treatment of printing and dyeing wastewater. The combination of iron–carbon micro-electrolysis and coagulation sedimentation improved the efficiency of COD removal and reduced the treatment cost. Ren Qingqing [21] removed four kinds of dyes in wastewater using iron–carbon micro-electrolysis, determined the optimal experimental conditions, and evaluated the influence degree of each factor. The iron–carbon micro-electrolysis process, as a pretreatment technology, yielded favorable treatment effects on the four types of wastewater. Evidently, in previous studies, the iron–carbon micro-electrolysis process for treating printing and dyeing wastewater mainly focused on wastewater pretreatment, aiming to improve the wastewater's biodegradability after pretreatment.

The wastewater containing azo dyes is characterized by a high chemical oxygen demand ( $\text{COD}_{\text{Cr}}$ ), a large number of refractory substances, and a high chroma, complicating the decolorization and degradation of dye wastewater [22,23]. Herein, Direct Scarlet 4BE with a typical azo structure was selected for experimental research. Effects of factors such as the initial pH value of the wastewater, reaction time, mass ratio of iron to carbon, and the mode of solid–liquid separation on the treatment effect were investigated. The optimal treatment conditions for the wastewater were determined. Subsequently, iron–carbon micro-electrolysis was coupled with coagulation or Fenton's reagent for wastewater treatment, achieving a superior decolorization effect. After treatment, the wastewater met the chromaticity emission standard of 80 times, as specified in Emission Standard for Water Pollutants in Textile Dyeing and Finishing Industry (GB4287-2012) [24].

## 2. Experimental Design and Sample Testing

### 2.1. Materials, Reagents, and Instruments

The printing and dyeing wastewater was formulated with Direct Big Red 4BE dye, with a concentration of 1500 mg/L, a salt content of 20 g/L, an initial pH of 8.34, and a chromaticity of 80,000 times. The main experimental chemicals included Direct Big Red 4BE dye, sodium chloride, iron powder, granular activated carbon, sodium hydroxide, concentrated sulfuric acid, etc. Main instruments were an electronic analytical balance (model BSA223S), an electric constant temperature blast drying oven (model DHG-9070), a pH meter (model PHS-3C), a rotary oscillator (model HZ-81B), a desktop centrifuge (model 800), as well as an ultraviolet and visible spectrophotometer (model SP-1105).

### 2.2. Material Pretreatment

Pretreatment of iron powder and granular activated carbon was required prior to the experiment. For the iron powder (60 mesh), the pretreatment steps were as follows: first, it was soaked in 10% sodium hydroxide for 6 min to remove oil and grease, then rinsed with tap water until neutral. Next, it was acid-washed with 5% sulfuric acid for 5 min to eliminate iron oxides and activate the iron powder, followed by rinsing with distilled water until neutral, and finally dried for use. The pretreatment of activated carbon was as follows: it was first rinsed with water until free of carbon black, soaked in the prepared wastewater for 48 h, and subsequently dried in an oven prior to use, aiming to eliminate interference from the activated carbon's adsorption effect on the experiment. In the experiment, iron powder should be prepared before use to avoid re-oxidation.

### 2.3. Experimental Design

Iron–carbon micro-electrolysis experiments were carried out to investigate the effects of different reaction times, initial pH values, and iron–carbon mass ratios on the degradation effects. Five 100 mL water samples were respectively poured into 250 mL conical flasks. Each conical flask was injected with a quantitative amount of iron powder and activated carbon. Upon oscillating for a specified time, it was left to stand for 20 min. The supernatant was filtered through a filter membrane (0.45  $\mu\text{m}$ ) for absorbance measurement.

The reaction time ranged from 50 to 130 min. The initial pH of the wastewater was adjusted to 3.0, 4.0, 5.0, 6.0, and 7.0. The amount of activated carbon and iron powder was adjusted according to the Fe/C mass ratios of 1:2, 1:1, 2:1, and 3:1, respectively. Moreover, the effects of different solid–liquid separation methods (centrifugal separation and microfiltration membrane filtration) on the degradation effect were investigated.

Under the optimal conditions of iron and carbon micro-electrolysis, the chromaticity of the treated wastewater remained high. It did not meet the emission standards for chromaticity in Emission Standards for Water Pollutants in Textile Dyeing and Finishing Industry (GB4287-2012) [24]. Coagulation sedimentation and Fenton oxidation were respectively combined with the iron–carbon micro-electrolysis process for further wastewater treatment.

### 2.4. Sample Testing and Data Processing Methods

The absorbance was measured using an ultraviolet and visible spectrophotometer. According to the standard curve, the concentration value was obtained, and the decolorization rate was calculated to judge the treatment effects of the iron–carbon micro-electrolysis process on Direct Red 4BE dye wastewater. Furthermore, the chromaticity was determined utilizing the dilution multiplier method in Water quality—Determination of colority—Dilution level method (HJ 1182-2021) [25]. The pH value was determined by a pH meter.

The absorbance of the treated dye wastewater was measured at 500 nm [26], and the corresponding wastewater concentration was derived from the standard curve. The decolorization rate  $\eta$  of the dye wastewater was calculated according to Equation (1):

$$\eta = (1 - C/C_0) \times 100\% \quad (1)$$

$C$ —concentration value of direct Big Red 4BE dye wastewater after treatment.

$C_0$ —concentration value of direct Big Red 4BE dye effluent before treatment.

Plotting of the standard curve of Direct Red 4BE dye wastewater: Direct Red 4BE solutions with dye concentrations of 0, 10, 20, 30, 40, and 50 mg/L were prepared, with a salt content of 20 g/L. Using distilled water as a reference, the absorbance of each water sample was determined by an ultraviolet-visible spectrophotometer. The standard curve was plotted with the concentration of direct scarlet 4BE as the abscissa and the absorbance value as the ordinate. The direct Big Red 4BE solution exhibited a good linear relationship between the dye concentration and absorbance within the concentration range of 0–50 mg/L, with the correlation coefficient  $R^2$  being 0.9923.

### 3. Results and Analysis

#### 3.1. Single Factor Experiment of Iron–Carbon Micro-Electrolysis

##### 3.1.1. Effects of Different Reaction Times

Five portions of 100 mL of dye wastewater were poured into 250 mL conical flasks, respectively. Quantitative iron powder and activated carbon (iron powder 20 g/L, activated carbon 40 g/L) were added to each water sample, which was then placed on the oscillator. After a 50 min reaction, water samples were collected every 20 min, and the absorbance value of each water sample was determined after standing and filtering. The absorbance of samples with reaction times of 50 min and 70 min was measured after 25-fold dilution, while the absorbance of samples with a reaction time of 90 min was measured after 10-fold dilution. The concentration value and decolorization rate of the samples are shown in Table 1.

**Table 1.** Effects of reaction times on treatment results.

| Reaction Time (min) | Absorbance After Treatment | Concentration After Treatment (mg/L) | Decolorization Rate (%) |
|---------------------|----------------------------|--------------------------------------|-------------------------|
| 50                  | 0.309                      | $20.7 \times 25$                     | 65.50                   |
| 70                  | 0.211                      | $14.58 \times 25$                    | 75.70                   |
| 90                  | 0.213                      | $14.70 \times 10$                    | 90.20                   |
| 110                 | 0.797                      | 51.20                                | 96.59                   |
| 130                 | 0.184                      | 12.89                                | 99.14                   |

Evidently, the decolorization rate increased with increasing reaction time. Within 50–130 min, the decolorization rate increased from 65.50% to 99.14%. After 110 min, the rate of color reduction slowed down, and the decolorization rate exceeded 96%. In the early stage, the Fe of the primary battery anode was sufficient ( $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ ), and there was also highly abundant cathode dissolved oxygen ( $\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$ ), providing enough electron acceptors for the reduction reactions ( $\text{Dye} + \text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Degradation Products}$ ). Due to the high concentration of reactants and favorable reaction conditions, the iron–carbon micro-electrolysis reaction proceeded at a relatively rapid rate. In the later stage, the dye concentration decreased. A large amount of  $\text{Fe}^{2+}$  was produced in the anode, which was further oxidized to  $\text{Fe}^{3+}$  under the action of dissolved oxygen ( $\text{Fe}^{2+} + \text{O}_2 \rightarrow \text{Fe}^{3+} + \text{O}_2^-$ ), and the micro-electrolysis reaction was weakened ( $\text{Dye} + \text{Fe}^{3+} \rightarrow \text{Degradation Products}$ ). The decolorization rate increased slowly under the enrichment of the micro-electric

field and the oxidation of dissolved oxygen. Following comprehensive consideration, the optimal reaction time of dye wastewater was set at 110 min.

### 3.1.2. Effects of Initial pH Values

The initial pH values of the wastewater were adjusted to 3.0, 4.0, 5.0, 6.0, and 7.0, respectively. Each water sample was added with a quantitative amount of iron powder and activated carbon (iron powder 20 g/L, activated carbon 40 g/L), and placed on an oscillator to oscillate for 110 min. Upon completion of the reaction, the samples were allowed to stand for 20 min, and the supernatant was filtered using a filter membrane to measure the absorbance value. The absorbance values of the two samples with initial pH values of 6 and 7 were measured by 10-fold dilution. The results are shown in Table 2.

**Table 2.** Effects of initial pH values on treatment results.

| Initial pH | Absorbance After Treatment | Concentration After Treatment (mg/L) | Decolorization Rate (%) |
|------------|----------------------------|--------------------------------------|-------------------------|
| 3          | 0.031                      | 3.33                                 | 99.78                   |
| 4          | 0.065                      | 5.45                                 | 99.64                   |
| 5          | 0.157                      | 11.20                                | 99.25                   |
| 6          | 0.111                      | $8.325 \times 10$                    | 94.45                   |
| 7          | 0.357                      | $23.70 \times 10$                    | 84.20                   |

As illustrated by Table 2, when the initial pH value fell in the range of 3–7, the decolorization rate of wastewater decreased with increasing initial pH value. When the initial pH value was 3, the decolorization rate of dye wastewater was the highest (99.78%). When the initial pH value was 3–5, the decolorization rate exceeded 99%. When the initial pH was 7, the decolorization rate reached the lowest (84.20%). This phenomenon can be attributed to two primary mechanisms: Firstly, when the initial pH was below 5, the high concentration of  $H^+$  in the water sample induced vigorous reactions with the anodic iron powder. Stronger acidity enhanced the potential difference of the galvanic cell in the solution, thereby intensifying the reaction kinetics. Secondly, lower initial pH promoted the generation of  $Fe^{2+}$  via the anodic reaction ( $Fe \rightarrow Fe^{2+} + 2e^-$ ) and  $H_2$  evolution through the cathodic reaction ( $2H^+ + 2e^- \rightarrow H_2$ ). The elevated  $Fe^{2+}$  content strengthened the redox capacity, facilitating the degradation and removal of dye molecules from the wastewater. When the initial pH value exceeded 5, the acidity of the water sample was reduced, and the active performance of iron was also substantially decreased, thus inhibiting the effects of the iron–carbon microcell. Considering comprehensively, the optimal initial pH value of this experiment was set at 5.

### 3.1.3. Effects of Different Fe/C Mass Ratios

There were four water samples. Quantitative iron powder (20 g/L) was added to each water sample. The amount of activated carbon was adjusted according to the Fe/C mass ratios of 2:1, 1:1, 1:2, and 1:3, implying activated carbon amounts of 10, 20, 40, and 60 g/L, respectively. The oscillation reaction was 110 min, and the absorbance value of each water sample was measured after standing and filtering. Samples with iron–carbon ratios of 2:1 and 1:1 were diluted 10 times, and the absorbance was measured. The results are shown in Table 3.

As shown in Table 3, when the mass ratios of iron to carbon were 2:1 and 1:1, the decolorization rate was low, with the lowest value being 90.20%. When the mass ratios were 1:2 and 1:3, the decolorization rate of dye wastewater was higher, which was basically maintained at approximately 99%. The reason for this phenomenon may be that when the amount of iron powder was relatively large (iron–carbon ratios of 2:1 and 1:1), the

internal electrolysis and flocculation precipitation of iron powder played a major role. With a decreasing mass ratio of iron to carbon, part of the iron powder and activated carbon formed the primary battery, and the effect of the iron powder itself was weakened. When the mass ratio of iron to carbon was less than 1:1, the iron–carbon micro-cell played a leading role, and the ability to remove organic matter was increasingly stronger. Upon comprehensive consideration, the best mass ratio of iron to carbon in this experiment was set at 1:2, the dosage of iron powder was 20 g/L, and the dosage of activated carbon was 40 g/L.

**Table 3.** Effects of iron–carbon ratios on treatment results.

| Iron–Carbon Ratio | Absorbance After Treatment | Concentration After Treatment (mg/L) | Decolorization Rate (%) |
|-------------------|----------------------------|--------------------------------------|-------------------------|
| 2:1               | 0.165                      | $11.70 \times 10$                    | 92.20                   |
| 1:1               | 0.213                      | $14.70 \times 10$                    | 90.20                   |
| 1:2               | 0.305                      | 20.45                                | 98.64                   |
| 1:3               | 0.055                      | 4.83                                 | 99.68                   |

### 3.1.4. Effects of Different Separation Methods

After the reaction, the solid–liquid separation was carried out in two ways: centrifugal separation and membrane filtration. In this experiment, membrane filtration was used for solid–liquid separation. Through a set of comparative experiments, the effects of different separation methods on the treatment of Direct Red 4BE dye wastewater by the iron–carbon micro-electrolysis process were investigated.

Ten dye wastewater samples were divided into two groups, and the dosage of activated carbon in each water sample was 40 g/L. Meanwhile, dosages of iron powder in each group were 20, 30, 40, 50, and 60 g/L, respectively. Following 90 min of oscillation reaction, the water samples were allowed to stand. The first group was separated by centrifugation, while the second group was filtered through a 0.45  $\mu\text{m}$  microporous membrane. The absorbance of wastewater was measured, as shown in Table 4.

**Table 4.** Effects of different separation methods on iron–carbon micro-electrolysis treatment.

| Separation             | Iron Powder Dosage (g/L) | Absorbance After Treatment (Dilute 10 Times) | Concentration After Treatment (mg/L) | Decolorization Rate (%) |
|------------------------|--------------------------|----------------------------------------------|--------------------------------------|-------------------------|
| centrifugal separation | 20                       | 0.244                                        | $16.638 \times 10$                   | 88.91                   |
|                        | 30                       | 0.268                                        | $18.137 \times 10$                   | 87.91                   |
|                        | 40                       | 0.251                                        | $17.075 \times 10$                   | 88.62                   |
|                        | 50                       | 0.202                                        | $14.013 \times 10$                   | 90.66                   |
|                        | 60                       | 0.185                                        | $12.950 \times 10$                   | 91.37                   |
| membrane filtration    | 20                       | 0.216                                        | $14.887 \times 10$                   | 90.08                   |
|                        | 30                       | 0.237                                        | $16.200 \times 10$                   | 89.20                   |
|                        | 40                       | 0.245                                        | $16.700 \times 10$                   | 88.87                   |
|                        | 50                       | 0.199                                        | $13.825 \times 10$                   | 90.78                   |
|                        | 60                       | 0.166                                        | $11.763 \times 10$                   | 92.16                   |

Figure 1 presents the variation curve of the decolorization rate with iron powder dosage under the two separation methods. As shown in the figure, the decolorization rates of the two samples were very close under the same iron powder dosage. The overall decolorization rate of centrifugal separation was slightly lower than that of membrane filtration. This discrepancy may be attributed to the experimental procedure, where the supernatant was first centrifuged and then subjected to membrane filtration. The intermediate time

difference led to some deviations in the decolorization rate of the two separation methods. Upon comprehensive consideration, it was concluded that there was no difference between the two solid–liquid separation methods of centrifugal separation and filter membrane filtration in the iron–carbon micro-electrolysis experiment. Herein, the convenient and quick filter membrane filtration was employed for solid–liquid separation.

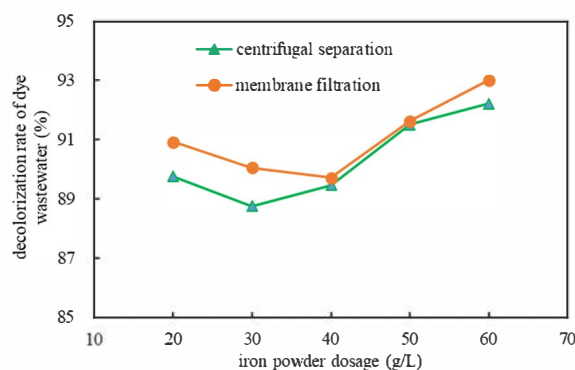


**Figure 1.** Variation of the decolorization rate of dye wastewater with iron powder dosage at different separation methods.

### 3.1.5. Iron–Carbon Micro-Electrolysis Experiments Under Optimal Conditions

Optimal conditions for iron–carbon micro-electrolysis treatment of wastewater were determined through single-factor experiments: a reaction time of 110 min, an initial pH value of 5, and an iron–carbon mass ratio of 1:2 (iron powder 20 g/L and activated carbon 40 g/L). The experiment was carried out under the optimal conditions. Furthermore, the absorbance and chroma of the supernatant were measured after filtration. The experimental results are shown in Table 5.

**Table 5.** Variations of dye wastewater quality before and after treatment by iron–carbon micro-electrolysis.

| Wastewater     | Color         | Dye Concentration (mg/L) | Chromaticity (Times) |
|----------------|---------------|--------------------------|----------------------|
| Pretreatment   | reddish-black | 1500                     | 80,000               |
| Post-treatment | light orange  | 14.51                    | 3000                 |

As shown in Table 5, after iron–carbon micro-electrolysis treatment, the concentration of wastewater was reduced to 14.51 mg/L, the chromaticity was 3000 times, and the decolorization rate reached 99.03%. It demonstrated the iron–carbon micro-electrolysis process’s favorable decolorization effect on the treatment of Direct Red 4BE dye wastewater.

### 3.2. Analysis of the Treatment Effect of Iron–Carbon Micro-Electrolysis Combined Processes

Under the optimal operating conditions, the chromaticity of the wastewater after iron–carbon micro-electrolysis treatment was 3000 times. However, it failed to meet the emission standard of 80 times the chromaticity in Discharge Standard of Water Pollutants for Textile Dyeing and Finishing Industry (GB4287-2012) [24]. In the field of refractory wastewater treatment, coagulation sedimentation [27–29], Fenton reagent oxidation [8,30–32], and other processes were generally employed or combined with other technologies to enhance the treatment effect. Therefore, in order to further improve the treatment effect of printing and dyeing wastewater, iron–carbon micro-electrolysis was integrated with coagulation sedimentation or Fenton oxidation to deeply treat Direct Red 4BE dye wastewater.

### 3.2.1. Analysis of the Treatment Effect of Iron–Carbon Micro-Electrolysis and Coagulation Sedimentation Combined Process

Iron–carbon micro-electrolysis and coagulation sedimentation [33–35] were combined to form a combined process for the treatment of printing and dyeing wastewater. The supernatant of iron–carbon micro-electrolysis under the optimal treatment conditions was taken for coagulation experiments, and the coagulant was  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . Effects of factors such as coagulant dosage, pH value, and coagulation standing time on the treatment effect were primarily considered. Optimal treatment conditions of the coagulation experiment were determined via the single-factor experiment involving a coagulant dosage of 100 mg/L, a pH value of 9.5, and a coagulation standing time of 50 min.

After the coagulation experiment, the supernatant was filtered to measure its absorbance and chromaticity. The experimental results are shown in Table 6.

**Table 6.** Variations of water quality of dye wastewater treated by combined process of iron carbon micro-electrolysis + coagulation sedimentation.

| Wastewater                                     | Color         | Dye Concentration (mg/L) | Chromaticity (Times) |
|------------------------------------------------|---------------|--------------------------|----------------------|
| Unpurified water                               | Reddish-black | 1500                     | 80,000               |
| After iron–carbon micro-electrolysis treatment | Orange-red    | 14.51                    | 3000                 |
| After coagulation and sedimentation treatment  | Light yellow  | 3.51                     | 60                   |

Figure 2 details the comparison before and after the treatment of dye wastewater by the combined process of iron–carbon micro-electrolysis + coagulation sedimentation.

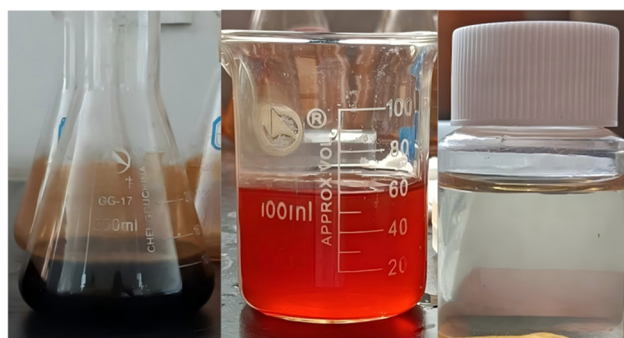


**Figure 2.** Comparison before and after treatment of dye wastewater by the combined process of iron–carbon micro-electrolysis + coagulation sedimentation (the **left**: the raw water; the **middle**: the supernatant of iron–carbon micro-electrolysis experiment; the **right**: the best coagulation sedimentation effluent).

As shown in Table 6, the concentration of wastewater decreased from 1500 mg/L to 3.51 mg/L, and the chromaticity decreased from 80,000 times to 60 times after the combined process of iron–carbon micro-electrolysis and coagulation sedimentation. The decolorization rate reached 99.77%. As indicated by Figure 2, the color of the dye wastewater gradually lightened as the experiment progressed, and its chromaticity reached the emission standard of 80 times specified in Discharge Standard of Water Pollutants for Textile Dyeing and Finishing Industry (GB4287-2012) [24].

### 3.2.2. Analysis of the Treatment Effect of Combined Process of Iron–Carbon Micro-Electrolysis + Fenton Oxidation

The combination of iron–carbon micro-electrolysis and Fenton oxidation [36–39] was employed to further treat the Direct Red 4BE dye wastewater. The supernatant of dye wastewater after iron–carbon micro-electrolysis treatment was collected. Effects of factors, including  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  dosage, pH value, reaction time, etc., on the degradation effect were separately considered. The optimal treatment conditions were determined through a single-factor experiment: the  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  dosages were 0.6 g/L and 20 mL/L, respectively, the pH was 2, and the reaction time was 40 min. Experiments were carried out under the optimal treatment conditions for Fenton oxidation. The supernatant was taken and filtered to measure its absorbance and chromaticity, with the experimental results shown in Table 7.

**Table 7.** Variations of water quality of dye wastewater treated by the combined process of iron–carbon micro-electrolysis + Fenton oxidation.

| Wastewater                                     | Color         | Dye Concentration (mg/L) | Chromaticity (Times) |
|------------------------------------------------|---------------|--------------------------|----------------------|
| Unpurified water                               | Reddish-black | 1500                     | 80,000               |
| After iron–carbon micro-electrolysis treatment | Orange-red    | 14.51                    | 3000                 |
| After Fenton oxidation                         | Light yellow  | 3.14                     | 40                   |

Figure 3 presents the comparison before and after the treatment of dye wastewater by the combined process of iron–carbon micro-electrolysis + Fenton oxidation.

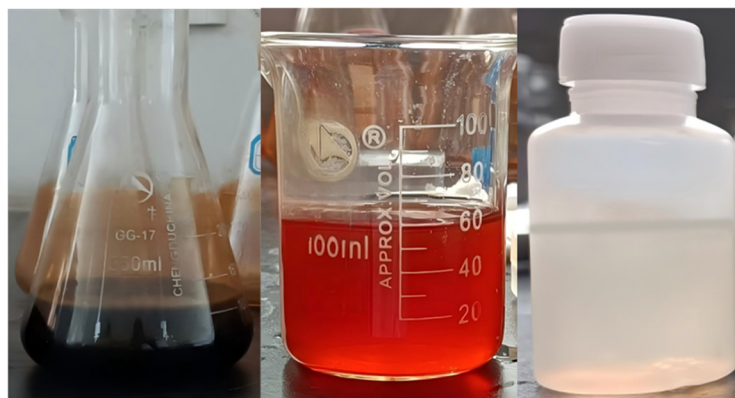


**Figure 3.** Comparison before and after treatment of dye wastewater by the combined process of iron–carbon micro-electrolysis + Fenton oxidation (the **left**: the raw water; the **middle**: the supernatant of iron–carbon micro-electrolysis experiment; the **right**: the water after Fenton oxidation).

As shown in Table 7, the concentration of the wastewater treated by the combined process of iron–carbon micro-electrolysis and the Fenton method was reduced to 3.14 mg/L, the chromaticity was reduced to 40 times, and the decolorization rate reached 99.79%. Figure 3 revealed that as the reaction progressed, the chromaticity of the dye wastewater was increasingly lowered, meeting the chromaticity emission standard of 80 times in Discharge Standard of Water Pollutants for Textile Dyeing and Finishing Industry (GB4287-2012) [24].

Obviously, the above two combined processes yielded superior treatment effects on dyeing wastewater. However, the Fenton oxidation method required the addition of hydrogen peroxide, and the dosage of ferrous sulfate (0.6 g/L) was higher than that of the

coagulation precipitation method (0.1 g/L), resulting in the generation of more sludge. Coagulation treatment of printing and dyeing wastewater boasts the advantages of a simple process, convenient operation and management, and low equipment investment. Therefore, the combination of iron–carbon micro-electrolysis and the coagulation sedimentation process demonstrated better cost-effectiveness in treating Direct Red 4BE dye wastewater.

#### 4. Conclusions

Herein, the experiment of iron and carbon micro-electrolysis treatment of direct Big Red 4BE dye wastewater was carried out to delve into the influence of different reaction times, initial pH values, and iron–carbon mass ratios on the treatment effects, aiming to determine the optimal treatment conditions. Data analysis showed that when the optimal reaction time of 110 min, the initial pH value of 5, and the iron–carbon mass ratio of 1:2 (iron powder dosage of 20 g/L, activated carbon dosage of 40 g/L) were involved, the decolorization rate of dye wastewater could reach 99.03%. Under such conditions, the concentration decreased from 1500 mg/L to 14.51 mg/L, and the chromaticity decreased from 80,000 times to 3000 times. However, it failed to meet the emission standard of dye wastewater. The dye wastewater treated under the optimal conditions of iron–carbon micro-electrolysis was subjected to coagulation precipitation and Fenton oxidation, respectively. The total decolorization rate of the wastewater could be improved up to 99.79%, and the chromaticity met the requirement of 80 times chromaticity specified in Discharge Standard of Water Pollutants for Textile Dyeing and Finishing Industry (GB4287-2012) [24].

**Author Contributions:** Validation, B.L.; Resources, J.X.; Data curation, X.S., J.X. and B.L.; Writing—original draft, X.S.; Writing—review and editing, X.K. and Y.Z.; Supervision, X.K. and Y.Z. All authors have read and agreed to the published version of the manuscript.

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