Experimental Study on Treatment of Dyeing Wastewater by Activated Carbon Adsorption, Coagulation and Fenton Oxidation

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Abstract: In this paper dyeing waste water was simulated by reactive brilliant blue XBR, activated carbon adsorption process, coagulation process and chemical oxidation process were used to treat dyeing waste water. In activated carbon adsorption process and coagulation process, the water absorbance values were measured. The CODcr value of water was determined in Fenton chemical oxidation process. Then, the decolorization rate and COD removal rate were calculated respectively. The results showed that the optimum conditions of activated carbon adsorption process were as follows: pH=2, the dosage of activated carbon was 1.2g/L, the adsorption reaction time was 60 min, and the average decolorization rate of the three parallel experiments was 85.30%. The optimum conditions of coagulation experiment were as follows: pH=8~9, PAC dosage was 70mg/L, stirring time was 20min, standing time was 45min, the average decolorization rate of the three parallel experiments was 74.48%. The optimum conditions for Fenton oxidation were Fe^{2+} 0.05g/L, H_2O_2 (30%) 14mL/L, pH=3, reaction time 40min. The average CODcr removal rate was 69.35% in three parallel experiments. It can be seen that in the three methods the activated carbon adsorption treatment of dyeing wastewater was the best one.

1. Introduction

Printing and dyeing industry is one of the important traditional industries in China. A lot of wastewater will be produced in printing and dyeing process. The wastewater has the characteristics of large amount, poor biodegradability, strong toxicity, deep color and so on[1]. If these wastewater is not properly treated, it will seriously pollute the local water environment and destroy the aquatic ecosystem[2]. Therefore, it is of great significance to strengthen the research of dyeing wastewater treatment.

There are many methods to treat dyeing wastewater at home and abroad. The main methods are chemical coagulation, biological method, membrane filtration, advanced oxidation and adsorption. The mechanism of chemical coagulation includes compressed double layer, net capture or volume sweep, electric neutralization and adsorption bridging[3]. Coagulation technology can remove suspended colloidal pollutants, which is the most widely used and mature technology in the world, its disadvantage is the need to deal with large amount of sludge produced by chemical coagulation. The biological method is a method which can degrade the organic matter in wastewater into simple inorganic matter or transform into various nutrients. The biological method is also widely used in dyeing wastewater. However, because of the poor biodegradability of dyeing wastewater, it is necessary to set up hydrolytic acidification tank to improve the biodegradability of dyeing wastewater before biological treatment. From recent research reports, the biological treatment of dyeing
wastewater is mainly in the aspects of microbial research, biological fixation technology, process improvement and so on[4]. The membrane filtration method includes microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO), and so on[5]. In the printing and dyeing industry, a large number of dyes in dyeing wastewater can be reused through application of membrane filtration technology. However, the membrane filtration method has high cost, and it is easy to cause membrane pollution, different dyeing wastewater needs to add different pretreatment facilities, and the filter concentration wastewater needs further treatment. General membrane treatment technology is combined with chemical and biological treatment, membrane treatment is used in depth treatment, and the water after treatment is reused. Advanced oxidation method is a method of removing or degrading pollutants in dyeing wastewater by producing hydroxyl radical (·OH) with strong oxidizing ability. At present, advanced oxidation technology mainly includes Fenton oxidation, wet oxidation, photocatalytic oxidation, electrochemical oxidation, ozone oxidation, and so on[6]. All kinds of oxidation processes have their own advantages and disadvantages. Developing new combination technology will be the development direction of advanced oxidation technology to treat dyeing wastewater. For example, the combination method of O₃-H₂O₂ is used to treat dyeing wastewater[7-8], ultrasonic is combined with Fenton oxidation to treat dyeing wastewater[9]. The adsorption method is the physical and chemical adsorption of various dyes on the surface of the adsorbent. The commonly used adsorbents are activated carbon, chitosan, fly ash, etc. The adsorption method can effectively deal with many dyes. Activated carbon is made from sawdust, shell and other organic matter rich in carbon, through dehydration, carbonization and activation. Activated carbon has a developed porous structure, a great specific surface area, good chemical inertia and electrical conductivity, excellent adsorption properties, which can be widely used in the pharmaceutical, chemical industry, environmental protection and other fields[10]. Therefore, it can be seen that different methods can be used to treat dyeing wastewater. In this paper, three economic feasible methods (activated carbon adsorption, coagulation, Fenton oxidation) are selected to treat dyeing wastewater. The optimal conditions are determined by experiments, and the effects of different methods on dyeing wastewater were compared.

2. Experimental scheme design and measurement

2.1 Experimental scheme design

The dyeing wastewater used in this experiment is a simulated dyeing wastewater prepared by reactive brilliant blue XBR and deionized water, with a concentration of 50 mg/l.

2.1.1 Adsorption experiment of activated carbon

The effects of pH value, dosage of activated carbon and adsorption time on the decolorization rate are studied. The decolorization rate of activated carbon adsorption treatment is calculated by three parallel experiments under the optimum conditions.

2.1.2 Coagulation experiment

The effects of pH value, PAC dosage (polyaluminum chloride), stirring time and standing time on the decolorization rate are studied. Under the optimum conditions, three parallel experiments are carried out to calculate the decolorization rate of coagulation treatment.

2.1.3 Fenton chemical oxidation experiment

In treatment of dyeing wastewater by Fenton chemical oxidation, the main affecting factors are the amount of FeSO₄, the amount of H₂O₂, pH value and reaction time. Because of the different effect of each factor on the treatment, and the single factor method takes a long time. In this paper, the orthogonal experiment is designed with four factors (the amount of FeSO₄, the amount of H₂O₂, pH value, reaction time) and three levels. The orthogonal factors and levels are shown in table 1. The concentration of Fe²⁺ is 0.5g/l, and the concentration of hydrogen peroxide is 30%.
100 ml of dyeing wastewater is put in 250 ml conical flask. According to the conditions of orthogonal design, adjust pH value and add medicine, then the experiment is carried on. After treatment, standing for 20 minutes, the absorbance and CODcr value of the supernatant are measured, and the COD removal rate is used as the index to analyze the orthogonal results. The COD removal rate of Fenton oxidation treatment is obtained by three parallel experiments under the optimum conditions.

2.2 Sample test method

For the evaluation of dyeing wastewater treatment effect of water quality indicators, there are decoloration rate and chemical oxygen demand in this paper. The determination of chemical oxygen demand is potassium dichromate method.

The absorbance A is measured at 565 nm by spectrophotometer, and the decolorization rate is calculated by the formula:

\[
\text{Decolorization rate} = \left( \frac{A_0 - A_1}{A_0} \right) \times 100\%
\]

A0, A1 are the absorbance of dyeing wastewater before and after treatment.

The determination of chemical oxygen demand by dichromate method(GB11914-89). The removal rate of CODcr= \( \left( \frac{\text{CODcr}_0 - \text{CODcr}_1}{\text{CODcr}_0} \right) \times 100\% \).

CODcr0, CODcr1 are the CODcr value of dyeing wastewater before and after treatment.

3. Results and Discussion

3.1 Experimental results of activated carbon adsorption

(1) Experiment results of pH effect on decolorization rate.

The absorbance of raw water is 0.294, and the decolorization rate of dyeing wastewater is calculated according to the absorbance value of the treated effluent, the experimental results are arranged in table 2. From table 2, it can be seen that the best pH value of the activated carbon adsorption experiment: pH=2.

| pH | Absorbance | Decolorization rate (%) | Activated carbon dosage (g/L) | Absorbance | Decolorization rate (%) |
|----|------------|-------------------------|-------------------------------|------------|-------------------------|
| 2  | 0.146      | 50.34                   | 0.2                           | 0.158      | 49.36                   |
| 3  | 0.179      | 39.12                   | 0.4                           | 0.123      | 60.58                   |
| 4  | 0.2        | 31.97                   | 0.6                           | 0.089      | 71.47                   |
| 5  | 0.211      | 28.23                   | 0.8                           | 0.069      | 77.88                   |
| 6  | 0.213      | 27.55                   | 1.0                           | 0.054      | 82.69                   |
| 7  | 0.228      | 22.45                   | 1.2                           | 0.045      | 85.58                   |
| 8  | 0.237      | 19.39                   | 1.4                           | 0.046      | 85.26                   |

(2) Experiment results of activated carbon dosage on decolorization rate

The absorbance of raw water is 0.312, the experimental results are arranged in table 2. It can be seen that the best condition of the activated carbon adsorption experiment is 1.2g/l.

(3) Experiment results of adsorption time on decolorization rate

The absorbance of raw water is 0.311, the experimental results are arranged in table 3. It can be seen that the best adsorption time of activated carbon adsorption experiment is 60 min.
Table 3. Effect of adsorption time on decolorization rate (AC)

| Adsorption time (min) | Absorbance | Decolorization rate (%) |
|-----------------------|------------|-------------------------|
| 20                    | 0.058      | 81.35                   |
| 40                    | 0.051      | 83.60                   |
| 60                    | 0.046      | 85.21                   |
| 80                    | 0.047      | 84.89                   |
| 100                   | 0.046      | 85.21                   |

(4) Result of parallel experiments

The optimum conditions for the adsorption of activated carbon are as follows: pH=2, the dosage of AC was 1.2g/l, and the adsorption time was 60 min. Under these conditions, three parallel experiments are carried out, the average maximum decolorization rate is 85.30 %.

3.2 Experimental results of coagulation

(1) Experiment results of pH effect on decolorization rate.

The absorbance of raw water is 0.314, and the decolorization rate of dyeing wastewater is calculated according to the absorbance value of the treated effluent, the experimental results are arranged in table 4. It can be seen that the decolorization rate reaches the maximum at pH 8~9.

Table 4. Effect of pH and PAC dosage on decolorization rate (coagulation)

| pH  | Absorbance | Decolorization rate (%) | PAC dosage (mg/L) | Absorbance | Decolorization rate (%) |
|-----|------------|-------------------------|-------------------|------------|-------------------------|
| 5   | 0.187      | 40.82                   | 30                | 0.243      | 22.12                   |
| 6   | 0.178      | 43.67                   | 50                | 0.102      | 67.31                   |
| 7   | 0.144      | 54.43                   | 70                | 0.077      | 75.32                   |
| 8   | 0.075      | 76.27                   | 90                | 0.096      | 69.23                   |
| 9   | 0.075      | 76.27                   | 110               | 0.225      | 27.88                   |
| 10  | 0.093      | 70.57                   |                   |            |                         |

(2) Experiment results of PAC dosage on decolorization rate

The absorbance of raw water is 0.312, the experimental results are arranged in table 4. It can be seen that the decolorization rate is maximum when the PAC dosage is 70mg/L.

(3) Experiment results of stirring time on decolorization rate

The absorbance of raw water is 0.309, the experimental results are arranged in table 5. According to the data of table 5, it can be seen that when the stirring time is 20 min, the decolorization rate reaches the maximum value.

Table 5. Effect of stirring time and standing time on decolorization rate (coagulation)

| Stirring time (min) | Absorbance | Decolorization rate (%) | Standing time (min) | Absorbance | Decolorization rate (%) |
|---------------------|------------|-------------------------|---------------------|------------|-------------------------|
| 10                  | 0.251      | 18.77                   | 15                  | 0.150      | 54.41                   |
| 20                  | 0.087      | 71.84                   | 30                  | 0.106      | 67.78                   |
| 30                  | 0.131      | 57.61                   | 45                  | 0.09       | 72.64                   |
| 40                  | 0.105      | 66.02                   | 60                  | 0.089      | 72.95                   |

(4) Experiment results of standing time on decolorization rate

The absorbance of raw water is 0.329, the experimental results are arranged in table 5. According to the data of table 5, it can be seen that the optimum standing time is 45 min.

(5) Result of parallel experiments

The optimum conditions of coagulation experiment are as follows: pH=8~9, PAC dosage of 70mg/L, stirring time of 20 min and standing time of 45 min. Under these conditions, three parallel experiments are carried out, the average maximum decolorization rate is 74.48 %.

3.3 Experimental results of Fenton chemical oxidation

Fenton chemical oxidation experiment is carried out according to the orthogonal table 1, the absorbance of raw water is 0.304, CODcr is 366.4mg/L. The decolorization rate and CODcr removal rate of dyeing wastewater are calculated according to the absorbance and CODcr values of the treated
effluent, the experimental results are arranged in Table 6.

**Table 6. Decolorization rate and CODcr removal rate of orthogonal experiment**

| NO. | Absorbance | CODcr(mg/L) | decolorization rate(%) | CODcr removal rate(%) |
|-----|------------|-------------|------------------------|-----------------------|
| 1   | 0.044      | 160         | 85.53                  | 56.33                 |
| 2   | 0.191      | 147.2       | 37.17                  | 59.83                 |
| 3   | 0.235      | 168.8       | 22.70                  | 53.93                 |
| 4   | 0.160      | 126.8       | 47.37                  | 65.39                 |
| 5   | 0.210      | 116         | 30.92                  | 68.34                 |
| 6   | 0.074      | 127.6       | 75.66                  | 65.17                 |
| 7   | 0.136      | 180.8       | 55.26                  | 50.66                 |
| 8   | 0.074      | 112.8       | 75.66                  | 69.21                 |
| 9   | 0.156      | 240.8       | 48.68                  | 34.28                 |

From the data of the decolorization rate and CODcr removal rate in Table 6, it can be seen that there isn’t obvious linear relationship between decolorization rate and CODcr removal rate. This is because that new substances are produced in degradation process of reactive brilliant blue XBR by Fenton chemical oxidation. Reactive brilliant blue XBR has the largest absorption at 565 nm, however the maximum absorption wavelength of these new substances is not necessarily at 565 nm. This means that the decolorization rate at 565 nm cannot be used as an evaluation of the chemical oxidation treatment of dyeing wastewater. Therefore, in the paper CODcr value is used as water quality index to study the effect of Fenton chemical oxidation on dyeing wastewater treatment.

**Table 7. Analysis of orthogonal experiment results**

| NO. | FeSO₄ | H₂O₂ | pH | Time | CODcr removal rate(%) |
|-----|------|------|----|------|-----------------------|
| 1   | 1    | 1    | 1  | 1    | 56.33                 |
| 2   | 1    | 2    | 2  | 2    | 59.83                 |
| 3   | 1    | 3    | 3  | 3    | 53.93                 |
| 4   | 2    | 1    | 2  | 3    | 65.39                 |
| 5   | 2    | 2    | 3  | 1    | 68.34                 |
| 6   | 2    | 3    | 1  | 2    | 65.17                 |
| 7   | 3    | 1    | 3  | 2    | 50.66                 |
| 8   | 3    | 2    | 1  | 3    | 69.21                 |
| 9   | 3    | 3    | 2  | 1    | 34.28                 |

| K1  | 170.09 | 172.38 | 190.72 | 158.95 |
| K2  | 198.91 | 197.38 | 159.50 | 175.66 |
| K3  | 154.15 | 153.38 | 172.93 | 188.54 |
| R   | 44.76  | 44.00  | 31.22  | 29.59  |

Taking CODcr removal rate as the index, the orthogonal experimental results are analyzed, as shown in Table 7. The results show that Fe²⁺ is the key factor, the next is H₂O₂, then pH, and finally the reaction time. The optimal conditions for the treatment of dyeing wastewater by Fenton oxidation are as follows: Fe²⁺ 0.05 g/L, H₂O₂ (30%) 14ml /L, pH=3, reaction time 40 min. Under these conditions, the average removal rate of cod is 69.35% in three parallel experiments.

### 4. Conclusion

In this paper, the treatment effect of coagulation process, activated carbon adsorption and Fenton chemical oxidation on dyeing wastewater were studied. The absorbency or CODcr value of the treated effluent was tested, and the best experimental conditions were determined. Under the optimum conditions, the decolorization rate of activated carbon adsorption was up to 85.30 %. The removal rate of CODcr in dyeing wastewater by Fenton oxidation is 69.35 %, which is due to that in the degradation of reactive brilliant blue dye, new organic substances were produced, which increased the CODcr value in water samples and lead to low removal rate of CODcr. Comprehensive consideration,
activated carbon adsorption treatment of dyeing wastewater was the best.

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