Degradation of Orange I by the zero-valent iron/hydrogen peroxide system

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Abstract. The zero-valent iron/hydrogen peroxide system was very effective for the oxidative degradation of high concentration Orange I solution. The effects of Orange I initial concentration, hydrogen peroxide concentration, zero-valent iron dosage and pH value of solution on the degradation of Orange I were studied in this article. The concentration of iron ion, pH value and the content of Orange I in the reaction solution were determined by UV-VIS spectrophotometer and pH meter, respectively. The intermediate degradation products were determined by LC-MS. The experimental results showed that the Orange I solution with high concentration could be effectively degraded with low hydrogen peroxide concentration and iron powder dosage under acid condition. In addition, it can be speculated that in the process of degradation, Orange I was first dissociated into 4-(4-hydroxy-1-naphthylazo) benzenesulfonate, and then its chromophore was oxidized and broken, decoloring the reaction solution, followed by the generation to benzene sulfonate, nitrogen and 1,4-naphthoquinone. After that, 1,4-naphthoquinone was further oxidized to phthalate.

1. Introduction

In recent years, zero-valent iron (ZVI) has attracted extensive attention in the field of soil and groundwater remediation[1,2,3]. Zero-valent iron is widely used in the degradation of organic and inorganic pollutants because of its active chemical nature, wide range of sources and environmental friendliness, such as hexavalent chromium[4], nitroaromatic hydrocarbons[5], etc. But for some more stable organic pollutants, the reduction rate with zero-valent iron alone is slower, so it is very necessary to adopt certain oxidation technology to accelerate the degradation rate[3].

In the past few decades, advanced oxidation processes have achieved good results in the degradation of refractory organic pollutants due to their strong oxidation capacity, and been increasingly favored by relevant researchers[6,7]. The Fenton method is very representative in advanced oxidation processes. Under acidic conditions, Fenton reagent uses divalent iron ion to catalyze the decomposition of hydrogen peroxide to generate hydroxyl radicals (·OH, E°=2.80 V), and the oxidation capacity of ·OH is second only to fluorine (E°=2.87 V) among common oxidants. Therefore, Fenton reagent can oxidatively degrade many organic pollutants, and hydrogen peroxide as an oxidant will not cause secondary pollution to the environment[8]. However, due to the shortcomings of the traditional Fenton reagent, such as large amount of hydrogen peroxide and the narrow pH range required for the reaction, it is restricted in practical applications[9,10], which also attracts many researchers to continuously study and improve Fenton reagent.

It has been reported that under acidic conditions, when hydrogen peroxide and zero-valent iron coexist, ·OH radicals can also be generated, thus triggering the oxidation reaction[11,12,13], so the
zero-valent iron/hydrogen peroxide system can be used to oxidize and degrade many organic pollutants. In this experiment, the representative azo dye, Orange I, was selected as the degradation object, to explore the optimal degradation reaction conditions and discuss the oxidative degradation mechanism.

2. Materials and method

2.1 Experimental agents and instruments

100-mesh zero-valent iron powder, 30% hydrogen peroxide solution, 36% hydrochloric acid solution, chromatographically pure methanol, Orange I, sodium hydroxide, hydroxylamine hydrochloride, o-phenanthroline, acetic acid, sodium acetate and others were analytical reagents. The instruments used in the experiment were TU-1901 dual-beam UV-VIS spectrophotometer, LC-MS-8040, FA2104 electronic analytical balance, TDL-5-A centrifuge, 85-1A magnetic stirrer, pHS-25 digital-display pH meter, etc.

2.2. Experimental method

A certain amount of Orange I dye solution of known concentration and pH was added to a 100ml conical flask, where then a certain amount of zero-valent iron powder and hydrogen peroxide were added. About 10ml of the upper reaction liquid was taken into a centrifuge tube every 10 minutes, which was repeated six times, and then centrifuge at 4000 rpm for 10 minutes. The upper liquid in the centrifuge tube was scanned on an UV-VIS spectrophotometer with a wavelength range of 200-600 nm. With other factors unchanged, when changing one factor, the effects of initial concentration of Orange I, hydrogen peroxide concentration, zero-valent iron dosage and pH value on the degradation of Orange I in zero-valent iron/hydrogen peroxide system were studied. The above experiments were conducted under the dark state.

The concentration of Orange I in the reaction solution at each time period could be calculated by making a standard curve with an UV-VIS spectrophotometer, so as to calculate the degradation rate of Orange I. For the determination of the concentration of iron ion in the solution, the o-phenanthroline colorimetric method was used.

The detection conditions of LC-MS were that: the mobile phase was water and methanol, gradient elution was used to increase the methanol from 10% to 100% within 15 minutes and maintained for 10 min, the flow rate was 0.2 mlꞏmin⁻¹, the injection flow injection was 0.3 ulꞏmin⁻¹, with ESI source, negative ion mode and mass-to-charge ratio scanning range of 50-700.

3. Results and analysis

3.1 Contrast experiment

Under normal conditions, the aqueous solution of Orange I was degraded by oxidation and reduction, respectively, and the experimental results are shown in Figure 1. In the experiment, the concentration of Orange I solution was 100 mgꞏL⁻¹, the pH value of the solution was 4.0, the dosage of zero-valent iron powder was 0.3 gꞏL⁻¹, and the concentration of H₂O₂ was 3 mmolꞏL⁻¹. It can be seen from Figure 1 that the addition of zero-valent iron without hydrogen peroxide has no obvious effect on the degradation of Orange, with the degradation rate of less than 10% within 60 minutes. If the air is blasted, the degradation rate will increase slightly; The degradation rate of Orange I reaches about 90% within 60 minutes with hydrogen peroxide and without zero-valent iron simultaneously, but the degradation rate will be reduced by about 10% if the air is blasted; Simultaneous addition of hydrogen peroxide and zero-valent iron has a good effect on the degradation Orange I, which can reach more than 95% within 10 minutes. If the air is blasted, the degradation rate changes little. Comprehensive comparison shows that the addition of hydrogen peroxide significantly improves the degradation rate of Orange I, and the oxidative degradation of Orange I in zero-valent iron/hydrogen peroxide system is very economical and feasible.
3.2. Effect of the initial concentration of Orange I on the reaction

As can be seen from the results of the contrast experiment, the degradation speed of the 100 mg·L\(^{-1}\) of Orange I solution was very fast with magnetic stirring, under the conditions that zero-valent iron dosage was 0.3 g·L\(^{-1}\), pH was 4.0 and the concentration of hydrogen peroxide was 3 mmol·L\(^{-1}\). The degradation rate after 10 minutes of reaction was over 95%. Therefore, in order to further explore the suitable concentration of Orange I, the Orange I solutions with the concentration of 0.2, 0.4, 0.6, 0.8 and 1.0 g·L\(^{-1}\) were selected for further experiments under the above conditions, and the experimental results are shown in Figure 2. As can be seen in Figure 2, the degradation rate gradually decreases to a steady level with the increase of the concentration of Orange I within 10 minutes; the degradation rates of Orange I solution at the concentrations of 0.1, 0.2 and 0.4 g·L\(^{-1}\) change slowly within 60 minutes, and finally reach more than 90%, without much difference between each other; the degradation rates of Orange I solution at the concentrations of 0.8 and 1.0 g·L\(^{-1}\) are below 5%; the degradation rate of 0.6 g·L\(^{-1}\) Orange I solution varies greatly, approximately increasing from 48% at 10 minutes to 70% at 60 minutes.

According to literature reports\([14,15,16]\), the reaction of oxidative and reductive degradation of pollutants based on zero-valent iron generally conforms to pseudo-first-order kinetics, so the pseudo-first-order kinetic equation was adopted in this experiment to describe the oxidative degradation of Orange I in zero-valent iron/hydrogen peroxide system. Table 1 shows the pseudo-first-order kinetic rate constants (K) of the oxidative degradation of Orange I at the different initial concentrations of Orange I. It can be seen from the data in Table 1 that as the concentration of Orange I increases, the reaction rate constant gradually declines. When the concentration is greater than 0.6 g·L\(^{-1}\), the reaction rate constant is very small. When the concentration of Orange I increases
from 0.1 g·L⁻¹ to 0.4 g·L⁻¹, the reaction rate constant decreases to about a quarter of the original.

![Figure 3](image3.png)

**Figure 3.** The influence of different hydrogen peroxide concentration on the degradation of Orange I.

![Figure 4](image4.png)

**Figure 4.** The influence of different Fe⁰ dosage on the degradation of Orange I.

| C₀ (g·L⁻¹) | 0.1  | 0.2  | 0.4  | 0.6  | 0.8  | 1.0  |
|------------|------|------|------|------|------|------|
| K (×10⁻³ min⁻¹) | 322.3 | 159.6 | 78.52 | 25.97 | 4.490 | 2.850 |
| R          | 0.9089 | 0.9093 | 0.9071 | 0.9300 | 0.9281 | 0.9012 |

| H₂O₂ (mmol·L⁻¹) | 3  | 6  | 9  | 12 | 15 |
|-----------------|----|----|----|----|----|
| K (×10⁻³ min⁻¹) | 25.97 | 86.94 | 92.75 | 71.59 | 117.5 |
| R               | 0.9300 | 0.9152 | 0.9357 | 0.9456 | 0.9427 |

### Table 1. The pseudo-first-order kinetic rate constant (K) under the different concentration of Orange I.

### Table 2. The pseudo-first-order kinetic rate constant (K) under the different concentration of H₂O₂.

3.3. **Effect of the concentration of hydrogen peroxide on the reaction**

According to the experimental method, under the conditions that the initial concentration of Orange I solution was 0.6 g·L⁻¹, the concentration of zero-valent iron was 0.3 g·L⁻¹ and the pH was 4.0, hydrogen peroxide solutions at the concentration of 3, 6, 9, 12 and 15 mmol·L⁻¹ were added, respectively, and degradation reaction was performed under magnetic stirring, with the experimental...
results shown in Figure 3. It can be seen from Figure 3 that the degradation rate of Orange I gradually increases when the initial concentration of hydrogen peroxide increases from 3 mmol·L\(^{-1}\) to 9 mmol·L\(^{-1}\) within 60 minutes; When the concentration of hydrogen peroxide continuously increases, the degradation rate of Orange I decreases first and then increases. Hydrogen peroxide plays an important role in Fenton-like reaction, and appropriate concentration of hydrogen peroxide can accelerate the speed of Fenton-like reaction, but excess hydrogen peroxide will become a trap for hydroxyl radicals\[17,18\], thereby reducing the rate of Fenton-like reaction, so the concentration of hydrogen peroxide should be properly controlled. In addition, Table 2 shows the pseudo-first-order reaction kinetic rate constants (K) of the degradation reaction of Orange I under the different concentrations of hydrogen peroxide. It can be seen that when the concentration of hydrogen peroxide is less than 9 mmol·L\(^{-1}\), the rate constant increases with the enlargement of hydrogen peroxide concentration; But when the concentration of hydrogen peroxide continues to arise, the rate constant decreases first and then increases.

Table 3. The pseudo-first-order kinetic rate constant (K) under the different concentration of Fe\(^0\).

| Fe\(^0\) (g·L\(^{-1}\)) | 0.2   | 0.3   | 0.4   | 0.5   | 0.6   |
|-------------------------|------|------|------|------|------|
| K (×10\(^{-3}\) min\(^{-1}\)) | 83.51 | 92.75 | 128.7 | 107.3 | 131.0 |
| R                       | 0.9294 | 0.9357 | 0.9034 | 0.9075 | 0.9087 |

Table 4. The pseudo-first-order kinetic rate constant (K) under different pH value.

| pH     | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
|--------|-----|-----|-----|-----|-----|
| K (×10\(^{-3}\) min\(^{-1}\)) | 130.1 | 110.2 | 128.7 | 2.790 | 1.010 |
| R     | 0.9124 | 0.9089 | 0.9034 | 0.9304 | 0.9504 |

3.4. Effect of the concentration of zero-valent iron

According to the experimental method, under the conditions that the initial concentration of Orange I solution was 0.6 g·L\(^{-1}\), the concentration of hydrogen peroxide was 9 mmol·L\(^{-1}\) and the pH was 4.0, zero-valent iron at concentration of 0.2, 0.3, 0.4, 0.5 and 0.6 g·L\(^{-1}\) were added, respectively. The degradation reaction was performed under magnetic stirring, and the experimental results are shown in Figure 4. As can be seen from Figure 4, the degradation rate of Orange I in each group of experiments has reached more than 70% within 10 minutes; When the concentration of iron powder is 0.4 g·L\(^{-1}\), the degradation rate of Orange I reaches more than 87% within 10 minutes and more than 93% within 60 minutes; When the concentration of iron powder is below 0.4 g·L\(^{-1}\), the degradation rate of Orange I arises with the increase of iron powder concentration; When the concentration of iron powder is greater than 0.4 g·L\(^{-1}\), the degradation rate of Orange I changes little. Furthermore, the Table 3 exhibits the pseudo-first-order reaction kinetic rate constants (K) of the degradation of Orange I at the different concentrations of zero-valent iron. As can be seen from Table 3, when the concentration of iron powder is less than 0.4 g·L\(^{-1}\), the rate constant enlarges with the increasing concentration of iron powder; But when the concentration of iron powder is greater than 0.4 g·L\(^{-1}\), the rate constant decreases first and then increases.

3.5. Effect of solution pH

In accordance with the experimental method, under the conditions that the initial concentration of Orange I solution was 0.6 g·L\(^{-1}\), the concentration of hydrogen peroxide was 9 mmol·L\(^{-1}\) and that of zero-valent iron was 0.4 g·L\(^{-1}\), the solutions with the original pH of 2.0, 3.0, 4.0, 5.0 and 6.0, respectively, were subjected to degradation action under magnetic stirring, and the experimental results are shown in Figure 5. It can be seen from Figure 5 that the degradation rates of Orange I in the two groups at pH 5.0 and 6.0 are less than 10% within 60 minutes; and the degradation rates of the other three groups are all around 90%, which has a wider range of pH compared with the traditional Fenton method. At the same time, the pseudo-first order reaction kinetic rate constants (K) of the degradation reaction of Orange I at the different pH of initial solutions are given in Table 4, from which as can be seen, when the pH of the initial solution is less than 4.0, the rate constant is relatively
large; However, when the pH of the initial solution is 5.0 and 6.0, the rate constant is relatively small, and the degradation effect at pH 4.0 is the best comprehensively.

Figure 5. The influence of different pH value on the degradation of Orange I.

3.6. Analysis of iron ion concentration and pH
The experiment group with the Orange I at concentration of 0.6 g⋅L⁻¹, pH=4.0, hydrogen peroxide at concentration of 9 mmol⋅L⁻¹ and zero-valent iron at concentration of 0.4 g⋅L⁻¹ was selected to determine the concentration of iron ion and the pH in the reaction solution at each time period. The measurement results of the changes of the iron ion concentration and pH in the reaction solution with the reaction time are shown in Figure 6. It can be seen from Figure 6 that both the concentrations of total iron ion and ferrous iron ion increase rapidly first and then gradually decrease during 0–60 minutes, reaching 110.6 mg⋅L⁻¹ and 103.7 mg⋅L⁻¹ at 10 minutes, respectively, while at 60 minutes, they decreased to 71.56 mg⋅L⁻¹ and 68.56 mg⋅L⁻¹, by 35% and 34%, respectively. The change trend of pH value of the reaction solution is similar to that of the concentration of iron ion, which also increases first and then gradually decreases. From the initial value of 4.0, the pH of the reaction solution increases to 4.83 within 10 minutes, then gradually decreases, and drops down to 4.4 at 60 minutes.

3.7. Analysis by UV spectroscopy and LC-MS
The experiment group with the Orange I at concentration of 0.6 g⋅L⁻¹, pH of 4.0, hydrogen peroxide at concentration of 9 mmol⋅L⁻¹ and zero-valent iron at concentration of 0.4 g⋅L⁻¹, was selected to perform
UV-VIS adsorption spectroscopic scanning for the reaction solution at each time period and determine the reaction solution at 60 minutes by LC-MS. The change over time of UV-VIS absorption spectrum of Orange I oxidatively degraded in zero-valent iron/hydrogen peroxide system is shown in Figure 7. 477 nm is the main absorption wavelength of Orange I, which is caused by the n-π* electron transition of azo structure of Orange I [16]. It can be seen from Figure 7 that the absorption intensity at the main wavelength of 477 nm gradually decreases with the extension of reaction time, indicating that the Orange I is gradually oxidatively degraded. After 10 minutes of reaction, the absorbance at 477 nm is reduced to 66% of the original Orange I solution, after 30 minutes to 58%, and after 60 minutes to 44%.

![Figure 7. The UV-VIS absorption spectra of degradation Orange I in the reaction process.](image)

The Orange I solution after 60 minutes of oxidative degradation was analyzed by LC-MS spectrometry, and the intermediate products, benzenesulfonate (C_{6}H_{5}O_{3}S\textsuperscript{-}, m/z=157) and phthalate (C_{8}H_{4}O_{4}\textsuperscript{2-}, m/z=164), were generated, which was consistent with the detected intermediate reported in the references [19,20,21], indicating that the azo double bond undergoes an electronic transition during the catalytic process, thereby activating the local structure of the dye molecule making the carbon...
atoms bonded to the azo double bond unstable. At this time, the strong oxidizing hydroxyl radicals in the system attacked these unstable carbon atoms, resulting in the first break of the C-N bond [22]. Therefore, it can be speculated that in the process of oxidative degradation, Orange I was first dissociated into 4-(4-hydroxy-1-naphthylazo) benzenesulfonate (C_{16}H_{11}N_{2}O_{4}S⁻), and then its chromophore was oxidized and broken, decoloring the reaction solution, followed by the generation to benzene sulfonate, nitrogen and 1, 4-naphthoquinone (C_{10}H_{6}O_{2}). After that, 1, 4-naphthoquinone was further oxidized to phthalate. The whole reaction process is shown in Figure 8.

4. Conclusions
The experimental results showed that the oxidation method could be used to oxidatively degrade the high-concentration Orange I solution at a lower cost, with a fast degradation rate and a good degradation effect. With other conditions unchanged, the effect of hydrogen peroxide on the degradation rate of Orange I firstly increased, then declined and then increased with the rising concentration of hydrogen peroxide. If the concentration of hydrogen peroxide was too low, the oxidative degradation rate was low, but if the concentration was too high, it would become the trapping agent of ·OH radical, so it is necessary to choose an appropriate concentration of hydrogen peroxide. The effect of zero-valent iron on the degradation rate of Orange I was firstly enlarged with the increase of the dosage and then changed little. Therefore, the dosage of zero-valent iron should not be too much. The initial pH value of the reaction solution was very important for the degradation of Orange I, and an appropriate pH can significantly increase the degradation rate of Orange I. As a result, under acidic conditions, the zero-valent iron/hydrogen peroxide system could effectively oxidize the azo structure of Orange I and destroy its chromogenic groups, thus to achieve an ideal oxidative degradation effect.

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