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Optimization and Interpretation of Fenton and UV/Fenton Processes for Degradation of Syringyl Lignin

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Abstract

The performances of syringyl lignin degradation by using Fenton and UV/Fenton processes were investigated in a self-designed cylindrical reactor. Many factors including pH, dosage of H_2O_2, concentration of Fe^{2+} initial concentration of syringyl lignin, reaction time and UV irradiation were optimized to reach the removal efficiency of syringyl lignin up to 87.5%. Specifically the optimum reactor time was 60 min, dosage of H_2O_2 was two times of its theoretical quantity and molar ratio of $[Fe^{2+}]/[H_2O_2]$ was 1:50 at pH 3. Furthermore, introducing UV-light into the Fenton system significantly improved the decomposition of syringyl lignin with the removal efficiency of 100% in first 30 min. In addition, the degradation mechanism of syringyl lignin by Fenton process was discussed in detail by using UV-visible spectroscopy and TOC analysis. It was found that syringyl lignin was oxidized by electron transfer of complex intermediates which contained high valence iron in homogeneous Fenton system.

Keywords: Fenton process; Homogeneous system; Syringyl lignin mechanism; Paper making wastewater

Introduction

In China, paper industry is not only one of the most important industries for national economy increasing, but also a major consumer of water resource, which produces environmental pollutants with various organic pollutants discharged in wastewater. The Chemical Oxygen Demand (COD) emission in China is reported to arrive at 719 thousand tons in 2010 which accounts for 20.3% of the national industrial emissions. The pollutant of paper-mill wastewater accounts for 90% of the total pollutants, causing a serious threat to people's health and ecological security [1].

Among the complex compositions of discharged wastewater from papermaking industries, lignin is the most difficult compound to be biodegraded due to its structure with phenyl propane [2,3]. The present treatment technique for papermaking wastewater is still limited owing to complex production processes, high operation cost, and high concentration of toxic substances. Nowadays, physicochemical methods are widely used for the treatment of papermaking wastewater. For example, Fenton oxidation process as an advanced oxidation technology has its superiorities in dealing with non-biodegradable organic matters, due to advantages of simple operation, accessible reagents, low treating cost, free of complicated equipment and low toxicity to the subsequent biochemical treatment. Fenton reaction mechanism and reaction rates were well concluded by Sychev et al. [4]. As a result, Fenton oxidation has been successfully used in a variety of industrial wastewater treatments [5-7]. Meanwhile, UV is introduced into Fenton system to improve performance of advanced oxidation process, since H_2O_2 can be efficiently decomposed into -OH under the irradiation of UV to enhance oxidation of Fenton reagent. The UV/Fenton process was reported to be more efficient than Fenton process but caused a comparatively high cost [8].

Additionally, Fe^{3+} generated from the reaction can form complex ion $Fe(OH)^{2+}$ with OH at low pH. These complex ions are transformed into Fe^{2+} producing -OH under UV, which not only improves Fe^{2+} concentration to enhance the catalytic performance of Fenton system, but also increases the amount of -OH.

Based on preliminary experimental study for the degradation of guaiacol [9], syringyl lignin from paper making wastewater was selected as a target compound in this study, which is a significant generated substance in the papermaking process. So far, study on degradation of syringyl lignin by Fenton process is still quite limit with few results and discussion. The homogeneous Fenton oxidation process was innovatively carried out in a self-designed cylindrical reactor, by using UV-Vis spectrophotometer to quantify syringyl lignin and discover potential complex intermediates. A number of potential factors that may impact the removal efficiency of syringyl lignin were investigated and optimized, including initial pH value, dosage of H_2O_2, concentration of Fe^{2+}, initial concentration of syringyl lignin, reaction time and UV irradiation. Furthermore, the mechanism of syringyl lignin degradation by Fenton and UV/Fenton reaction has been initially explored by analyzing the change of UV-visible spectral of syringyl lignin during the degradation and comparing removal efficiency and mineralization efficiency of syringyl lignin.

Methods and Materials

Reactor set-up

The degradation of syringyl lignin by Fenton and UV/Fenton processes was carried out in a double glass heat-resistant reactor (Figure 1).

The outer layer was the circulated cooling water (diameter 10 cm, temperature 20°C), and the inner was the reaction zone (height 15 cm, inner diameter 8 cm and total volume 750 cm³). A high pressure

mercury lamp (TianJing ZiJing Special Light Source ZSZ, China) was introduced into UV/Fenton system to provide UV light. The nominal power of ultraviolet lamp was 11 w. Solution was mixed by a thermostatic magnetic mixer (Shanghai Sile Instrument 85-2, China).
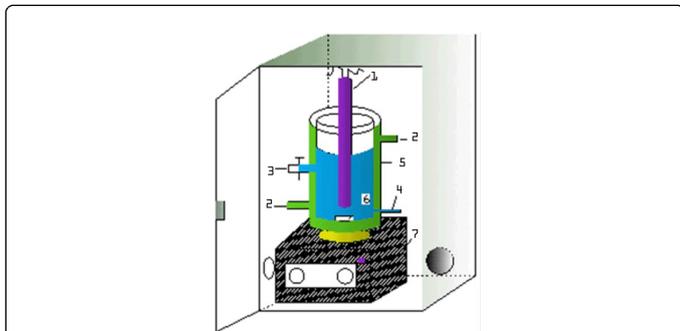
Figure 1: Diagram of Photocatalytic reactor 1. Ultraviolet lamp; 2. Circulating cooling water; 3. Sampling place; 4. Aeration place; 5. Reactor zone; 6. Magnetic stirrer; 7. Magnetic mixer.

The formula of syringyl lignin (SL) is $OHC_6H_3 (OCH_3)_2$ and its main structure contains a phenyl alkoxy, a phenolic hydroxyl group and a methoxy group with the maximum absorption wavelength λ_{max}=267 nm, whose molecular structure is shown in Figure 2.
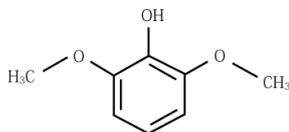
Figure 2: Molecular formula of syringyl lignin

Treatment design

Syringyl lignin (analytical purity, Nanjing Odyssey Chemical Industry Co., Ltd) was dissolved in 500 mL deionized water in the photocatalytic reactor that was place on the thermostatic magnetic mixer. Sulfuric acid (analytical purity, Tianjin Yingdaxigui Chemical Reagent) or NaOH (analytical purity, Tianjin Kaitong Chemical Reagent Co., Ltd.) was used to adjust pH to be 2.0, 3.0, 4.0, 5.0, 6.0, 9.0 and 10.0, respectively. In this test, other factors were controlled to be [SL]=50 mg/L, $[H_2O_2]$=2.0Q_{th} and $[Fe^{2+}]$/ $[H_2O_2]$=1:50.

Then 10 mg/L $FeSO_4$ (analytical purity, Tianjin Beifang Chemical Reagent) was added and stirred uniformly in solution. The molar ratio of $[Fe^{2+}]$/$[H_2O_2]$ was changed to 1 : 100, 1 : 80, 1: 50, 1 : 25 and 1 : 20, respectively in conditions of [SL]=50 mg/L, $[H_2O_2]$=2.0Q_{th}, pH=3 and reaction time for Fenton and UV/Fenton=60 min and 30 min, respectively.

Theoretical H_2O_2 amount (Q_{th}) is the required amount of H_2O_2 to completely oxidize the organic pollutant into CO_2 and H_2O. Taking syringyl lignin solution as an example, according to Eq. (1), 198.7 mg/L H_2O_2 was needed to completely mineralize syringyl lignin to CO_2 and H_2O. Considering the density of H_2O_2 (30% w/w) of 1.110 g/mL, theoretical H_2O_2 amount was 0.6 mL/L.

$$C8H10O3+18H2O2 \rightarrow 8CO_2+23H_2O \quad (1)$$

Dosage of H_2O_2 in the study was based on this theoretical amount and different amounts of H_2O_2 (30% w/w) (analytical purity, Tianjin Beifang Chemical Reagent) were added into Fenton and UV/Fenton systems: 0.25Q_{th}, 0.5Q_{th}, 1.0Qth, 2.0Q_{th} and 3.0Q_{th} in conditions of [SL]=50 mg/L, $[Fe2+]$/ $[H2O2]$=1:50, pH=3 and reaction time for Fenton and UV/Fenton=60 min and 30 min, respectively.

For sample analysis, 5 mL solution was taken separately at reaction time of 5, 10, 20, 30, 60 and 90 min in conditions of [SL]=50 mg/L, $[H_2O_2]$=2.0Q_{th}, $[Fe^{2+}]$/$[H_2O_2]$=1:50 and pH=3, and then mixed with Na_2SO_3 to terminate the reaction.

Physicochemical analysis

UV/Vis spectra were recorded by using an UV-Vis spectrophotometer (LabTech UV-1000, USA) pH was measured by an acidimeter (Tianjin Shengbang Technology pHS-3C, China). Total organic carbon (TOC) was measured by a TOC analyzer (OI Analytical 1010, USA). TOC values were mainly represented by non-purgeable organic carbon (NPOC).

Absorbance value of solution was measured at a wavelength of 267 nm. The removal efficiency of syringyl lignin could be calculated according to Eq. (2)

Removal efficiency=(C0-C)/C0 x 100% (2)

Where C0 was the mass concentration of syringyl lignin solution before the reaction, mg/L; C was the mass concentration of syringyl lignin solution after the reaction, mg/L.

The intermediates during degradation process were difficult to be monitored by gas chromatography or liquid chromatography, because they may instantly disappear or their concentrations are too low to be detected in the organic phase after the samples were extracted with organic solvent. So, UV-visible spectrophotometer and TOC analyzer were used to investigate the degradation process in this study. The samples were scanned by UV-visible spectrophotometer at the wavelength ranging from 200 to 600 nm.

Results and Discussion

Initial pH

The effect of different initial pH on removal efficiency of syringyl lignin is shown in Figure 3, Which indicates that the removal efficiency of syringyl lignin was significantly high at pH 3.0-4.0 with the maximum value of 87.5% at pH=3.0. However, the removal efficiency of syringyl lignin was 43.2% and almost zeros at pH 6.0 and 2.0, respectively. This phenomenon could be explained by two reasons, Fe^{2+} starts to precipitate under alkaline condition with the increase of pH, and thus it can significantly reduce catalytic decomposition of H_2O_2. Besides, H_2O_2 is not stable in alkaline solution and is decomposed into O_2 and H_2O and thus lose oxidative capacity [10]. Regarding with extreme low pH, it enhances the stability of H_2O_2 and slows decomposition of H_2O_2 to produce -OH, resulting in the decrease of removal efficiency of syringyl lignin. In addition, the high concentration of H^+ inhibits the reduction of Fe^{3+} to Fe^2. Therefore, H_2O_2 and Fe^{2+} are difficult to form an effective redox system under a high or extreme low pH condition. In this study, optimized pH value for Fenton process was assumed to be 3.0. Similarly, Jung et al. [11] found that pH buffered to acidic condition maintained relatively high levels of dissolved iron in the aqueous solution, contributing to

effective production of hydroxyl radical and degradation of organic contaminants.
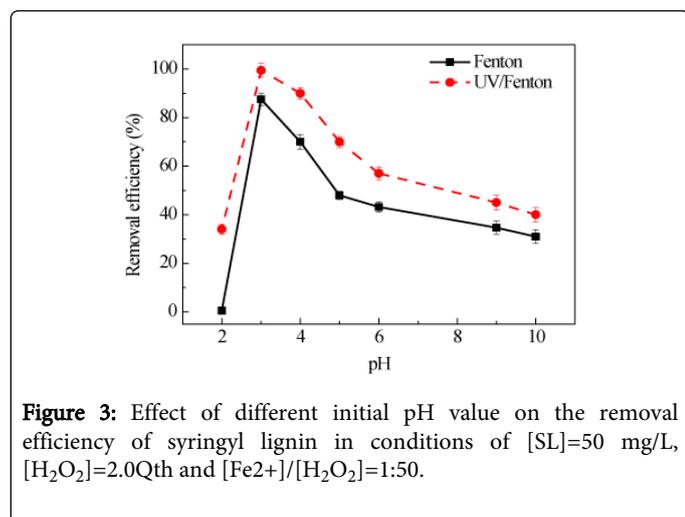
Figure 3: Effect of different initial pH value on the removal efficiency of syringyl lignin in conditions of [SL]=50 mg/L, [H_2O_2]=2.0Qth and [Fe2+]/[H_2O_2]=1:50.

Figure 3 also shows that the syringyl lignin degradation in UV/Fenton system was very efficient with removal efficiency up to 100% at the same pH of 3.0 in Fenton system. Introducing ultraviolet light in Fenton system contributed to comparative high removal efficiency at extreme high and low pH.

H_2O_2 dosage

As shown in Figure 4, the removal efficiencies of syringyl lignin increased at first and then decreased along with the increase of H_2O_2 dosage in both systems, and finally reached a maximum value at the H_2O_2 amount of 2.0Q_{th}. Although the high H_2O_2 concentration was reported to be a dominating parameter for the high removal efficiency of phenol by Fenton's reagent [12], its adding concentration should be estimated. Because H_2O_2 can both generate and eliminate -OH, optimum H_2O_2 amount to yield high concentration of -OH stayed in a certain range. When the dosage of H_2O_2 exceeds this range, further H_2O_2 addition leads to scavenging effect on -OH, resulting in decrease of -OH utilization. Therefore it is extremely important to select an appropriate concentration of H_2O_2. According to the result of experiment, good treatment effect efficiency can be achieved when the dosage of H_2O_2 is 2.0Q_{th}
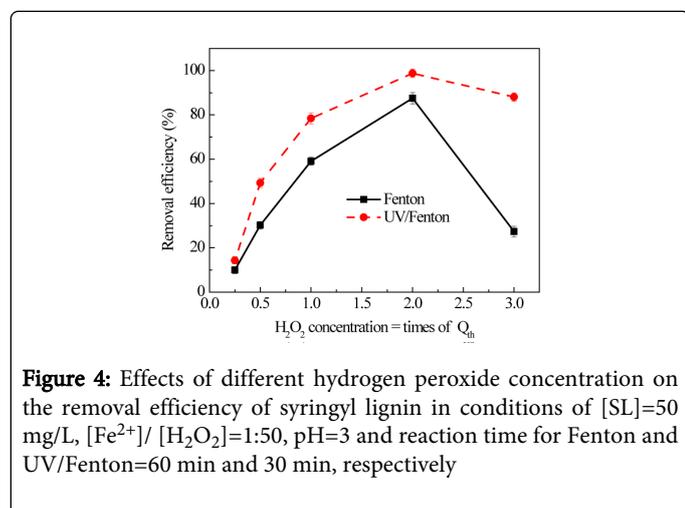
Figure 4: Effects of different hydrogen peroxide concentration on the removal efficiency of syringyl lignin in conditions of [SL]=50 mg/L, [Fe^{2+}]/ [H_2O_2]=1:50, pH=3 and reaction time for Fenton and UV/Fenton=60 min and 30 min, respectively

[Fe^{2+}]/ [H_2O_2] ratio

The effect of different concentrations of Fe^{2+} on removal efficiency of syringyl lignin is shown in Figure 5, which indicates that the removal efficiency of syringyl lignin increased at first and then decreased as the concentration of Fe^{2+} increases, and finally reached a maximum value at [Fe^{2+}]/[H_2O_2]=1 : 50. Consequently, Fe^{2+} was a necessary element to catalyze the generation of radical. Otherwise, H_2O_2 was hard to decompose to generate radical without Fe^{2+}. Additionally, the changing trend of curves was similar to the curve in Figure 4. When the dosage of Fe^{2+} was low, the removal efficiency of syringyl lignin continuously increased due to the accumulation of generated -OH, whereas excessive Fe^{2+} was detrimental to the removal efficiency because the oversupplied Fe^{3+} yields Fe^{2+} that may act as a significant scavenger by quenching the -OH. Another reason is that excessive concentration of Fe^{2+} promotes H_2O_2 decomposing into large amount of -OH. Thus a high concentration of -OH leads to scavenging effect by itself. Both reasons lead to a decline in utilization efficiency of -OH. Chan et al. [13] suggested that the oxidation capacity of Fenton process had a nonlinear correlation to the doses of [Fe^{2+}]/[H_2O_2] due to the involvement of some unwanted side reactions at both high and low [Fe^{2+}]/[H_2O_2] ratios. So appropriate dosage of Fe^{2+} is necessary to increase the reaction efficiency and reduce the cost of wastewater treatment at the same time.
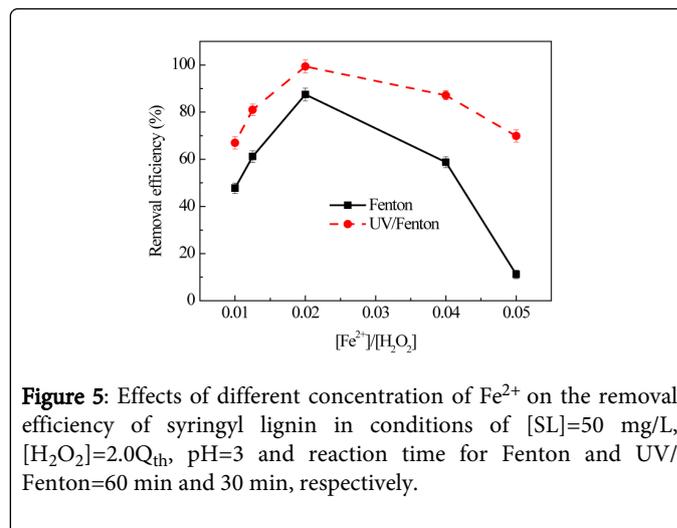
Figure 5: Effects of different concentration of Fe^{2+} on the removal efficiency of syringyl lignin in conditions of [SL]=50 mg/L, [H_2O_2]=2.0Q_{th}, pH=3 and reaction time for Fenton and UV/Fenton=60 min and 30 min, respectively.

Reaction time

The effect of reaction time on removal efficiency of syringyl lignin is shown in Figure 6 which demonstrates that the removal efficiency of syringyl lignin was more than 70% and about 54% in UV/Fenton and Fenton system, respectively after 30 min, indicating the high rate of reaction at the beginning of Fenton reagent. After 30 min, syringyl lignin was totally removed in UV/Fenton system, while the removal efficiency of syringyl lignin in Fenton reaction increased to the maximum value about 87% at 60 min. This phenomenon suggests that Fenton reaction was very quick, and -OH produced during the reaction could basically oxidize syringyl lignin in the first 60 min of the reaction, after that the concentration of -OH decreased and it slowed down the reaction rate.

Comparison in different systems

In order to understand the role of Fe^{2+} and UV in Fenton system, the removal efficiency of syringyl lignin was separately investigated in H_2O_2, homogeneous Fenton and homogeneous UV/Fenton system. The comparison of removal efficiency of syringyl lignin in different systems is also shown in Figure 6.

H_2O_2 system only contributed to the removal efficiency being about 21.7%. But the removal efficiency was significantly improved after addition of Fe^{2+} with removal efficiency up to 87.5% at 60 min, which was 4 times higher than that in H_2O_2 system. Moreover, the removal efficiency of syringyl lignin was even higher when UV irradiation was introduced into the Fenton system, where syringyl lignin was completely removed in first 30 min. Similarly, Hu et al. [14] compared UV/Fenton, UV/H_2O_2 and Fenton reagent to treat landfill leachate, who suggested that the UV/Fenton process was the most effective approach oxidation process to enhance the biodegradability and eliminate the color of the leachate. This is in accordance to the theory that UV irradiation can efficiently enhance the decomposition of H_2O_2 to produce -OH, which consequently increases the oxidation of syringyl lignin. Meanwhile, complex ion $Fe(OH)_2$ formed by Fe^{3+} and OH at pH 3 also produces -OH and Fe^{2+} under UV irradiation. Thus the catalytic capacity of Fenton was enhanced to improve the removal efficiency of syringyl lignin.

Interpreting degradation of syringyl lignin
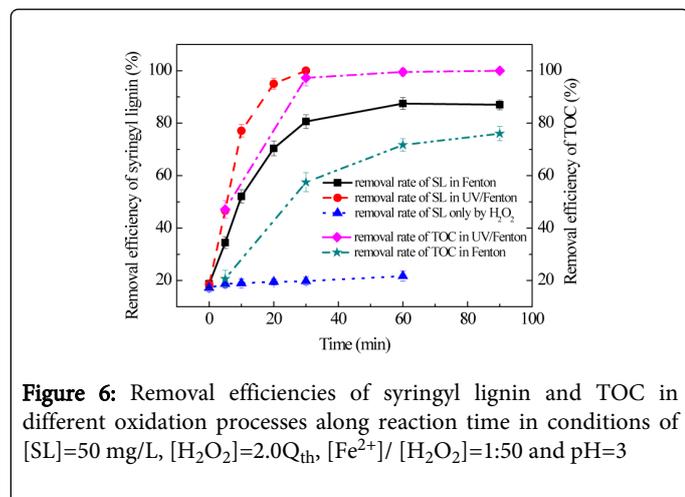
Figure 6: Removal efficiencies of syringyl lignin and TOC in different oxidation processes along reaction time in conditions of [SL]=50 mg/L, $[H_2O_2]=2.0Q_{th}$, $[Fe^{2+}]/$ $[H_2O_2]=1:50$ and pH=3

By comparing removal efficiencies of syringyl lignin and TOC in Fenton and UV/Fenton system in Figure 6,

It can be found that the removal efficiency of TOC was lower than that of syringyl lignin in Fenton and UV/Fenton systems. This phenomenon proposes a hypothesis that syringyl lignin was degraded into some other organic intermediates first and then completely mineralized slowly instead of one-step oxidizing syringyl lignin into CO_2 and H_2O. Therefore, further analysis was done to reveal the mechanism by analyzing UV-Vis spectra.

The UV-Vis spectra of UV/Fenton system are shown in Figure 7a, which demonstrates the absorption peak of syringyl lignin at around 267 nm immediately disappeared once H_2O_2 was added into the system and a strongly absorbed spectral band was detected in the range of 200-400 nm simultaneously. It can be inferred that a large amount of complex intermediates was generated with a strong

absorption in UV-Vis range. The absorbance decreased rapidly in the first 30 min of reaction and then kept stable, which implies that conjugate structure of phencyclidine is destroyed by oxidation of UV and Fenton reagent. According to Figure 6, the mineralization efficiency reached 100% after 30 min, indicating that syringyl lignin was completely mineralized; however the absorption spectrum bands in ultraviolet regions still existed and the colorless solution immediately turned to brown as H_2O_2 was added. So it can be concluded that the Fenton reaction is not a simple radical reaction. Combining with the theory of other researchers [15-17], an assumption was proposed that a complex (Fe is +IV or +V) with a large absorption spectra band was generated by the reaction of Fe (II) and syringyl lignin. The pollutant was oxidized by electron transfer of complex compound, which is another important pathway of Fenton reaction.
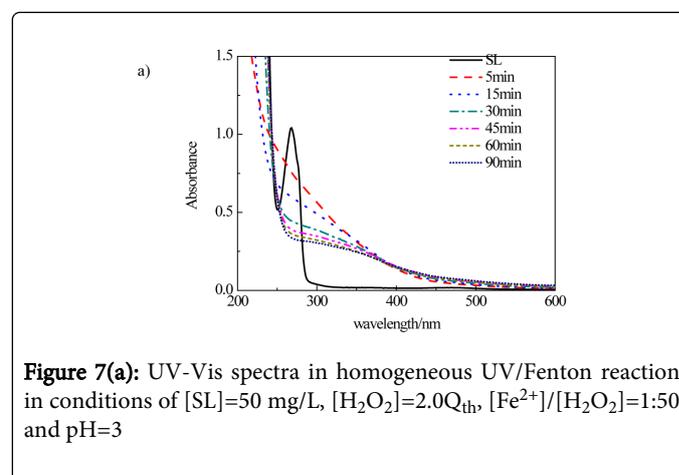
Figure 7(a): UV-Vis spectra in homogeneous UV/Fenton reaction in conditions of [SL]=50 mg/L, $[H_2O_2]=2.0Q_{th}$, $[Fe^{2+}]/[H_2O_2]=1:50$ and pH=3
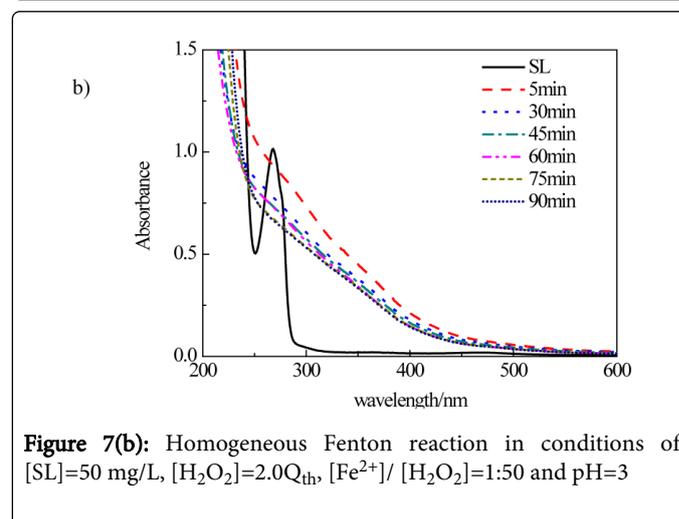
Figure 7(b): Homogeneous Fenton reaction in conditions of [SL]=50 mg/L, $[H_2O_2]=2.0Q_{th}$, $[Fe^{2+}]/$ $[H_2O_2]=1:50$ and pH=3

The UV-Vis spectra of syringyl lignin changing with the time of Fenton reaction are shown in Figure 7b, Which shows that the UV-Vis spectral change of syringyl lignin in homogeneous Fenton system was very similar to UV/Fenton system? The absorption peak at 267 nm disappeared when H_2O_2 was added into the system, suggesting that the reaction mechanisms of both systems are similar. However, a larger absorbed spectral band was detected in the range of 250-600 nm in Fenton system than that in UV/Fenton system in the range of 250-400 nm, suggesting that the oxidation of UV/Fenton was stronger than

Fenton reaction, and the synergistic effect between UV and Fenton reagent improved the removal efficiency of organic compounds.

Conclusion

The factors in Fenton and UV/Fenton processes such as initial pH value, dosage of H_2O_2 and Fe^{2+}, reaction time and UV irradiation were optimized in a self-designed cylindrical reactor. The optimum factors including dosage of H_2O_2 of $2.0Q_{th}$ (0.6 mL), $[Fe^{2+}]/[H_2O_2]$ ratio of 1:50, initial pH of 3.0, and reaction time of 90 min gave rise to removal efficiency of syringyl lignin being 87.5%. UV irradiation increase the removal efficiency of syringyl lignin that was completely removed in first 30 min. Reaction mechanisms of both Fenton system and UV/Fenton system were similar, that complex intermediates (Fe is +IV or +V) were generated with a large absorption spectra band when H_2O_2 was added. Thus syringyl lignin was degraded into organic intermediates firstly and then completely mineralized slowly instead of one-step oxidized into CO_2 and H_2O. The present study is believed to provide a valuable foundation for the treatment of papermaking wastewater by Fenton reagent.

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