Degradation of Orange II by the Fe\textsuperscript{0}/H\textsubscript{2}O\textsubscript{2} system

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Abstract. The degradation of Orange II by the Fe\textsuperscript{0}/H\textsubscript{2}O\textsubscript{2} system was examined. The effects of Orange II concentration, H\textsubscript{2}O\textsubscript{2} concentration, Fe\textsuperscript{0} dosage, initial solution pH value on the degradation of Orange II were investigated. The experimental results showed that Fe\textsuperscript{0} was exhibited high catalytic activity on the activation of H\textsubscript{2}O\textsubscript{2} for the degradation of Orange II. The reactive hydroxyl radical (\bullet OH) produced in the Fe\textsuperscript{0}/H\textsubscript{2}O\textsubscript{2} system was significant the key for the degradation of Orange II. The mechanism of the degradation of Orange II was discussed by the UV-Vis spectra analysis and determining intermediate products of the reaction solution by LC-MS. It was speculated that in the process of oxidative degradation, Orange II was first dissociated into 4-(2-hydroxy-1-naphthylazo) benzenesulfonate, and then its azo structure was oxidized and destroyed by hydroxyl radicals (\bullet OH). Secondly, the reaction solution faded to produce benzenesulfonate and 1, 2-naphthoquinone, and then 1, 2-naphthoquinone was further oxidized by \bullet OH to phthalate. Finally, phthalate and benzenesulfonate could be further mineralized into CO\textsubscript{2}, H\textsubscript{2}O and SO\textsubscript{4}\textsuperscript{2-}.

1. Introduction

The azo dye is a kind of dye with azo group (-N=N-) in molecular structure. It can be divided into monoazo, bisazo, triazo and polyazo dyes according to the number of azo groups in the molecule. It is the most widely used organic synthetic dye in the industry at present. It is widely used in food, textile, cosmetic, leather and other industries\cite{1}. However, the wide application of azo dyes also brings water pollution. In addition, azo dye wastewater is a kind of refractory organic wastewater because of its stable azo structure and benzene ring. Many azo dyes are made of aniline by organic diazotization and then coupling with phenols, anilines and methylene compounds. As a result, the organic components of azo dye wastewater are complex, which is recognized by researchers as one of the refractory organic wastewater\cite{2}. There are many treatment methods for azo dye wastewater, such as chemical reduction or oxidation, physical adsorption, biodegradation, etc. In these methods, the degradation of azo dyes by zero valent iron (Fe\textsuperscript{0}) has always been a research focus\cite{3,4}.

Zero valent iron (Fe\textsuperscript{0}) is extensively used in the degradation of inorganic or organic pollutants on account of its active chemical properties and extensive sources. For example, nitroaromatic compounds\cite{5}, heavy metal ion\cite{6}, etc. It has been reported that hydroxyl radicals (\bullet OH) can be produced when Fe\textsuperscript{0} and H\textsubscript{2}O\textsubscript{2} coexist under acidic conditions\cite{7,8,9}. Fe\textsuperscript{0} can be corroded by acid to produce Fe\textsuperscript{2+}, which can catalyze the disintegration of hydrogen peroxide to produce hydroxyl radicals. In common oxidants, the oxidation capacity of hydroxyl radicals (E\textsubscript{th}=2.80V) is second only to that of fluorine (E\textsubscript{th}=2.87V), which can oxidize and degrade many organic pollutants\cite{10}. Therefore, using the Fe\textsuperscript{0}/H\textsubscript{2}O\textsubscript{2} system to degrade azo dye wastewater is very significance. The representative azo dye, Orange II, was chose as the degradation object to explore the best degradation reaction conditions and discuss its degradation mechanism in this experiment.
2. Materials and method

2.1. Experimental agents and instruments
The analytical agents include Orange II, sodium hydroxide, hydroxylamine hydrochloride, acetic acid, isopropanol, o-phenanthroline and sodium acetate. The purity of methanol is chromatographic pure. The mass fraction of hydrochloric acid solution is 36%. The particle size of zero valent iron powder is 100-mesh. The volume fraction of hydrogen peroxide solution is 30%. The instruments including TU-1901 dual-beam UV-VIS spectrophotometer, LC-MS-8040, TDL-5-A centrifuge, 85-1A magnetic stirrer and pHS-25 digital-display pH meter were used in the experiment.

2.2. Procedure and approach
A certain amount of Orange II dye solution of known concentration and pH, a certain amount of 100-mesh zero valent iron powder, and known concentration of H_2O_2 were added to a 100 ml conical flask. In the experiment, about 10 ml of the upper reaction solution every 10 minutes was taken into a centrifuge tube, and then centrifuged at 4000 rpm for 10 minutes. The above operation was repeated for 6 times. After centrifugation, the supernatant of centrifuge tube was scanned by UV-Vis spectrophotometer at a wavelength range of 200-600 nm. In addition, the above experiments were carried out in the dark state. When changing one factor including initial concentration of Orange II, hydrogen peroxide concentration, zero valent iron dosage and pH value, the effects of which on the oxidative degradation of Orange II were examined with other factors unchanged.

The concentration of Orange II in each time period could be determined by UV-Vis spectrophotometer. The degradation rate of Orange II was calculated by monitoring the reduction of its concentration. The concentration of iron ion could be determined by o-phenanthroline colorimetric method. The intermediate degradation products of Orange II could be detected by LC-MS. The detection conditions were as follows: water and methanol were mobile phase; the gradient elution was used; the methanol dosage was increased from 10% to 100% within 15 minutes; hold time was set to 10 minutes; the flow rate was set to 0.2 mlꞏmin^{-1}; the injection flow injection was set to 0.3 ulꞏmin^{-1}, with ESI source, the negative ion mode; the scanning range of mass to charge ratio was 50-700.

3. Results and analysis

3.1. Comparative experiment
Five different methods were used to degrade the Orange II solution under normal conditions. The experimental results are shown in the Figure 1. The reaction conditions including initial 100 mgꞏL^{-1} Orange II solution, pH=4.0, 0.3 gꞏL^{-1} iron powder, 3 mmolꞏL^{-1} H_2O_2, 2 mm cross section diameter of iron wire and 3 mmolꞏL^{-1} isopropanol (IPO) were selected in the experiment. It can be seen from Figure 1 that neither zero valent iron powder nor H_2O_2 can effectively degrade Orange II, but when zero valent iron powder and H_2O_2 coexist, Orange II can be rapidly degraded, and the degradation rate reaches about 80% within 10 minutes. This proofs that the reduction of Fe⁰ or the oxidation of H_2O_2 can not rapidly destroy the molecular structure of Orange II, but when zero valent iron powder and H_2O_2 coexist, it can degrade Orange II significantly. In the acid solution because zero valent iron was corroded to produce Fe^{2⁺} which could catalyze the decomposition of H_2O_2 to produce hydroxyl radicals (ꞏOH). And then ꞏOH could quickly oxidize the molecular structure of Orange II[11,12]. In addition, when isopropanol, the scavenger of hydroxyl radicals, was added to the Fe⁰/H_2O_2 system, the degradation rate of Orange II was significantly decreased, which proved that ꞏOH played a key role in the degradation of Orange II[13]. We can also see from the Figure 1 that when iron wire and H_2O_2 coexist, Orange II can not be effectively degraded. Although iron wire can also be used as the source of Fe⁰, the specific surface area of iron wire is far less than iron powder, and the corrosion rate in the reaction solution is slower than iron powder, which can not provide enough Fe^{2⁺} for the decomposition of H_2O_2, resulting in the oxidation capacity of iron wire/H_2O_2 system is less than iron powder/H_2O_2 system under the same conditions. Therefore, the iron powder/H_2O_2 system is suitable for the
degradation of Orange II.

3.2. Effect of the concentration of Orange II
Orange II was oxidized and degraded by the Fe⁰/H₂O₂ system. Using the experimental method, under the conditions of zero valent iron powder 0.3 g·L⁻¹, pH value 4.0 and H₂O₂ 3 mmol·L⁻¹, the Orange II solution with the concentration of 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 g·L⁻¹ was added respectively, and the degradation reaction was carried out under magnetic stirring. The experimental results are shown in Figure 2. We can also see from the Figure 2 that with the increase of concentration of Orange II in 10 minutes, the degradation rate gradually decreases to a stable level. The degradation rate of 0.1 g·L⁻¹ Orange II solution reached 78% in 10 minutes. In 60 minutes, the degradation rate of 0.2 g·L⁻¹ Orange II solution gradually increased with the extension of reaction time. The degradation rate of 0.4, 0.6, 0.8, 1.0 g·L⁻¹ Orange II solution tended to be stable after 10 minutes.

Generally, the reaction of oxidation and reduction of organic pollutants based on zero valent iron conforms to the pseudo-first-order kinetics, so this experiment adopted the pseudo-first-order kinetics equation to describe the oxidative degradation of Orange II by the Fe⁰/H₂O₂ system[5,14]. The reaction kinetic rate constant (K) at different Orange II initial concentrations is given in Table 1. By analyzing the data in Table 1, we can see that the reaction kinetic rate constant (K) decreases with the increase of the concentration of Orange II. When the concentration of Orange II increases from 0.1 g·L⁻¹ to 0.2 g·L⁻¹, the reaction rate constant (K) decreases to about one third of the original value. This showed that when the concentration of Orange II was too high, there would be a certain competition between the degradation intermediates and excessive Orange II for the limited ·OH, which was not conducive to the further degradation of Orange II intermediates[12].

3.3. Effect of the concentration of H₂O₂
Using experimental method, when the iron power dosage was 0.3 g·L⁻¹, pH=4.0 and the initial concentration of Orange II solution was 0.2 g·L⁻¹, 3, 4, 5, 6 and 7 mmol·L⁻¹ H₂O₂ were added respectively, and the degradation reaction was carried out under the magnetic stirring. The experimental results are shown in Figure 3. According to the analysis in Figure 3, when the initial concentration of H₂O₂ increases from 3 to 7 mmol·L⁻¹ in 60 minutes, the degradation rate of Orange II increases gradually; when the dosage of H₂O₂ is greater than 6 mmol·L⁻¹, the degradation rate of Orange II does not change much. In Table 2, the reaction kinetic rate constant (K) at different H₂O₂ initial concentrations is given. By analyzing the data in Table 2, we can see that the reaction rate constant (K) gradually increases with the increase of dosage of H₂O₂, but the reaction rate constant (K) tends to be gentle when the concentration of hydrogen peroxide is more than 6 mmol·L⁻¹. In the Fe⁰/H₂O₂ system, it is ·OH that can oxidize and degrade the Orange II, and ·OH is produced from the disintegration of H₂O₂. Therefore, increasing the concentration of H₂O₂ in a certain extent is conducive to the production of ·OH, thus providing ·OH needed for the oxidative degradation of Orange II[12,15].
Table 1. The kinetic rate constant (K) at the different concentration of Orange II.

| C₀ (g·L⁻¹) | 0.1 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|------------|-----|-----|-----|-----|-----|-----|
| K (×10⁻³ min⁻¹) | 54.56 | 18.65 | 8.040 | 5.430 | 4.560 | 4.400 |
| R          | 0.9547 | 0.9740 | 0.9620 | 0.9629 | 0.9781 | 0.9554 |

Table 2. The kinetic rate constant (K) at the different dosage of H₂O₂.

| H₂O₂ (mmol·L⁻¹) | 3 | 4 | 5 | 6 | 7 |
|-----------------|---|---|---|---|---|
| K (×10⁻³ min⁻¹) | 18.65 | 22.91 | 29.89 | 45.67 | 48.24 |
| R               | 0.9740 | 0.9588 | 0.9633 | 0.9749 | 0.9427 |

Table 3. The kinetic rate constant (K) at the different dosage of Fe⁰.

| Fe⁰ (g·L⁻¹) | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 |
|-------------|-----|-----|-----|-----|-----|
| K (×10⁻³ min⁻¹) | 24.31 | 45.67 | 55.10 | 71.65 | 76.54 |
| R            | 0.9589 | 0.9749 | 0.9653 | 0.9553 | 0.9527 |

Table 4. The kinetic rate constant (K) at different initial pH value.

| pH  | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
|-----|-----|-----|-----|-----|-----|
| K (×10⁻³ min⁻¹) | 65.42 | 55.23 | 45.67 | 4.170 | 2.810 |
| R   | 0.9624 | 0.9533 | 0.9749 | 0.9815 | 0.9873 |
3.4. Effect of the dosage of $Fe^0$

Using the experimental method, when the initial concentration of Orange II solution was 0.2 g·L$^{-1}$, the pH value was 4.0 and the H$_2$O$_2$ concentration was 6 mmol·L$^{-1}$, 0.2, 0.3, 0.4, 0.5 and 0.6 g·L$^{-1}$ zero valent iron powder were added respectively, and the degradation reaction was carried out under the magnetic stirring. The experimental results are shown in Figure 4. According to the analysis in Figure 4, the degradation rate of Orange II enlarges gradually with the increase of Fe$^0$ dosage in 10 minutes. When the dosage of Fe$^0$ is greater than 0.3 g·L$^{-1}$, the degradation rate of Orange II is over 92% at 60 minutes, and there is little difference between them. In Table 3, the reaction kinetic rate constant (K) at different iron powder initial concentrations is given. By analyzing the data in Table 3, we can see that the reaction rate constant (K) enlarges gradually with the increase of the dosage of Fe$^0$, but when the Fe$^0$ dosage is greater than 0.5 g·L$^{-1}$, the increase of reaction rate constant (K) slows down. Therefore, the dosage of iron powder should be properly controlled in the degradation of Orange II. It is not only necessary to guarantee a high degradation rate of Orange II within a certain reaction time, but also to facilitate recycling of iron powder, so as to achieve the purpose of cost saving.

3.5. Effect of the solution pH value

On the basis of the experimental method, when the H$_2$O$_2$ concentration was 6 mmol·L$^{-1}$, iron powder dose was 0.3 g·L$^{-1}$ and the initial concentration of Orange II was 0.2 g·L$^{-1}$, 2.0, 3.0, 4.0, 5.0 and 6.0 initial solution pH value were added respectively, and the degradation reaction was carried out under the magnetic stirring. The experimental results are shown in Figure 5. According to the analysis in Figure 5, the degradation rate of Orange II is below 20% in 60 minutes, and the degradation effect is not good under pH 5.0 and pH 6.0. Under the condition of pH 2.0 and 3.0, the degradation rate of Orange II is more than 80% and faster in 10 minutes. when the initial solution pH value is 4.0, the degradation rate of Orange II shows a certain tendency within 60 minutes, and the overall degradation effect can reach more than 90%. In Table 4, the reaction kinetic rate constant (K) at different initial solution pH value is given. We can see that the rate constant (K) is larger, and vice versa when the pH value is lower than 4.0 by analyzing the data in Table 4. When the solution pH value reduces, it is beneficial to the corrosion of iron powder, and the production of Fe$^{2+}$ is accelerated, so it is beneficial to the decomposition of H$_2$O$_2$ and the production of ‘OH. When the solution pH value increases, the corrosion of zero valent iron powder is inhibited, thereby reducing the presence of Fe$^{2+}$ in the system, resulting in hindered the decomposition of H$_2$O$_2$, the amount of ‘OH is decreased, and the degradation rate of organic pollutants is reduced[16,17].

3.6. Analysis of pH value and iron ion concentration

The concentration of pH value and iron ion in the reaction solution were determined in the
experimental group with the concentration of Orange II of 0.2 g·L⁻¹, pH=4.0, hydrogen peroxide of 6 mmol·L⁻¹ and zero valent iron of 0.3 g·L⁻¹. The results are shown in Figure 6. According to the analysis in Figure 6, both the concentrations of total iron and Fe²⁺ decrease with the increase of reaction time in 10-60 minutes. The concentrations of total iron ion and Fe²⁺ are 110.1 and 94.3 mg·L⁻¹ at 10 minutes, respectively, and decrease to 38.1 and 27.4 mg·L⁻¹ at 60 minutes, respectively, with a reduction of 65% and 71% respectively. The change trend of iron ion concentration in the reaction solution is similar to that of pH value, which increases first and then decreases gradually. Both the concentrations of total iron ion and Fe²⁺ decrease with the extension of reaction time, which indicate that zero valent iron plays an indirect catalytic role in oxidative degradation. The zero valent iron can be converted into Fe²⁺ in the reaction. The Fe²⁺ can catalyze disintegration of H₂O₂ to produce hydroxyl radicals (·OH) that can oxidize Orange II. The corrosion of iron powder consumes H⁺ in the system, resulting in the increase of pH value of the solution. However, with the progress of degradation reaction, there may be carboxylic acid formation in the degradation process of Orange II, which makes the solution pH value decrease[18].

3.7. Determination of UV spectroscopy and LC-MS

The reaction solution in each time period was scanned by the UV-Vis absorption spectrum and determined by LC-MS after 60 minutes reaction in the experimental group with the concentration of Orange II of 0.2 g·L⁻¹, pH=4.0, hydrogen peroxide of 6 mmol·L⁻¹ and zero valent iron of 0.3 g·L⁻¹. The UV-Vis absorption spectrum of degradation Orange II changes with time is shown in Figure 7. As a result of the n-π* electron transition of azo structure of Orange II, the main UV absorption wavelength of Orange II appears near 484 nm[14]. According to the analysis in Figure 7, the absorption intensity at 484 nm decreases with the extension of reaction time, and both the absorbance at 228 nm and 308 nm also decrease, which indicates that Orange II is degraded gradually. Therefore, the Fe⁰/H₂O₂ system can oxidize and break the azo structure of Orange II, and gradually reduce the absorbance of its main absorption wavelength (484 nm), which shows that the Fe⁰/H₂O₂ system can achieve the purpose of oxidative degradation of Orange II[19].

According to the test method, the reaction solution after 60 minutes was analyzed by LC-MS. It was found that the intermediate products were benzenesulfonate (C₆H₅O₃S⁻, m/z=157) and phthalate (C₈H₄O₄²⁻, m/z=164), which was consistent with the reported intermediates[20, 21, 22]. It shows that the electron transition of azo double bond occurs in the catalytic process, which can activate the local structure of dye molecules and make the carbon atoms connected with azo double bond unstable. At the same time, the C-N bond is first broken because the highly active hydroxyl radicals attack these unstable carbon atoms[23]. In conclusion, We can speculate that in the reaction of oxidative degradation, Orange II is first dissociated into 4-(2-hydroxy-1-naphthylazo) benzenesulfonate (C₁₆H₁₁N₂O₄S⁻), and then its azo structure is oxidized and destroyed by ·OH. Secondly, the reaction
solution fades to produce intermediates such as benzenesulfonate (C₆H₅O₃S⁻) and 1, 2-naphthoquinone (C₁₀H₆O₂), and then 1, 2-naphthoquinone is further oxidized by ·OH to phthalate (C₈H₄O₄²⁻). Finally, phthalate and benzenesulfonate can be further mineralized into CO₂, H₂O and SO₄²⁻. The approximate degradation pathway is shown in Figure 8.

4. Conclusions
Under the premise of keeping other reaction conditions unchanged, the degradation rate of Orange II gradually decreased to a steady level with the increase of Orange II initial concentration. At a certain H₂O₂ concentration, the total amount of ·OH provided by the Fe⁰/H₂O₂ system was limited, so only a certain amount of Orange II could be degraded. If the concentration of H₂O₂ was too low, it was not enough to provide enough ·OH for the oxidation of Orange II, but if it was too high, the degradation rate would be limited by the Orange II initial concentration, resulting in the waste of H₂O₂. The degradation rate of Orange II was first decreased with the increase of the dosage of iron powder, and then tended to be gentle. Therefore, the excessive addition of iron powder was not conducive to the degradation reaction. However, the solution pH value was more important for the corrosion of iron powder, and the proper pH value was conducive to the degradation reaction.

Under acid condition, zero valent iron can be corroded to produce Fe²⁺, and Fe²⁺ can catalyze the disintegration of H₂O₂ to produce ·OH with high oxidation activity. These new ·OH can oxidize the azo structure of Orange II, destroy its chromogenic group, and transform Orange II into benzenesulfonate, 1, 2-naphthoquinone. And then these intermediates can be further oxidized by ·OH to open the ring, mineralized into CO₂, H₂O, and SO₄²⁻. The whole degradation process is rapid and mild, so the Fe⁰/H₂O₂ system can provide an effective new method for the degradation of azo dyes.

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