

Analysis of a complex produced in the Fenton oxidation process

Chang Wang, Siyue Zhang, Sakai Yuji and Zongpeng Zhang

ABSTRACT

The absorbances of different concentrations of Fe^{2+} , Fe^{3+} and H_2O_2 were investigated by UV-visible spectrophotometry without separating the substances. The law of complex formation was studied by considering changes in the UV-vis spectra of mixtures of these three substances. The results show that upon eliminating the influence of the substrate, an iron-based complex was present in the Fenton reaction, which exhibited substantial absorbance from 190 to 500 nm. Therefore, the presence of an unknown complex in the Fenton oxidation process was verified and its concentration varied with a change in the concentration of hydrogen peroxide. This study provides a strong foundation for further studies into the mechanism of traditional hydroxyl radical theory of the Fenton reaction.

Key words | Fenton, intermediate complex, reaction mechanism

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INTRODUCTION

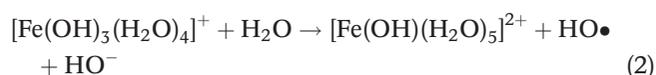
For the treatment of refractory organic wastewater, the Fenton oxidation is a well-studied and widely applied technology, which has the advantages of short reaction time, easy operation and automatic flocculant generation. Fenton oxidation has been used to treat many types of wastewater including dye wastewater (Gu *et al.* 2011), paper production wastewater (Rodríguez *et al.* 1999; Lucas *et al.* 2012), oily wastewater and sludge (Zhang *et al.* 2013), coking wastewater and pharmaceutical wastewater (Badawy *et al.* 2009), and good results have been achieved. The Fenton method has drawn increasing attention in the environmental field because of its high mineralization rate and fast reaction rate. However, as a theoretical guide to the practical application of Fenton oxidation technology its mechanism is still controversial, which restricts the wider use of Fenton oxidation in industrial applications.

The Fenton reagent is a combination of ferrous ions and hydrogen peroxide and it was introduced by Fenton (1894). Haber & Weiss (1934) proposed a hydroxyl radical mechanism for the Fenton oxidation. This theory proposes that hydroxyl radicals are the main intermediate products in the Fenton reaction and it has been developed by many scholars (Kang *et al.* 2002; Tang *et al.* 2011; Cui *et al.* 2012) for the treatment of various organic pollutants. Specifically, ferrous ions in the Fenton reaction act as catalysts and

generate hydroxyl radicals ($\text{HO}\cdot$) with a high oxidation potential ($E^0 = 2.8 \text{ V}$), and they tend to attack high electron density locations while the ferrous ions are oxidized to iron ions.

However, thermodynamic calculations have shown that an outer-sphere electron transfer reaction between Fe^{2+} and H_2O_2 cannot take place because the formation of intermediate H_2O_2^- is not favored (Goldstein *et al.* 1993). However, the formation of a hydrated iron (II)- H_2O_2 complex is thermodynamically favored. Therefore, the classic Fenton oxidation mechanism wherein hydroxyl radicals are the main intermediate has been questioned. Bossmann *et al.* (1998) found 2,4-dimethylphenol during the degradation of 2,4-dimethylaniline by a photo-Fenton oxidation and this cannot be explained by a hydroxyl radical chain reaction. They regarded this intermediate product as a result of electron transfer and a high-valent iron ion oxidation mechanism was thus proposed. Lei & He (2003) obtained evidence contradictory to the classic hydroxyl radical chain mechanism wherein small-molecule organic acids were not found upon the degradation of polyvinyl alcohol (PVA) by photo-Fenton oxidation. The high-valent iron ion oxidation mechanism proposes that the reactive intermediate is an iron (IV) complex or chelate for the oxidation of organic pollutants by the Fenton reagent in which the

strong oxidizing high-valent iron ion oxidizes organic pollutants by accepting electrons. Specifically, an inner-sphere two-electron transfer reaction slowly takes place within $[\text{Fe}(\text{OH})(\text{H}_2\text{O}_2)(\text{H}_2\text{O})_4]^+$ and the intermediate iron (IV) complex, $\text{Fe}_{\text{aq}}^{4+}$ ($[\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_4]^+$), is formed; see Equation (1). This intermediate iron (IV) complex may react further, leading to the formation of a free hydroxyl radical and $\text{Fe}_{\text{aq}}^{3+}$ ($[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$), as shown in Equation (2):



Currently, much research has been carried out to clarify the mechanism by considering pollutant degradation upon Fenton oxidation. However, the study of a specific pollutant cannot be used to explain the behavior of a wide range of pollutants. Although *Lei's* (2003) measurements were carried out on complex intermediates of degradation for different pollutants, their degradation mechanism focused on one substrate rather than being a universal mechanism and their photon yield rate discussion was only related to the photo-Fenton system. To investigate the formation of an unknown complex in the Fenton reaction, this study was based on an analysis of UV-vis spectra without substrate degradation or UV irradiation.

EXPERIMENTAL

Chemicals

Dilute sulfuric acid was purchased from the Tianjin Yingdaxigui Chemical Reagent Co. $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3$ and H_2O_2 (30% w/w) were supplied by the Tianjin Jiangtian Chemical Reagent Co. All the reagents were of analytical purity and the water used was double distilled.

Measurements

UV-vis spectra were recorded using a Lab Tech UV-1000 UV-vis spectrophotometer (LabTech, USA). A J500 precision electronic balance (OHAUS, USA), a pH3210 SET2 precision acidimeter (WTW, Germany) and an 85-2 magnetic mixer (Shanghai Sile Instruments, China) were also used.

Methods

250 mL of deionized water (250 mL) was poured into a beaker, which was placed on a magnetic mixer at room temperature; dilute sulfuric acid was used to adjust the pH to 3. A specific amount of fresh 0.06579 mol/L FeSO_4 was then added and the mixture was stirred. A specific amount of H_2O_2 (30% w/w) was then added to start the reaction. After reacting for a certain time (normally 2 min but further mixing of 1 hour was required for the tests in *Figure 3*, *Figure 4* and *Figure 5*) a sample was taken and its UV-visible spectrum was obtained from 190–500 nm.

RESULTS AND DISCUSSION

Comparison of UV-vis spectra before and after mixing FeSO_4 with different concentrations of H_2O_2

In the figures below the abscissa is the wavelength of light and the ordinate is the absorbance. UV-vis spectra of 0.144 mmol/L FeSO_4 and different concentrations of H_2O_2 (0.392 mmol/L–3.918 mmol/L) were investigated separately and are shown in *Figure 1*. From this figure, H_2O_2 absorbs in the ultraviolet region (<300 nm) and does not absorb from 300–500 nm. FeSO_4 shows little absorption throughout the whole range (190–500 nm).

Next, 0.144 mmol/L FeSO_4 was added to the various concentrations of H_2O_2 mentioned above. The UV-vis spectra of the mixtures and the 0.144 mmol/L $\text{Fe}_2(\text{SO}_4)_3$ solution are shown in *Figure 2*. This figure shows that the baseline in the UV-vis spectra of the FeSO_4 and H_2O_2 mixtures increases significantly with an increase in H_2O_2 content. Additionally, the absorption of the mixture increases with an increase in hydrogen peroxide concentration. If these Fenton reactions follow the classic hydroxyl radical mechanism, shown in Equation (3), the strongly oxidizing excess H_2O_2 would instantly oxidize all Fe^{2+} (0.144 mmol/L) to Fe^{3+} , and thus the absorption curve of the mixture should coincide with the Fe^{3+} spectrum from 300–500 nm where the absorption of Fe^{2+} and H_2O_2 are approximately zero. However, the absorption curves of the mixtures are significantly higher than that of Fe^{3+} from 300–400 nm, which indicates the presence of another substance in the mixed system in addition to Fe^{3+} . The spectrum of this substance is different from that of Fe^{2+} , Fe^{3+} or H_2O_2 within the range of

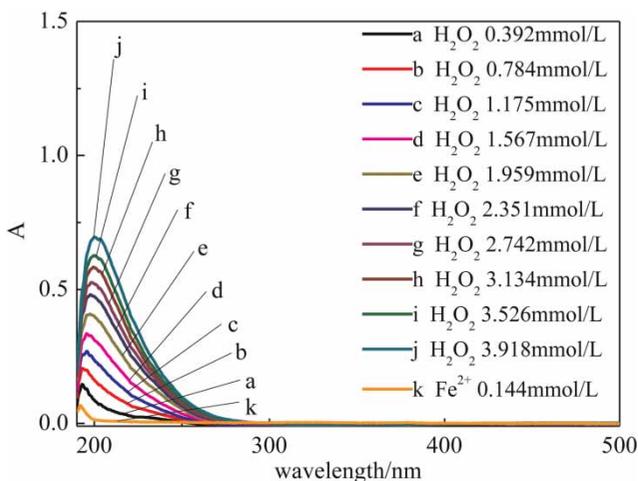


Figure 1 | UV-vis spectra of the FeSO_4 solution and H_2O_2 solutions of different concentrations.

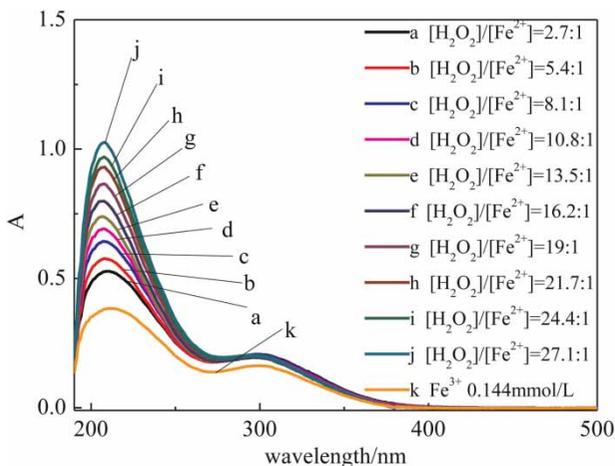


Figure 2 | UV-vis spectra of FeSO_4 and H_2O_2 solution mixtures at different concentrations.

300–400 nm, indicating that it is an unknown compound with significant absorbance:



Comparison of UV-vis spectra before and after mixing $\text{Fe}_2(\text{SO}_4)_3$ and different concentrations of H_2O_2

According to the classic Fenton mechanism, H_2O_2 oxidizes Fe^{2+} to Fe^{3+} because of its strong oxidation property and hydroxyl radicals are produced. Fe^{2+} and H_2O_2 do not absorb from 300–500 nm while Fe^{3+} has a considerable absorption band in the same range. Interestingly, an even stronger absorption emerges in this range after mixing

Fe^{2+} and H_2O_2 . To investigate whether a new compound is formed by Fe^{3+} and H_2O_2 in this wavelength range, several experiments were carried out and the results are shown in Figures 3 and 4. Both figures show the spectra of separate solutions of $\text{Fe}_2(\text{SO}_4)_3$ and H_2O_2 and their mixtures, as well as a comparison of the spectra of the mixtures after reacting for different times.

Of the five lines in Figure 3, line b is the UV-vis spectrum of 0.144 mmol/L Fe^{3+} , which has the same as the Fe^{2+} in Figure 1. Line a is the spectrum of 0.392 mmol/L H_2O_2 , which is the minimum concentration of H_2O_2 shown in Figure 1. Line c is the spectrum of a mixture of H_2O_2 and Fe^{3+} at a ratio of 2.7:1, and line d is the spectrum of the same solution after mixing for one hour. Line e is the sum of line a and line b.

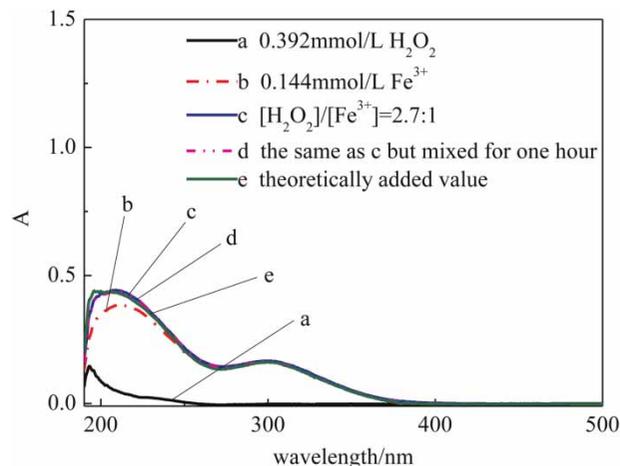


Figure 3 | Comparison of the UV-vis spectra of single and mixed systems of $\text{Fe}_2(\text{SO}_4)_3$ and H_2O_2 at $[\text{H}_2\text{O}_2]/[\text{Fe}^{3+}] = 2.7:1$.

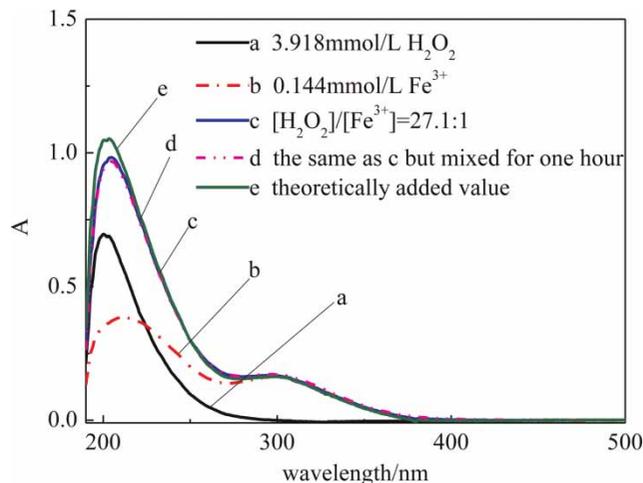


Figure 4 | Comparison of UV-vis spectra of single and mixed systems of $\text{Fe}_2(\text{SO}_4)_3$ and H_2O_2 at $[\text{H}_2\text{O}_2]/[\text{Fe}^{3+}] = 27.1:1$.

As shown in Figure 3, the spectrum of the H_2O_2 and Fe^{3+} mixed solution (line c) almost coincides with the superposition of the separate spectra of H_2O_2 and Fe^{3+} , which was generated under the same conditions (line e). This indicates that the addition of H_2O_2 has no impact on the Fe^{3+} solution since Fe^{3+} is in the highest possible oxidation state under these conditions, which means it is relatively stable and will be difficult to oxidize further. From the spectrum of the solution that was mixed for 1 hour (line d), the extended reaction time did not result in any changes, indicating that H_2O_2 and Fe^{3+} are relatively independent and the absorption of the mixture from 300–500 nm was only from the Fe^{3+} solution. Therefore, this mixture does not form a new complex.

To further investigate the influence of H_2O_2 concentration on Fe^{3+} , the H_2O_2 concentration in Figure 4 was increased from 0.392 mmol/L in Figure 3 to the maximum concentration in Figure 1 (3.918 mmol/L). Interestingly, the theoretical superposition of the separate spectra of H_2O_2 and Fe^{3+} is slightly higher than the actual absorption curve of the mixture, which probably results from the application scope of the UV-vis spectrophotometer being 0.2–0.8 absorbance. Once the curve exceeds this range the line will be compressed so that the theoretical values are slightly higher than the measured values. However, when the absorption decreases to within the application scope beyond 250 nm, the theoretical values (line e) and the measured values (line c) are similar. This indicates that even though the H_2O_2 concentration is higher, as shown in Figure 4, H_2O_2 does not react with Fe^{3+} , proving that H_2O_2 and Fe^{3+} are relatively stable in the system and no chemical reaction takes place to form new compounds.

From the absorption intensity between 300–500 nm in Figure 2 and in addition to Fe^{3+} , a new compound is present in the H_2O_2 and Fe^{2+} mixed system, and it is closely linked to the complex mechanism of the Fenton reaction proposed by Bossmann *et al.* (1998).

Comparison of UV-vis spectra before and after equimolar mixing of Fe^{2+} and Fe^{3+}

In the initial Fenton reaction solution, Fe^{2+} is oxidized to Fe^{3+} by H_2O_2 and hydroxyl radicals are generated. There is a dynamic equilibrium between Fe^{2+} and Fe^{3+} in this system. To investigate the interaction between Fe^{2+} and Fe^{3+} , 0.144 mmol/L Fe^{2+} and Fe^{3+} were mixed in equimolar amounts. Spectra of the solutions before and after mixing and solution mixing for 1 hour are all shown in Figure 5. As shown in Figure 5, the spectrum of the admixture is

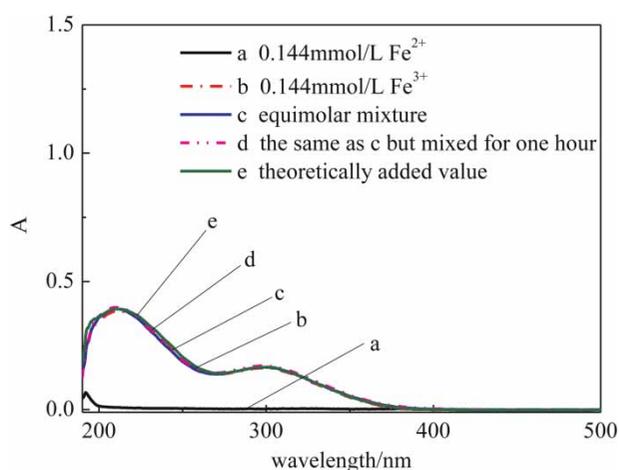


Figure 5 | Comparison of the UV-vis spectra of the single and mixed $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 solutions.

similar to the theoretical spectrum and the spectrum does not change upon extending the reaction time, which means that Fe^{2+} and Fe^{3+} do not combine with each other to form a new substance. Therefore, the conversion of iron to different valences in the Fenton system is achieved by the strong oxidant H_2O_2 .

We thus conclude that a new substance was formed in the Fenton system in addition to Fe^{3+} , which is assumed to be an iron complex. This study shows that this complex is not generated by Fe^{3+} and H_2O_2 because Fe^{2+} and Fe^{3+} are independent, which indicates that this complex can only be obtained when using Fenton reagents. To determine the composition of the new complex is an important task in complex mechanism theory, and it plays a significant role in the further development of Fenton theory and the study of the elementary reaction initiated by hydroxyl radicals, which is a future study topic.

CONCLUSIONS

We compared the spectra of separate solutions of FeSO_4 and H_2O_2 and their mixtures and show that a new substance, presumably an iron complex, is formed in the Fenton system in the absence of Fe^{3+} , and it is simply generated by the Fenton reagents. The absorbance of the iron complex is very high from 300–400 nm, and it increases with an increase in the H_2O_2 concentration. The absorption of an admixture of Fe^{3+} and H_2O_2 is similar to their theoretical absorption, demonstrating that these two substances are stable and independent. For an equimolar mixture of

Fe^{2+} and Fe^{3+} , the two substances are independent with no formation of new substances occurring. Moreover, the unknown iron complex may contribute to the generation of $\cdot\text{OH}$, which is highly oxidative.

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