Fe-S Co-doped Porous Carbon Catalyzed Oxidation and Degradation of Dye Wastewater

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Abstract: In this paper, Fe-S co-doping method of "one-step blending + high temperature carbonization activation" was used to prepare highly efficient Fenton-like catalyst. Rhodamine B (Rh B) was used as the research object, and H2O2 was used as the oxidant to catalyze the oxidation and degradation of Rh B. The important process conditions (reaction pH, reaction temperature, H2O2 addition, catalyst addition) were optimized, and the reaction mechanism and stability of the catalyst were investigated. The experimental results show that the initial concentration of Rh B is 50 mg/L, n(Fe): n(S) = 1.8:1, C source 9 g; Under the conditions of reaction pH = 2, reaction temperature 50℃ and catalyst dosage 0.02 g, the degradation rate of Rh B can reach 91.17%. XRD, BET and FT-IR results show that the prepared catalyst has good pore structure and abundant functional groups on its surface. The kinetic results show that the oxidation and degradation of Rh B by Fe-S co-doped Fenton-like catalyst conforms to the quasi-first-order kinetic model. The experiment results of free radical quenching show that the reaction process is controlled by many kinds of free radicals. After repeated use for 3 times, the degradation rate of the catalyst decreased from 91.05% to 85.76%, and recovered to 88.32% after thermal regeneration, showing good repeatability and thermal stability.

Keywords: Fenton Reaction; Fe-S Co-doping; Porous Carbon; Dye Wastewater.

1. Introduction

As a typical coloring agent, dye has the characteristics of high toxicity, difficult degradation and so on, and has potential harm to the environment and human beings. Dye wastewater has become one of the typical refractory wastewater in recent years, so it is very important to accelerate the research of efficient and economical treatment methods [1].

Fenton-like oxidation technology catalyzes H2O2 chain reaction by Fe2+ to produce active free radicals with strong oxidation, thus efficiently treating organic pollutants. It has the advantages of simple operation, rapid reaction and wide application conditions. The key lies in how to prepare an efficient and stable Fenton-like catalyst [2].

Zero-valent Fe and Fe fund oxide are cheap and widely sourced, and are commonly used as active components of Fenton catalyst[3]. On the one hand, supported heterogeneous Fenton catalyst can make metal Fe stably and uniformly supported inside the carrier structure, on the other hand, it can also increase the specific surface area of the catalyst, thus significantly improving its reaction activity[4]. Due to its good electrical conductivity and adsorption properties, carbon material as a carrier of Fe-based catalyst can increase the active site of catalyst and facilitate the redox cycle of Fe2+/Fe3+ [5, 6].

On the basis of Fe or Fe oxide alone, doping other elements can significantly improve the catalytic performance of the catalyst [7]. It is found that the S-doped modification process can produce bending, off-site and other structural defect sites on porous carbon materials, and increase the active site by changing the local surface electronic structure [8, 9]. These active sites can improve the electron transfer effect or adsorption or desorption between carbon materials and reactants, or enhance the interaction between carbon materials and metals, and improve the dispersion and stability of nano-metal particles [10]. This is due to the fact that by introducing elements to coordinate the formation of new structures, the electron transfer number can be increased to a large extent, and the apparent reactivity can be greatly improved [11]. Therefore, if S heteroatom can be introduced into Fe/C catalyst to form Fe-S co-doped porous carbon catalyst, the catalytic activity and stability of traditional Fe/C catalyst can be effectively improved [4, 12].

In this study, heterogeneous Fenton catalyst was prepared by the method of "one-step blending + high-temperature carbonization activation", and the important influencing conditions in the material preparation process were investigated, as well as the important technological conditions. The pH application range of the catalyst is expanded, the dissolution rate of iron ions is reduced, and the catalytic effect is finally improved. XRD, BET, FT-IR and other methods were used to characterize the structural and surface properties of the prepared catalyst, explore the relationship between Fe-S/AC structure and catalytic activity, explore the reaction mechanism of Fe-S/AC catalyst catalytic oxidation active factor and RhB removal, and fit the kinetic model according to the experimental results. Stability experiments were carried out to check the repeatability of the catalyst.

2. Experimental

2.1. Experimental Reagents and Instruments

Experimental reagents: anhydrous ferric chloride, L-cysteine, soluble starch, sodium chloride, nitric acid, H2O2, methanol, ethylenediamine tetracetic acid, tert-butanol, ascorbic acid, Rh B, sodium hydroxide, all AR, and the experimental water was deionized water.

Experimental equipment: intelligent magnetic stirrer, electronic analysis balance, electric blast drying oven, UV-visible spectrophotometer, pH composite electrode,
catalyst, then add 2 mL H2O2. Sampling was performed at 0, 2, 5, 8, 12 h. Then calcination was carried out in the tube furnace, CO2 was injected, the temperature was raised to 550℃ at 5℃/min, and then calcined for 2 h. The resulting black expanded solid is ground and transferred to the filter device, washed first to remove excess impurities, then pickled with 5% nitric acid for 12 h, and finally washed to neutral. After drying for 12 h, Fe-S co-doped Fenton-like catalyst is obtained, which is denoted as NFe-S/AC, where N is the value of n (Fe): n (S).

2.3. Materials Characterization

(1) XRD analysis: Bruker/D2 PHASER X-ray diffractometer of Bruker Company was used for analysis.

(2) BET analysis: The 3H-2000PS2 specific surface and aperture measuring instrument of Best Company was used for analysis.

(3) FT-IR analysis: Thermo Scientific NICOLET 6700 Fourier transform infrared spectrometer was used to identify active carbon functional groups.

2.4. Catalytic Oxidation Degradation of Rh B Experiment

Prepare 50 mg/L Rh B solution 200 mL in a beaker and start stirring at 50℃ and 1200 r/min. Add nitric acid to adjust pH, then add 2 mL H2O2. Sampling was performed at 0, 2, 5, 10, 20, 30, 40, 50, 60 min. The corresponding absorbance was measured, and the Rh B concentration was calculated using the fitted Rh B standard curve.

3. Result Analysis and Discussion

3.1. Catalyst Characterization Result

3.1.1. XRD Analysis

The crystal structures of different catalysts were characterized by X-ray diffraction (XRD). It can be seen from Fig.1 that the characteristic diffraction peak of S at 32.89° and Fe at 37.12° are the characteristic diffraction peaks [14]. After Fe and S co-doped, the characteristic diffraction peaks still exist on the catalyst, indicating that Fe and S have no effect on the crystal structure of porous carbon materials [15]. 1.5Fe-S/AC, 1.8Fe-S/AC, 2.0Fe-S/AC characteristic diffraction peaks corresponding to the supported Fe and S elements appear in the XRD patterns of the catalysts, while the corresponding characteristic diffraction peaks appear in the XRD patterns of 1.5Fe-S/AC catalysts, which may be due to too little iron oxide supported on the carrier surface. With the increase of n (Fe): n (S), the characteristic diffraction peak of the catalyst becomes more obvious, indicating that Fe and S elements are successfully loaded into the porous carbon.

3.1.2. BET Analysis

The properties and number of active sites on the catalyst surface are the key factors affecting the catalytic activity, and a larger specific surface area is conducive to the generation and dispersion of active sites, and increasing the contact area can improve the catalytic efficiency [5, 16]. The N2 adsorption/desorption test results of different Fe-S/AC catalysts are shown in Table 1. With the increase of Fe content, the specific surface area also increases gradually. This may be because the carbon material reacts with the iron source at high temperatures to form iron carbides, which can effectively promote the activation of carbon and generate more microporous and mesoporous structures [17, 18]. However, Fe/AC has the largest specific surface area, but its catalytic activity is weak, which indicates that other factors may affect its catalytic activity [14, 19]. Therefore, other characterization methods were used to further analyze and study.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area [m²g⁻¹]</th>
<th>Pore diameter [nm]</th>
<th>Pore Volume [cm³g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/AC</td>
<td>106.66</td>
<td>3.03</td>
<td>0.0808</td>
</tr>
<tr>
<td>1.5Fe-S/AC</td>
<td>146.79</td>
<td>2.73</td>
<td>0.1003</td>
</tr>
<tr>
<td>1.8Fe-S/AC</td>
<td>179.14</td>
<td>2.17</td>
<td>0.0973</td>
</tr>
<tr>
<td>2.0Fe-S/AC</td>
<td>217.43</td>
<td>2.24</td>
<td>0.1526</td>
</tr>
<tr>
<td>Fe/AC</td>
<td>390.61</td>
<td>2.15</td>
<td>0.2103</td>
</tr>
</tbody>
</table>

3.1.3. FT-IR Analysis

As shown in Fig.2, Fe-S/AC catalysts of different proportions were characterized by infrared spectroscopy and their surface functional groups were qualitatively analyzed. The wider absorption peak of 3475 cm⁻¹ is caused by the -OH or -CH functional groups [20]. The absorption peak at 1123 cm⁻¹ is caused by C-C, the absorption peak at 1625 cm⁻¹ is caused by C=O, and the absorption peak at 3768 cm⁻¹ belongs to the vibration peak of S-H [21]. Comparing different catalysts, it is found that the catalyst without S source does not have obvious vibration peak[22]. With the increase of S content, the vibration peak of S-H becomes more obvious, indicating that the addition of L-cysteine can successfully incorporate S element into the catalyst.

Figure 1. XRD Spectra of Fe-S/AC

Table 1. Specific Surface Area and Pore Volume of Fe-S/AC
3.2. Catalyst Activity Evaluation

3.2.1. Catalyzed Oxidative Degradation Rh B Wastewater of Fe-S/AC.

Under the conditions of Rh B concentration of 50 mg/L, catalyst dosage of 0.1 g/L, solution pH = 4, and reaction temperature of 50 ℃, the results of catalytic oxidation of Rh B wastewater with different Fe-S/AC are shown in Fig.3. When only H₂O₂ is added, Rh B is almost not degraded, indicating that the oxidation of H₂O₂ is not enough to decompose Rh B [23]. Fe/AC and S/AC catalysts also showed the same results, indicating that a single active component could not catalyze the decomposition of H₂O₂ to generate active free radicals to degrade Rh B. The degradation rate of Fe-S/AC catalysts with different proportions is higher than that of single active component, indicating that Fe-S co-doping can improve the ability of catalytic material to activate H₂O₂. The degradation rate of 1.8Fe-S/AC was the highest, which increased from 64.14% when the load ratio was 1.5Fe-S/AC to 80.60% (1.8Fe-S/AC). This may be because with the increase of Fe sources, the catalyst produces more Fe-based active sites, which generates more active free radicals, helping to catalyze the reaction. However, the degradation rate decreased to 69.12% when Fe loading was further increased. This may be the result of less Fe³⁺ being loaded on a certain specific surface area [12].

3.2.2. Influence of C Source Addition.

Under the same experimental conditions above, the effects of different C source additions on the activity of Fe-S/AC catalyst were investigated, and the results were shown in Fig.4. The catalytic degradation effect is the best when the C source is 9 g. When the amount of C source is small, the degradation rate is 67.73%. It may be that the specific surface area of the prepared catalyst is not large enough, and the volume is not enough, resulting in poor catalytic adsorption effect [24]. When the C source was increased to 9 g, the degradation rate increased to 81.47%. However, when the addition of more C sources increases, the pore structure of the prepared catalyst may be blocked [25], resulting in a decline in the catalytic performance of the catalyst and a low degradation rate [26]. The addition of C source in catalyst preparation was determined to be 9 g.

3.2.3. The Effect of Reaction Ph.

Based on the optimum preparation conditions, the effects of technological parameters on the H₂O₂ activation activity of Fe-S/AC catalyst were investigated. The influence rule of reaction pH is shown in Fig.5. The degradation effect of Rh B wastewater decreases with increasing pH [27]. When the pH increases from 4 to 8, the degradation rate decreases from 60.07% to 37.74%, which is because Fenton reaction needs to be carried out in an acidic environment [6]. When pH = 2, the degradation rate was 86.84%. This is due to the fact that the surface charge of the catalyst will be changed under acidic conditions, and the catalytic activity of the catalyst will be improved, thus improving the degradation efficiency of the catalyst for Rh B [28].
3.2.4. The Effect of Reaction Temperature.

Reaction temperature also has a great impact on Fenton reaction. At a higher temperature, the reaction rate is faster, but more energy is consumed. The degradation rate of Rh B at different reaction temperatures is shown in Fig. 6. When the reaction temperature increased from 40 °C to 60 °C, the degradation rate of Rh B increased from 69.07% to 90.78%. This indicates that the higher the reaction temperature is, the more beneficial it is to increase the activity of the catalyst and facilitate the reaction [29]. This is mainly because the increase in temperature can accelerate the mass transfer efficiency between the substrate and the catalyst, resulting in an increase in the number of reactive activated molecules [25]. At the same time, because high temperature helps to produce more active free radicals, it can enhance its oxidation capacity, thus accelerating the reaction [30]. The increase of temperature will also accelerate the formation rate of •OH [31]. It can help •OH react with organic matter, effectively decompose refractory macromolecules into small molecules, and realize Rh B mineralization [32]. However, considering the cost and time of actual wastewater treatment, 50 °C was chosen as the temperature of catalytic oxidation experiment.

![Figure 6. Fe-S/AC Catalyzed Oxidation and Degradation of Rh B At Different Temperature](image)

3.2.5. The Effect of Catalyst Addition.

As shown in Fig. 7, when the amount of catalyst is 0.015 g, the degradation rate of Rh B is 75.35%. It may be that the amount of catalyst is too small, resulting in not enough active sites to catalyze oxidative degradation of Rh B wastewater. When the addition of catalyst increases from 0.02 g to 0.03 g, the degradation rate increases from 90.92% to 96.18%, and the degradation rate further increases, which may be because the increase of catalyst will enable enough Fe^{2+} and H_{2}O_{2} in the solution to react to generate strong oxidizing •OH, thus rapidly degrading Rh B [33]. However, since the degradation rate has reached 90.92% at 0.02g, continuing to increase will not significantly improve the degradation rate, but also increase the cost, so the subsequent selection of catalyst addition is 0.02g.

In summary, the experimental results show that the initial concentration of Rh B is 50 mg/L, n(Fe): n(S) = 1.8:1, C source 9 g; Under the conditions of reaction pH = 2, reaction temperature 50°C and catalyst dosage 0.02 g, the degradation rate of Rh B can reach 91.17%.

![Figure 7. Fe-S/AC Catalyzed Oxidation and Degradation of Rh B Under Different Addition](image)


The experiment was carried out under the above optimal catalyst and optimal process conditions, and the reaction was repeated under the same operation, and the results were shown in Fig. 8. After repeated use for 3 times, the degradation rate of Rh B wastewater decreased from 91.05% to 85.76%, but after one calcination, the degradation rate increased to 88.32%. After the third experiment, the degradation rate decreased slightly, which may be due to the fact that when Rh B reacted with the catalyst surface, a covering layer or physical adsorption layer would be formed on the catalyst surface. The residual covering of organic matter would reduce the specific area of the catalyst, resulting in some active sites on the catalyst surface being obscured, thus affecting the activity and selectivity of the catalyst. At the same time, impurities or pollutants in the reactants may also be deposited on the catalyst surface during the catalytic reaction, thus affecting the degradation effect of the catalyst [34]. The catalytic activity was partially recovered after calcination, which may be due to the fact that some small organic molecules covered the active site during the use of the catalyst and blocked the pore channels, thus resulting in the inactivation of porous carbon [10]. Through thermal regeneration treatment, the organic matter covering the active site can be shed and the catalytic activity can be restored.

![Figure 8. Stability Of 1.8Fe-S/AC](image)

3.3. Dynamics Research

Taking Rh B as the research object, under the conditions of initial concentration of Rh B being 50 mg/L, pH = 2, volume...
of H₂O₂ being 2 mL and catalyst being 0.02 g, the effect of reaction temperature on catalytic oxidative degradation of Rh B was studied and the Arrhenius curve was fitted, as shown in Fig.9. When the reaction temperature increased from 30 °C to 60 °C, the degradation rate of Rh B increased from 58.11% to 91.78%. This is mainly due to the fact that the higher the temperature is, the more active free radicals are generated by thermal activation, thus accelerating the degradation of Rh B [26]. According to the quasi-first-order kinetic equation \( C_t/C_0 = e^{-kt} \), the obtained temperature data were fitted, and the linear fitting correlation \( R^2 > 0.97 \) was obtained, indicating that the degradation rate of Rh B prepared at different reaction temperatures was in line with the quasi-first-order kinetic model [35]. The Arrhenius formula is used to calculate the reaction activation energy of 37.81 kJ/mol, which is lower than the corresponding activation energy when it is used as a catalyst, which confirms the good catalytic activity of the co-doped Fenton-like catalyst prepared in the experiment. It can be seen from kinetic analysis that S doping modification is an effective means to enhance its catalytic activity [36]. Combined with the characterization data, it can be seen that although it has the largest specific surface area, its catalytic activity is not optimal, indicating that the specific surface area is not the key factor affecting its activity, but mainly depends on the number and type of surface active functional groups [34].

![Figure 9. Dynamics Research Results Of 1.8Fe-S/AC](image)

**3.4. Reaction Mechanism**

In order to explore the reaction mechanism of this process, different free radical masking agents were added in the reaction process, and 2mM MeOH, TBA, EDTA and VC were added respectively as \( \cdot OH \), SO₄⁻, \( \cdot O_2^- \) and \( ^1O_2 \) free radical quenching agents for masking experiments, as shown in Fig.10. After 60 min, the degradation rates of Rh B were 26.30%, 32.47%, 26.56% and 19.02%, respectively. After the quenching agent was added, the degradation rate decreased significantly, indicating that a variety of active free radicals co-existed in the process and jointly participated in the oxidative degradation process of Rh B, thus showing a good degradation rate [35, 37].

**4. Summary**

(1) The optimal experimental conditions are: \( n(Fe): n(S) = 1.8:1 \), C source 9 g; When pH = 2, reaction temperature 50 °C and catalyst dosage 0.02 g, the degradation rate of Rh B can reach 91.17% after 60 min. Compared with Fe and S alone, the catalyst supported by Fe and S has better degradation of Rh B wastewater, among which 1.8Fe-S/AC has the highest degradation rate and has good stability.

(2) XRD results show that S doping has no effect on the crystal structure. The BET results showed that the specific surface area increased with the increase of Fe content.

(3) The kinetic analysis results show that the degradation of Rh B by Fe-S co-doped Fenton-like catalyst conforms to the quasi-first-order kinetic model. The activation energy calculated by Arrhenius formula is 37.81 kJ/mol (> 29 kJ/mol), which belongs to the surface reaction control process.

(4) The results of free radical quenching show that a variety of active free radicals co-exist in the catalytic oxidation reaction system, indicating that the catalyst degradation of Rh B is an oxidation process dominated by free radicals.

**CONFLICTS OF INTEREST**

The authors declare that they have no conflict of interest.

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