Study on Fe (II) Type Heterogeneous Fenton Decolorized Rhodamine B Supported by Aminophosphoric Chelate Resin

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Abstract. The main objective of this work was to study the decolorization of the rhodamine B in aqueous solution using Fenton process. Ls-5000 chelating resin loaded Fe2+ Fenton reagent was prepared by shaking impregnation method. The effects of various factors on the treatment of rhodamine B were preliminarily investigated. The results show that the optimal process conditions for photo-assisted heterogeneous Fenton decolorized rhodamine B with Ls-5000 chelating resin loaded Fe2+ is: 0.60g Ls-5000 chelate resin loaded Fe2+ + 1.5mL H2O2 + 60W visible light power + solution pH=2. 96.21% of decolorization efficiency could be achieved after 180 minutes under the Ls-5000 chelate resin loaded Fe2+/H2O2 reaction system.

1. Introduction
China is a big country where organic dyes are produced and used. Meanwhile Rhodamine B, an anthraquinone dye with a molecular formula of C28H31ClN2O3, is among the organic dyes that are most used worldwide [1]. The dye wastewater has high chromaticity, high concentration of organic pollutants and poor biodegradability, which is usually difficult to remove or inefficiency to remove from water by using conventional physical, chemical and biological treatment methods [2].

In 1894, the Fenton, French chemist, discovered that Fe2+ and H2O2 exhibited strong oxidizing properties in an acidic environment and could catalyze the oxidation of tartaric acid during the research. Later, the oxidation reaction from the Fe2+/H2O2 system was called Fenton oxidation Reaction [3]. Therefore, the application of Fenton oxidation reaction was started in chemical industry, pesticide, medicine, environmental pollution control and other fields [4, 5]. Fenton oxidation Reaction has emerged as an important alternative to decolorization for wastewater treatment. It has also been demonstrated to be effective for decolorization of some organic dyes.

In this paper, amino phosphoric acid chelating resin immobilized Fe (II) heterogeneous Fenton reagent was prepared by shaking impregnation method. The effects of solution conditions including the Fe-chelating resin quality, H2O2 dose, illumination power, solution pH, RhB concentration on rhodamine B removal performance were evaluated. Also the optimum process conditions discoloured with Rhodamine B was investigated. The degradation of rhodamine B by Ls-5000 amino phosphoric
acid type chelating resin loaded Fe (II) Fenton reagent was investigated under the condition of the presence of visible light radiation.

2. Experimental

2.1. Materials
Ls-5000 amino phosphoric acid type chelating resin was obtained from Xi’an Lanshen Special Resin Co. The solutions of Fe\(^{2+}\) at concentration of 4 mg ml\(^{-1}\)and the solutions of Rhodamine B at concentration of 1 mg ml\(^{-1}\) was prepared.

2.2. The Fe (II) fixed load
100g of pretreated Ls-5000 aminophosphate chelating resin was accurately weighed and placed in 1000mL beakers, and the mass concentration of 4mg/mL of Fe\(^{2+}\) solution was added to 500mL, and the solution oscillated for 24h. The resin was left overnight for extraction and filtration, and washed with distilled water. When it is dry, it is removed for later use.

2.3. Heterogeneous Fenton Decolorized Rhodamine B.
A 0.50g Ls-5000 amino phosphoric acid type chelating resin loaded Fe (II) was accurately weighed in a 250mL beaker (diameter: 8.0cm) and poured into a 50g/mL rhodamine B x-grl solution prepared in a 50mL volumetric flask. 1mL H\(_2\)O\(_2\) with a volume ratio of 1:100 was added and the beaker was placed on a magnetic stirrer for stirring. 60W incandescent lamp was placed 10cm above the beaker for irradiation. The residual dye concentration in the reaction solution was measured for 180min, the decolorization efficiency of Rhodamine B could be simply described as presented in Equation (1).

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R\% = \frac{C_0 - C_t}{C_0} \times 100\%
\]  

Where \(C_0\) and \(C_t\) are the concentration of Rhodamine B in aqueous solution at reaction time 0 and t min, respectively.

3. Results and discussion

3.1. Single factor experiment

3.1.1. Effect of Fe-chelating resin quality. The experiment was carried out in accordance with the experimental method of 2.3. To observe the influence of Fe-chelating resin quality decolourization on the rates of Rhodamine B, initial Fe-chelating resin dosages were varied in the range of 0-0.6g and Rhodamine B decolourization is shown in Fig 1.
In all cases, there was an increase in the decolorization of rhodamine B as Fe-chelating resin quality increased from 0 to 0.6g. As Fe-chelating resin increased, the total active surface area and the photoactivated volume of solution increased as well. 83.37% of decolorization efficiency could be achieved after 180 minutes when the catalyst dose reached 0.6g under the Ls-5000 chelate resin loaded Fe²⁺/H₂O₂ reaction system. However, when the mass of the catalyst was increased to 0.6g, the quality of the catalyst was never increased, the decolorization rate of Rhodamine B was basically stable. Fe-chelating resin quality above 0.6g would not induce significant change in decolorization efficiency. It is indicated that Ls-5000 chelate resin loaded Fe²⁺ exert different degrees of photocatalytic oxidation performance, which significantly improves the decolorization rate of Rhodamine B. But it is not necessary to add too much catalyst, because the more the amount of catalyst is, the more the amount of adsorbed dye will increase, and the dye adsorbed into the carrier is not conducive to further oxidative degradation. And too much Fe²⁺ will consume the •OH in the solution, and the decolorization rate of Rhodamine B will not continue to increase significantly.

3.1.2. Effect of H₂O₂. The experiment was carried out in accordance with the experimental method of 2.3, the influence of H₂O₂ volume on the decolorization rate of rhodamine B is shown in figure 2.

Most researches have demonstrated that the rates and efficiencies of photo-assisted degradation of organic substances are significantly improved in the presence of hydrogen peroxides when the proper amount is added. It was observed that higher the H₂O₂ volume, higher increased the decolorization efficiency of rhodamine B by Fenton oxidation reaction. Though H₂O₂ is an oxidant, its addition at concentration of 1.5 ml inhibited the decolorisation of rhodamine B. This is probably due to the scavenging effect of H₂O₂ on •OH. At high dosage, the hydrogen peroxide scavenges the photocatalytic surfaces formed, hindering •OH and the photo-generated hole (h⁺) Our experiments showed that H₂O₂ can effectively promote the decolorization of Rhodamine B.

3.1.3. Effect of illumination power. The experiment was carried out in accordance with the experimental method of 2.3, the Impact of the power of incandescent on decolourization of rhodamine B is shown in figure 3.
Regarding the effects of power, it is not surprising that this power contributed slightly to the rhodamine B decolourization in our experiments. It can be seen from Fig. 3 that the decolorization rate of Rhodamine B is slightly lower in the absence of visible light irradiation; the decolorization rate of Rhodamine B is more and more with the increase of illumination power. At the optimal illumination power, a maximum decolorization of 79.41% was obtained with the Fenton process. And the decolorization rate of Rhodamine B tends to be stable with the increase of illumination power. It is shown that visible light can effectively promote the decolorization of rhodamine B. This phenomenon can be explained by the fact that the dye molecules can absorb dye and can be transferred to Fe$^{3+}$ to obtain Fe$^{2+}$ and dye positive ion radicals, which can promote the decomposition of H$_2$O$_2$ by Fe$^{2+}$ to produce strong oxidizing OH, thereby improving the utilization efficiency of H$_2$O$_2$ and further oxidizing decolorizing dye.

3.1.4. **Effect of initial pH value.** The experiment was carried out in accordance with the experimental method of 2.3, the influence of the initial pH on decolourization of rhodamine B is shown in Fig 4. A series of experiments were carried out to study the influence of solution pH on rhodamine B decolourisation. The initial pH values were set at 2.0, 3.0, 4.0, 5.0 and 6.0, and the rest of parameters remained constant. Fig. 4 shows that the favourable pH values were 2.0 where the maximum decolorization rate is above 95.00% after 180min, which indicates that the photo-assisted heterogeneous Fenton system can solve the problem of narrow pH range for Fenton reaction. It is shown that pH has different effects on different heterogeneous Fenton system decolorization dyes, and suitable pH conditions should be determined through experiments during the application process.

3.1.5. **Effect of initial concentration of Rhodamine B.** The experiment was carried out in accordance with the experimental method of 2.3, Fig.5 shows the relationship between decolorization of the dye at different initial Rhodamine B concentrations.
As seen in Fig. 5, the decolorization rate of Rhodamine B decreases when the initial concentration of the dye solution increases from 0 to 200 mg L\(^{-1}\). 71.84\% of decolorization efficiency could be achieved when the initial concentration of the rhodamine B solution was 200 \(\mu\)g/mL under the Ls-5000 chelate resin loaded Fe\(^{2+}\)/H\(_2\)O\(_2\) reaction system. The decolorization rate of the decolorization rate is tend to be stable while the initial concentration of the dye is increasing.

3.2. Orthogonal experiment

According to the results of single factor experiment, the four factors affecting the decolorization rate of Rhodamine B were determined, namely catalyst dosage, solution pH, H\(_2\)O\(_2\) dosage and illumination power. In addition, the horizontal parameters of each factor were selected to carry out the orthogonal test according to the 4-factor 3 level orthogonal test table. The decolorization rate of Rhodamine B was comprehensively considered. The test results are shown in Table 1.

Table 1 Orthogonal experiment results of chelate resin loaded Fe\(^{2+}\) decolorizing rhodamine B

| Column number | test number | H\(_2\)O\(_2\) V/mL | pH | illumination power P/W | Catalyst m/g | Decolorization rate R\/% |
|---------------|-------------|---------------------|----|------------------------|-------------|--------------------------|
| 1             | 1           | 1.5                 | 2.0| 60                     | 0.4         | 95.7                     |
| 2             | 2           | 1.5                 | 4.0| 40                     | 0.6         | 90.8                     |
| 3             | 3           | 1.5                 | 6.0| 100                    | 0.2         | 84.0                     |
| 4             | 4           | 1.0                 | 2.0| 40                     | 0.2         | 94.2                     |
| 5             | 5           | 1.0                 | 4.0| 100                    | 0.4         | 72.5                     |
| 6             | 6           | 1.0                 | 6.0| 60                     | 0.6         | 92.5                     |
| 7             | 7           | 2.0                 | 2.0| 100                    | 0.6         | 87.3                     |
| 8             | 8           | 2.0                 | 4.0| 60                     | 0.2         | 81.4                     |
| 9             | 9           | 2.0                 | 6.0| 40                     | 0.4         | 84.5                     |
| I/3           | I/3         | 90.2                | 92.4| 89.9                  | 84.3        |                          |
| II/3          | II/3        | 86.4                | 81.6| 89.8                  | 90.2        |                          |
| III/3         | III/3       | 84.4                | 87.0| 81.3                  | 86.6        |                          |
| Range R       |             | 5.8                 | 10.9| 8.6                   | 6.0         |                          |

Factors affect the order of strength and weakness:
- pH
- illumination power
- Catalyst
- H\(_2\)O\(_2\) (From big to small)

Optimum process conditions: 0.60g Fe\(^{2+}\)/Ls-5000 chelate resin + 1.5mL H\(_2\)O\(_2\)+60W visible light power + solution pH=2
The differential analysis of the 9 sets of test data in Table 1 shows that the effect of catalyst quality, H$_2$O$_2$ volume, light power and solution pH on the decolorization rate of Rhodamine B was tested by Ls-5000 chelate resin loaded Fe$^{2+}$: pH of solution > Lighting power > Ls-5000 Chelating resin quality loaded Fe$^{2+}$ > H$_2$O$_2$ volume. The best process conditions for photo-assisted heterogeneous Fenton decolorized rhodamine B with Ls-5000 chelate resin loaded Fe$^{2+}$ is: 0.6 g Ls-5000 amino phosphoric acid type chelating resin loaded Fe$^{2+}$ + 1.5 mL H$_2$O$_2$ + 60 W visible light power + solution pH = 2.

4. Conclusion
The treatment of a solution containing rhodamine B by Fenton oxidation process has been taken into account in this study. The degradation rate and percentage are influenced by the Fe-chelating resin quality, H$_2$O$_2$ dose, illumination power, solution pH, rhodamine B concentration. The optimal conditions for degradation of RhB in the Fenton were observed at a pH of 2, with an initial Ls-5000 amino phosphoric acid type chelating resin loaded Fe$^{2+}$ quality of 0.6 g, 60 W visible light power and an initial H$_2$O$_2$ concentration of 1.5 mL for an rhodamine B concentration of 50g/mL. Heterogeneous Fenton reagent supplemented with visible light radiation is very suitable for the treatment of coloured waters, very effective and less expensive than conventional processes such as adsorption and extraction-liquid–liquid which implement pollution from one phase to another. To some extent, it solves the problem that the Fenton oxidation process has a narrow pH range and causes secondary pollution of iron sludge, which provides a theoretical and experimental basis for the study of wastewater treatment of anion and cationic dyes. The advantages of the heterogeneous Fenton reagent supplemented with visible light radiation as an oxidative treatment are low cost, rapid degradation, and simple handling. Therefore, this system could be applied to treat wastewater from dyeing operations.

Acknowledgements
This work was supported by the National Natural Science Foundation for Young Scientists of China (No.31800319)

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