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Comparison of Different Enhanced Coagulation Methods for Azo Dye Removal from Wastewater

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Abstract: Printing and dyeing wastewater (PDW) is considered to be one of the most difficult industrial wastewaters to treat because of its large quantities, high pH values, and high color and toxicity, which may endanger the lives of animals and humans. In this study, we assessed the chemical decolorization process of Congo Red in azo dyes using response surface methodology (RSM), and the effect of different enhanced coagulation pretreatment processes (ECPPs) on the microbial community structure of PDW using high-throughput sequencing technology. We concluded that, based on the initial concentration and pH of Congo Red, different decolorants can be selected for decolorization reactions. In addition, it was found that the microbial community of the wastewater after three different ECPP treatments was similar to the raw wastewater and the oxidation ditch wastewater from a treatment plant. We also found that the ECPPs with polymeric iron sulfate had the smallest effect on the microbial community. In practical applications, these findings provide a reference for an established link between the physicochemical and biochemical treatment of PDW.

Keywords: azo dye; decolorization; coagulation and flocculation; bacterial community; response surface methodology (RSM)

Highlights

Parameters of enhanced coagulation pretreatment processes (ECPPs) were optimized by response surface methodology (RSM).

Different chemical decolorization processes can be selected according to the initial pH and concentration of Congo Red.

A relationship was developed between the physicochemical and biochemical treatment of printing and dyeing wastewater (PDW).

1. Introduction

Coloring agents and dyes are widely used in the modern textile industry, as well as other manufacturing industries. Any dyes left in the effluent after treatment (printing and dyeing wastewater; PDW) are discharged into the water environment, and can cause surface water pollution [1,2]. The coloring material usually only absorbs about 80% of the dye [3]. PDW is toxic and could endanger human and animal life. It is also very difficult to remove from industrial wastewater; thus, it is widely concerning for society [4].

Mass et al. (2005) estimated that 2.8×10^5 tons of textile dyes are discharged into the water with textile industry wastewater every year around the world. Among them, azo dyes account for about

half of all synthetic dyes [5]. Azo reactive dyes have nitrogen–nitrogen double bonds [6], and some azo dyes and their decomposition products are toxic and may mutate living organisms [7]. Azo dyes also have poor biodegradability because they possess electron-withdrawing groups in their structures, which generate electron-deficient dye molecules [8].

PDW has a high pH value, color content, water temperature, and toxicity, as well as other characteristics, and a lot of wastewater is created in the printing and dye process; thus, it is difficult for certain technologies to treat it. Physical, chemical, and biological treatment technologies should, therefore, be combined for its treatment [4,9,10]. Among them, coagulation–flocculation is one of the physicochemical treatment methods currently used for PDW [11]. It is often used in the pretreatment process of PDW, and can effectively remove most of the dyes, thus reducing the load for the subsequent biochemical treatment facilities [12,13]. Coagulation technology adds high-dose coagulants that maintain a particular pH value to sewage in order to improve the removal of pollutants using conventional treatments [14]. Factors affecting the coagulation effect include water temperature, pH, dosage, hydraulic conditions, and raw water quality [15]. In actual wastewater, it is often used to treat wastewater with varying water quality by adjusting pH and dosage.

There are a large number of microorganisms indigenous to the wastewater-regulating pools of printing and dyeing industrial parks. Different enhanced coagulation pretreatment processes (ECPPs) have different effects on these microorganisms [12,16]. High-throughput sequencing technology can be used to analyze any changes in microbial community composition in PDW from industrial parks before and after ECPPs, which can then be used to compare microbial community composition in any subsequent biological treatment facilities.

In this study, we wanted to test the capability of ECPPs for PDW treatment. Firstly, we studied azo dye removal efficiency using different ECPP methods and simulation tests. Next, we explored the relationship between using different ECPPs and the associated microbial community changes in industrial park PDW. These results provide a reference for further research studying the relationship between physicochemical and biological PDW treatment methods.

2. Materials and Methods

2.1. Water Samples

Based on our experimental design, water samples were divided into two categories. The first was simulated wastewater. Congo Red in azo dyes was selected as the target pollutant for our wastewater simulations. The second category was actual wastewater, and these samples were taken from the regulating tank of the Datang Printing and Dyeing Industrial Park wastewater treatment plant in Foshan city, Guangdong province, China. The actual characteristics of the wastewater are shown in Table A4 (Appendix A).

2.2. Chemicals

The following chemical agents were selected to use in the coagulation process: calcium hydroxide ($\text{Ca}(\text{OH})_2$, analytically pure, used as a neutralizing base, no synergistic effect of complexation and flocculation in a parallel experiment with NaOH), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, analytically pure, used as a coagulant), aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, analytically pure, used as a coagulant), polymeric iron sulfate ($[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_3 - n/2]_m$ (where $n < 2$, $m = f(n)$), analytically pure, used as a coagulant), and non-ionic polyacrylamide (analytically pure, used as a flocculant).

2.3. Jar Tests of Simulated Wastewater

The chemical agents were tested using the 1000-mL raw water samples and a programmable Jar test instrument using the following standard procedure: rapid stirring at 200 rpm for 2 min during neutralization, stirring at 200 rpm for 5 min after adding coagulant, stirring at 100 rpm for 10 min after adding flocculant, and then settling for 30 min.

2.4. ECPPs of Actual Wastewater

The chemical agents were pretreated using the following procedure: $\text{Ca}(\text{OH})_2$ was added to 1000 mL of actual wastewater until a pH of 9.0 was achieved, and then stirred at 200 rpm for 5 min; ferrous sulfate was added with a dosage of 150 mg/L, and then stirred at 200 rpm for 5 min, before stirring at 100 rpm for 10 min after adding flocculant, and then settling for 30 min; the supernatant was collected and labeled sample L1.

The same procedure was used for the coagulants aluminum sulfate and polymeric iron sulfate, with the collected supernatant samples labeled as L2 and L3, respectively.

2.5. Optimal Design of Response Surface Methodology (RSM)

In this study, we used three surface response experiments at indoor temperature. In the first experiment, ferrous sulfate was used as the decolorizing agent; in the second experiment, aluminum sulfate was used as the decolorizing agent; in the third experiment, polymeric iron sulfate was used as the decolorizing agent. On the basis of single-factor experiments, the numerical ranges of the influencing factors of all three experiments were determined.

The first experiment was designed with three factors at three levels (+1, −1, 0) at pH 6, 8, and 10, with initial Congo Red concentrations of 50 mg/L, 100 mg/L, and 150 mg/L, and chemical doses of 80 mg/L, 140 mg/L, 200 mg/L. Seventeen experiments were designed using Design-Expert (version 8.06) software design (Table A1, Appendix A). The second-order polynomial equation was based on Shao et al. (2018) and Su et al. (2016) [10,17].

The second experiment was designed with three factors at three levels (+1, −1, 0) at pH 5, 7, and 9, with initial Congo Red concentrations of 100 mg/L, 200 mg/L, and 300 mg/L, and chemical doses of 20 mg/L, 50 mg/L, 80 mg/L. Seventeen experiments were designed using Design-Expert (version 8.06) software design (Table A2, Appendix A). The second-order polynomial equation was based on Shao et al. (2018) and Su et al. (2016) [10,17].

The third experiment was designed with three factors at three levels (+1, −1, 0) at pH 5, 7, and 9, with initial Congo Red concentrations of 50 mg/L, 100 mg/L, and 150 mg/L, and chemical doses of 50 mg/L, 100 mg/L, 150 mg/L. Seventeen experiments were designed using Design-Expert (version 8.06) software design (Table A3, Appendix A). The second-order polynomial equation was based on Shao et al. (2018) and Su et al. (2016) [10,17].

2.6. Analytical Methods of Chemical Indexes

The pH was measured directly using a digital pH meter (PHS-3C, China), and Congo Red concentrations were measured by a method with a wavelength equal to 496 nm using an HACH instrument (DR5000, USA).

2.7. Sequencing Analysis of Microorganisms

The microbial community of raw wastewater, water samples pretreated by enhanced coagulation, and water samples from the oxidation ditch of the wastewater treatment plant were analyzed. Two-milliliter samples were extracted from each water sample and sent to Biomarker Technologies CO., LTD (Beijing, China) for high-throughput sequencing. The microbial diversity calculations were based on the Illumina HiSeq sequencing platform, and a small fragment library was constructed using a paired-end sequencing method. Primers used were as follows: 338 forward (F): 5′-ACTCCTACGGGAGGCAGCA-3′; 806 reverse (R): 5′-GGACTACHVGGGTWTCTAAT-3′.

3. Results and Discussion

3.1. Box–Behnken Design for Optimizing Factors in the First Experiment

RSM with a Box–Behnken design was used to analyze the interaction between the basic variables affecting the decolorization removal ratio of Congo Red by ferrous sulfate. These included the pH of the reaction, the initial Congo Red concentration, and the dosage of ferrous sulfate. The interaction between two independent variables was determined using response surface curves and contours. The quadratic polynomial equation constructed by the coding factor was as follows:

$$R_{CR} = 69.44 + 13.41A + 11.94B - 8.38C - 7.28AB + 5.85AC - 1.15BC + 7.14A^2 - 0.26B^2 + 1.82C^2,$$

where R_{CR} is the decolorization ratio of Congo Red, and A, B, and C represent the pH of the reaction, the dosage of ferrous sulfate, and the initial Congo Red concentration, respectively.

Table 1 shows the regression coefficient, standard error, F-value, and *p*-value. The model F-value of 43.85 implies that the model was significant. There was only a 0.01% chance that a value that large could be caused by noise. Table 1 shows that the linear coefficient ($p < 0.0001$) of pH of the reaction, the linear coefficient ($p < 0.0001$) of dosage of ferrous sulfate, and the linear coefficient ($p < 0.0001$) of initial Congo Red concentration ($p = 0.0001$) were all vitally significant and had the largest effect on the decolorization ratio of Congo Red. Furthermore, the linear coefficient of the pH of the reaction with ferrous sulfate dosage ($p = 0.0021$), the linear coefficient of the pH of the reaction with initial Congo Red concentration ($p = 0.0067$), and the quadratic coefficient of the pH of the reaction ($p = 0.0020$) were also all significant (Table 1).

Table 1. Regression analysis of least square fitting in the first experiment.

Source	Regression Coefficient	Standard Error	F-Value	<i>p</i> -Value Prob > F
Model	-	-	43.85	<0.0001
A—pH of the reaction	13.41	1.09	152.27	<0.0001
B—dosage of ferrous sulfate	11.94	1.09	120.62	<0.0001
C—initial Congo Red concentration	−8.38	1.09	59.37	0.0001
AB	−7.28	1.54	22.40	0.0021
AC	5.85	1.54	14.48	0.0067
BC	−1.15	1.54	0.56	0.4788
A ²	7.14	1.50	22.73	0.0020
B ²	−0.26	1.50	0.030	0.8684
C ²	1.82	1.50	1.47	0.2644

$R^2 = 0.9826$; adjusted $R^2 = 0.9602$; coefficient of variation = 4.18%. “0.01 < *p*-value < 0.05” and “*p*-value > 0.1” in model terms with “Prob > F” were considered to be significant and insignificant, respectively (Su et al., 2016; Shao et al., 2018).

Figure 1 shows the three-dimensional (3D) response surface (a) and contour (b) of the decolorization ratio of Congo Red as a function of the independent variables, the pH of the reaction and the dosage of ferrous sulfate. At low doses of ferrous sulfate, the decolorization ratio of Congo Red increased rapidly with an increase in pH. However, at high doses of ferrous sulfate, the decolorization ratio of Congo Red increased slowly with an increase in pH. In addition, at lower pH levels, the decolorization ratio of Congo Red increased significantly with an increase in the dosage of ferrous sulfate. At higher pH levels, the decolorization ratio of Congo Red increased a small amount with an increase in the dosage of ferrous sulfate. The highest decolorization ratio of Congo Red (96.14%) could, therefore, be obtained with an optimal pH of 10.00 and dosage of 159.64 mg/L.

Figure 1. The three-dimensional (3D) response surface (a) and contour plot (b) for the decolorization ratio of Congo Red under different reaction pH levels and ferrous sulfate dosages. The 3D response surface (c) and contour plot (d) for the decolorization ratio of Congo Red under different reaction pH levels and initial Congo Red concentrations.

The effects of the two significant factors, the pH of the reaction and the initial Congo Red concentration, on the decolorization ratio of Congo Red can be seen in Figure 1c,d. As the initial Congo Red concentrations increased, the decolorization ratio decreased. The decolorization ratio increased with an increase in pH of the reaction. At a reaction pH of 10.00 and an initial Congo Red concentration of 50.24 mg/L, a decolorization ratio of Congo Red of 96.14% was obtained.

The comparison and analyses of the three influencing factors showed that (1) when the pH of the reaction, the dosage of Ferrous Sulfate, and the initial Congo Red concentration were 10.00, 159.64 mg/L, and 50.24 mg/L, respectively, the decolorization ratio of Congo Red reached its maximum value, and (2) a maximum decolorization ratio of Congo Red of 96.14% was obtained with simulations using optimal conditions.

3.2. Box–Behnken Design for Optimizing Factors in the Second Experiment

RSM with a Box–Behnken design was used to analyze the interaction between basic variables affecting the decolorization removal ratio of Congo Red by aluminum sulfate. These included the pH of the reaction, initial Congo Red concentration, and dosage of aluminum sulfate. The interaction between two independent variables can be easily understood by using response surface curves and contours. The quadratic polynomial equation constructed by the coding factor was as follows:

$$R_{CR} = 82.68 - 21.16A + 34.61B - 9.33C - 2.48AB + 11.50AC - 2.60BC - 20.88A^2 - 10.13B^2 - 19.55C^2,$$

where R_{CR} is the decolorization ratio of Congo Red, and A, B, and C represent the pH of the reaction, the dosage of aluminum sulfate, and the initial Congo Red concentration, respectively.

Table 2 shows the regression coefficient, standard error, F-value and p -value. The model F-value of 12.03 implies that the model was significant. There was only a 0.17% chance that a value this large could be caused by noise. Table 2 shows that the linear coefficients of the pH of the reaction ($p < 0.0026$) and dosage of aluminum sulfate ($p < 0.0001$) were vitally significant and had the largest effect on the decolorization ratio of Congo Red. Furthermore, the quadratic coefficients of the pH of the reaction ($p = 0.0139$) and of the initial Congo Red concentration ($p = 0.0186$) were significant.

Table 2. Regression analysis of least square fitting in the second experiment.

Source	Regression Coefficient	Standard Error	F-Value	p -Value Prob > F
Model	-	-	12.03	<0.0017
A—pH of the reaction	−21.16	4.65	20.71	<0.0026
B—dosage of aluminum sulfate	34.16	4.65	55.40	<0.0001
C—initial Congo Red concentration	−9.33	4.65	4.02	<0.0850
AB	−2.48	6.58	0.14	0.7178
AC	11.50	6.58	3.06	0.1238
BC	−2.60	6.58	0.16	0.7044
A ²	−20.88	6.41	10.61	0.0139
B ²	−10.13	6.41	2.50	0.1581
C ²	−19.55	6.41	9.30	0.0186

$R^2 = 0.9393$; adjusted $R^2 = 0.8612$; coefficient of variation = 22.34%. “ $0.01 < p\text{-value} < 0.05$ ”, and “ $p\text{-value} > 0.1$ ” in model terms with “Prob > F” were considered to be significant and insignificant, respectively (Su et al., 2016; Shao et al., 2018).

As a function of the independent variables, the pH of the reaction and the dosage of aluminum sulfate, Figure 2 shows the 3D response surface (a) and contour (b) of the decolorization ratio of Congo Red. With an increase in the reaction pH level, the decolorization ratio of Congo Red decreased significantly. Meanwhile, with an increase in the aluminum sulfate dosage, the decolorization ratio of Congo Red rapidly increased. The highest decolorization ratio of Congo Red (84.37%) was obtained with an optimal pH and aluminum sulfate dosage of 8.26 and 80 mg/L, respectively.

Figure 2. Cont.

Figure 2. The 3D response surface (a) and contour plot (b) for the decolorization ratio of Congo Red under different reaction pH levels and aluminum sulfate dosages. The 3D response surface (c) and contour plot (d) for the decolorization ratio of Congo Red under different aluminum sulfate dosages and initial Congo Red concentrations.

The effects of the two significant factors, the aluminum sulfate dosage and the initial Congo Red concentration, on the decolorization ratio of Congo Red can be seen in Figure 2c,d. With an increase in the initial concentration of Congo Red, the decolorization ratio firstly increased and then decreased. The inflection point occurred near the initial Congo Red concentration of 175 mg/L. At an aluminum sulfate dosage of 80.00 mg/L and an initial Congo Red concentration of 187.92 mg/L, a decolorization ratio of Congo Red of 84.37% was achieved.

The comparison and analyses of the three influencing factors showed that (1) when the pH of the reaction, the aluminum sulfate dosage, and the initial Congo Red concentration were 8.26, 80.00 mg/L, and 187.92 mg/L, respectively, the decolorization ratio of Congo Red reached its maximum value, and (2) under the optimal model conditions, a maximum decolorization ratio of Congo Red of 84.37% was obtained.

3.3. Box–Behnken Design for Optimizing Factors in the Third Experiment

RSM with a Box–Behnken design was used to analyze the interaction between basic variables affecting the decolorization removal ratio of Congo Red by polymeric iron sulfate. These included pH of the reaction, initial Congo Red concentration, and dosage of polymeric iron sulfate. The interaction between two independent variables can be easily understood by using response surface curves and contours. The quadratic polynomial equation constructed by the coding factor was as follows:

$$R_{CR} = 80.16 - 5.89A + 29.63B - 6.06C + 2.17AB - 1.50AC + 1.08BC - 5.000 \times 10^{-3}A^2 - 14.88B^2 + 1.85C^2,$$

where R_{CR} is the decolorization ratio of Congo Red, and A, B, and C represent the pH of the reaction, the polymeric iron sulfate dosage, and the initial Congo Red concentration, respectively.

Table 3 shows the regression coefficient, standard error, F-value, and *p*-value. The model F-value of 21.85 implies that the model was significant. There was only a 0.03% chance that a value this large could be caused by noise. Table 3 shows that the linear coefficient ($p < 0.0001$) of the polymeric iron sulfate dosage was vitally significant and had the largest effect on the decolorization ratio of Congo Red. Furthermore, the linear coefficient of the pH of the reaction ($p = 0.0396$), the linear coefficient of initial Congo Red concentration ($p = 0.0355$), and the quadratic coefficient of dosage of polymeric iron sulfate ($p = 0.0024$) were significant.

Table 3. Regression analysis of least square fitting in the third experiment.

Source	Regression Coefficient	Standard Error	F-Value	p-Value Prob > F
Model	-	-	21.85	0.0003
A—pH of the reaction	−5.89	2.33	6.37	0.0396
B—dosage of polymeric iron sulfate	29.63	2.33	161.19	<0.0001
C—initial Congo Red concentration	−6.06	2.33	6.75	0.0355
AB	2.17	3.30	0.43	0.5309
AC	−1.50	3.30	0.21	0.6632
BC	1.08	3.30	0.11	0.7541
A ²	−5.000 × 10 ^{−3}	3.22	2.417 × 10 ^{−6}	0.9988
B ²	−14.88	3.22	21.40	0.0024
C ²	1.85	3.22	0.33	0.5842

$R^2 = 0.9656$; adjusted $R^2 = 0.9214$; coefficient of variation = 8.92%. “0.01 < p-value < 0.05”, and “p-value > 0.1” in model terms with “Prob > F” were considered to be significant and insignificant, respectively (Su et al., 2016; Shao et al., 2018).

As a function of the independent variables, the pH of the reaction and polymeric iron sulfate dosage, Figure 3 shows the 3D response surface (a) and contour (b) of the decolorization ratio of Congo Red. With an increase in the reaction pH level, the decolorization ratio of Congo Red showed a decrease. On the other hand, the decolorization ratio of Congo Red increased rapidly with an increase in polymeric iron sulfate dosage. The highest decolorization ratio of Congo Red (98.28%) was obtained at an optimal pH of 6.35 and polymeric iron sulfate dosage of 141.66 mg/L.

Figure 3. The 3D response surface (a) and contour plot (b) for the decolorization ratio of Congo Red under different reaction pH levels and polymeric iron sulfate dosages. The 3D response surface (c) and contour plot (d) for the decolorization ratio of Congo Red under different polymeric iron sulfate dosages and the initial Congo Red concentrations.

The effects of the two significant factors, the polymeric iron sulfate dosage and initial Congo Red concentrations, on the decolorization ratio of Congo Red can be seen in Figure 3c,d. With an increase in initial Congo Red concentration, the decolorization ratio decreased. The decolorization ratio of Congo Red also increased rapidly with an increase in the polymeric iron sulfate dosage. At a polymeric iron sulfate dosage of 141.66 mg/L and initial Congo Red concentration of 77.82 mg/L, a decolorization ratio of Congo Red of 98.28% was achieved.

The comparison and analyses of the three influencing factors showed that (1) when the pH of the reaction, the polymeric iron sulfate dosage, and the initial Congo Red concentration were 6.35, 141.66 mg/L, and 77.82 mg/L, respectively, the decolorization ratio of Congo Red reached its maximum value, and (2) under optimal model conditions, a maximum decolorization ratio of Congo Red of 98.28% was achieved.

3.4. Characteristics of Microbial Community Structure

3.4.1. Bacterial Community Structures

As shown in Figure 4, after three types of ECPPs were implemented, in comparison to raw wastewater, the microbial community structure of industrial park PDW did not change much, but the relative abundance was slightly different. Proteobacteria, Tenericutes, and Epsilonbacteraeota were the three dominant phyla present. The microbial community structure of L0, L1, L2, L3, and the oxidation ditch (Figure A1, Appendix A) was nearly the same. At the phylum level, the dominant bacteria included Proteobacteria, Firmicutes, and Bacteroidetes. This was also consistent with Zhu et al. (2018) [16], where Proteobacteria, Firmicutes, and Bacteroidetes were the dominant functional microorganisms found after the treatment of PDW. These results demonstrate that ECPPs had no adverse effect on biological treatment.

Figure 4. Microbial community structure in different samples at the phylum level. L0 is raw wastewater; L1 is the enhanced coagulation pretreatment process (ECPP) with ferrous sulfate; L2 is the ECPP with aluminum sulfate; L3 is the ECPP with polymeric iron sulfate. The horizontal ordinate is the name of the sample, and the longitudinal coordinate is the relative abundance percentage.

3.4.2. Heat Map

A heat map is a graphical display in which color gradients represent the values in the data matrix and cluster according to the abundance similarity of species or samples. Colors represent the species abundance in heat map clustering [17]. Vertical clustering represents the similarity in abundances of different species in the samples. The closer the distance between two species is, the shorter the branch length is, indicating that the abundance of these two species is more similar between samples. Horizontal clustering represents the similarity of species abundances of different samples. Just like vertical clustering, the closer the distance between two samples is, the shorter the branch length is, indicating that the abundance of species of these two samples is more similar. The color gradient from blue to red indicates the relative abundance from low to high [18].

It can be seen in Figure 5 that the relative abundance value of the microbial community in L0 was the highest, followed by L3. The upper clustering tree indicates that the bacteria in L0 and L3, as well as L1 and L2, were similar. Therefore, ECPPs with polymeric iron sulfate had the lowest effect on the microbial communities in the PDW from the industrial park.

Figure 5. Heat map of different samples at the phylum level. The horizontal clustering is sample information, and the vertical clustering is species information. The left clustering tree is species clustering, the upper clustering tree is sample clustering, and the middle one is the heat map. L0 is raw wastewater, L1 is the ECPP with ferrous sulfate, L2 is the ECPP with aluminum sulfate, and L3 is the ECPP with polymeric iron sulfate.

4. Conclusions

In the simulated wastewater examples, using Congo Red as the target pollutant of azo dye, when ferrous sulfate was used as decolorizing agent and the initial concentration of Congo Red was 50.24 mg/L, the reaction pH value was 10.00, the ferrous sulfate dosage was 159.64 mg/L, and the maximum decolorizing ratio of Congo Red optimized by RSM was 96.14%. When aluminum sulfate was

used as a decolorizing agent and the initial concentration of Congo Red was 187.92 mg/L, the reaction pH value was 8.26, the aluminum sulfate dosage was 80 mg/L, and the maximum decolorization ratio of Congo Red optimized by RSM was 84.37%. When the initial concentration of Congo Red was 77.82 mg/L, the reaction pH was 6.35, the polymeric iron sulfate dosage of was 141.66 mg/L, and the maximum decolorization ratio of Congo Red optimized by RSM was 98.28%. It can, therefore, be concluded that, based on the initial concentration and pH of Congo Red, different decolorants can be selected for decolorization reactions.

In addition, we found that the microbial community of PDW from the industrial park after three different ECPP treatments was similar to the raw wastewater and oxidation ditch wastewater from the treatment. Proteobacteria, Firmicutes, and Bacteroidetes were the dominant bacteria at the phylum level, meaning that subsequent biological treatment can occur. It was also found that the pretreatment of PDW from the industrial park using polymeric iron sulfate had the smallest effect on the microbial community structure. These results provide a reference for an established link between the physicochemical and biochemical treatment of PDW.

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Appendix A

Table A1. Seventeen experiments were designed using Design-Expert (version 8.06) software design.

Std	A: pH of the Reaction	B: Dosage of Ferrous Sulfate (mg/L)	C: Initial Congo Red Concentration (mg/L)	Decolorization Ratio of Congo Red (%)
1	6.00	80.00	100.00	42.2
2	10.00	80.00	100.00	87.2
3	6.00	200.00	100.00	80.0
4	10.00	200.00	100.00	95.9
5	6.00	140.00	50.00	79.5
6	10.00	140.00	50.00	91.0
7	6.00	140.00	150.00	54.1
8	10.00	140.00	150.00	89.0
9	8.00	80.00	50.00	67.5
10	8.00	200.00	50.00	94.3
11	8.00	80.00	150.00	50.0
12	8.00	200.00	150.00	72.2
13	8.00	140.00	100.00	71.0
14	8.00	140.00	100.00	70.4
15	8.00	140.00	100.00	70.7
16	8.00	140.00	100.00	69.6
17	8.00	140.00	100.00	65.5

Table A2. Seventeen experiments were designed using Design-Expert (version 8.06) software design.

Std	A: pH of the Reaction	B: Dosage of Aluminum Sulfate (mg/L)	C: Initial Congo Red Concentration (mg/L)	Decolorization Ratio of Congo Red (%)
1	5.00	20.00	200.00	25.6
2	9.00	20.00	200.00	11.1
3	5.00	80.00	200.00	97.2
4	9.00	80.00	200.00	72.8
5	5.00	50.00	100.00	98.3
6	9.00	50.00	100.00	10.1
7	5.00	50.00	300.00	51.4
8	9.00	50.00	300.00	9.2
9	7.00	20.00	100.00	21.2
10	7.00	80.00	100.00	98.2
11	7.00	20.00	300.00	13.0
12	7.00	80.00	300.00	79.6
13	7.00	50.00	200.00	84.2
14	7.00	50.00	200.00	83.7
15	7.00	50.00	200.00	75.5
16	7.00	50.00	200.00	88.9
17	7.00	50.00	200.00	81.1

Table A3. Seventeen experiments were designed using Design-Expert (version 8.06) software design.

Std	A: pH of the Reaction	B: Dosage of Polymeric Iron Sulfate (mg/L)	C: Initial Congo red Concentration (mg/L)	Decolorization Ratio of Congo Red (%)
1	5.00	50.00	100.00	42.5
2	9.00	50.00	100.00	28.1
3	5.00	150.00	100.00	98.1
4	9.00	150.00	100.00	92.4
5	5.00	100.00	50.00	98.1
6	9.00	100.00	50.00	87.6
7	5.00	100.00	150.00	79.4
8	9.00	100.00	150.00	62.9
9	7.00	50.00	50.00	40.2
10	7.00	150.00	50.00	96.6
11	7.00	50.00	150.00	35.5
12	7.00	150.00	150.00	96.2
13	7.00	100.00	100.00	71.2
14	7.00	100.00	100.00	83.2
15	7.00	100.00	100.00	79.2
16	7.00	100.00	100.00	84.1
17	7.00	100.00	100.00	83.1

Table A4. The actual characteristics of the wastewater.

pH	Chemical Oxygen Demand (mg/L)	PO ₄ ³⁻ -P (mg/L)	Total Phosphorus (mg/L)	Suspended solids (mg/L)	SO ₄ ²⁻ (mg/L)	Color (mg Pt/L)
8.68	1550	9.3	53.4	3150	3800	1900

Table A5. List of abbreviations.

Abbreviation	Full Name
PDW	Printing and dyeing wastewater
RSM	Response surface methodology
ECPPs	Enhanced coagulation pretreatment processes

Figure A1. The microbial community structure of the oxidation ditch.

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