



Degradation of Methylene Blue Wastewater by Fe²⁺ Coupling Persulphate Using Online UV-Vis Spectrophotometry

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ABSTRACT

Online UV-Vis spectrophotometer technology as accurate, convenient and fast monitoring method was used to detect instantaneous dye concentration in aqueous medium. Ferrous ion coupling with Persulphate to degrade methylene blue (MB) exhibited a very high degradation rate, and therefore online UV-Vis spectrophotometer showed great advantage in this study. The effects of ferrous ion concentration, sodium Persulphate concentration, pH value and initial MB concentration on MB degradation were investigated. The online spectrophotometer could minimize the systematic error caused by the termination of adding chemicals and manual operation. At room temperature, the optimal condition was acquired with 73.6% MB removal after 100s at neutral medium when initial ferrous dosage and sodium Persulphate were 1.25 mmol/L and 0.2 mmol/L, respectively. Fe²⁺/S₂O₈²⁻ system exhibited a great degradation efficiency in acidic or neutral environment.

INTRODUCTION

Dyes are widely used in textile industry, leather industry, printing industry and food industry. According to statistics, one million tons of dyes were produced in the world every year, of which about 15% dyes entered the natural environment in the process of production and usage (Yang et al. 2011). The dye entering the natural environment not only influenced the natural water colour, but also had a negative impact on the ecological environment (Zhu et al. 2013). Conventional wastewater treatment such as adsorption, filtration and flocculation mainly transferred pollutants to other phases which were easy to cause secondary pollution (Zhang et al. 2015).

Advanced oxidation technology (AOP) has been proved to be a very effective method to remove organic pollutants from water because of fast degradation speed, high treatment efficiency and little secondary pollution (Jia et al. 2017, Feng et al. 2015). The reason was that high active hydroxyl radical could be produced during AOP and hydroxyl radical could non-selectively destroy the structure of organic matter in water. Because hydroxyl radical only stably existed in acidic medium, this problem restricted its application in wastewater treatment. Sulphate radical was another high active radical to use pollutant degradation especially in neutral and acidic medium (Deng et al. 2015) which was more beneficial for wastewater treatment.

Fenton reagent (ferrous ions/hydrogen peroxide) was one of the AOPs which could produce hydroxyl radical and display a high degradation performance in acidic medium (2-4 pH value). Ferrous ion also could catalyse Persulphate to produce sulphate radical for the degradation of organic pollutants. In this study, methylene blue (MB) was used as the target pollutant which was degraded by ferrous ion coupling sodium Persulphate. Because of very high reactive speed, the online UV-Vis spectrophotometry was used to monitor instantaneous concentration of MB in dyeing wastewater (Xu et al. 2018, Xu et al. 2016). The effects of ferrous ion concentration, sodium Persulphate (SP) concentration, pH value and initial MB concentration on MB degradation were investigated.

MATERIALS AND METHODS

Experimental Reagents

The methylene blue (MB), ferrous sulphate (FeSO₄), sodium Persulphate (Na₂S₂O₈, SP), sodium hydroxide (NaOH), hydrochloric acid (HCl) were of analytical grade and purchased from Tianjin Chemical Reagent Technology Company (China).

Experimental Apparatus

The online reaction and spectrophotometric analysis system are shown in Fig. 1. This system consisted of a reaction

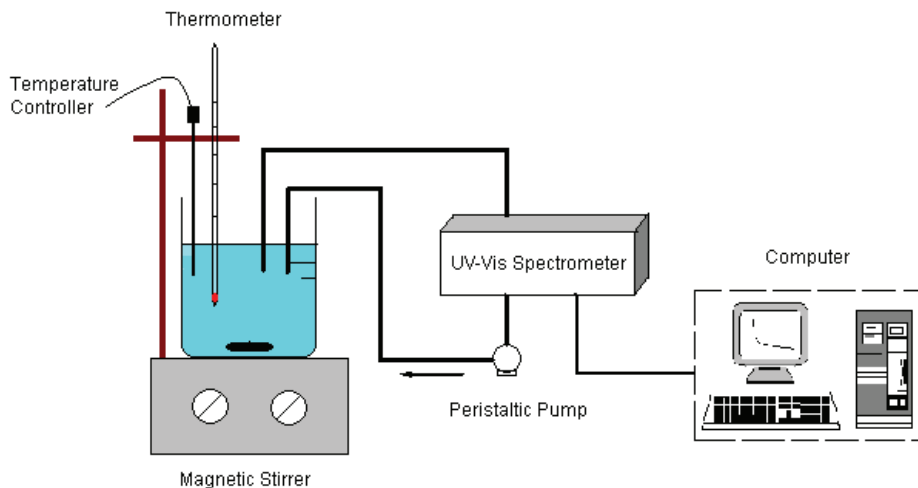


Fig. 1: Online spectrophotometric system.

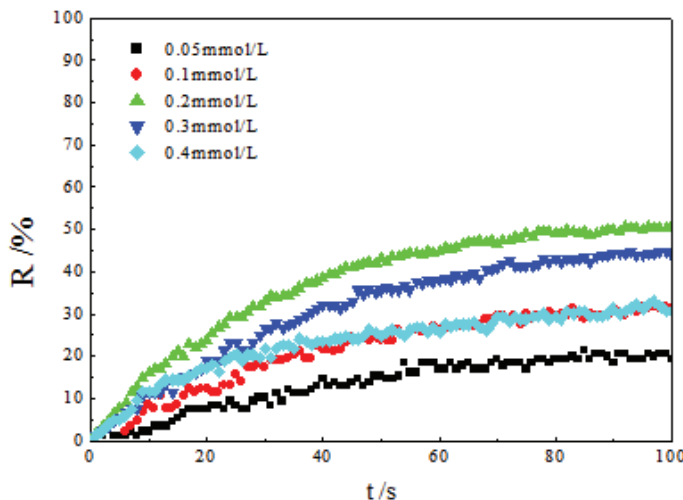


Fig. 2: Effect of initial Fe^{2+} concentration on MB degradation (MB = 7.5mg/L, SP = 0.5mmol/L, pH = 6.99, room temperature).

container, a digital display thermostat magnetic stirrer (85-2 Shanghai instrument manufactory), a digital pH meter (PHS-3C-01 experimental pH meter Hangzhou instrument limited corporation), a UV-Vis spectrophotometer (SP-756PC Shanghai spectrometric instrument manufactory), a peristaltic pump (HL-1D Beijing instrument manufactory) and a computer. A plastic hose with an inner diameter of 2 mm linked the reactive solution with the flowing cell cuvette within the spectrophotometer with the solution pumped by the peristaltic pump. The return liquid was sent back to beaker to form the cycle. UV-Vis spectrophotometry was used to monitor the colour change in the flowing cell cuvette at 1s^{-1} .

Experimental Method

200 mL MB wastewater was added in 250 mL beaker. Next, the ferrous sulphate and hydrochloric acid were added in MB wastewater. The detected wavelength was adjusted to 664 nm. When the sodium Persulphate was added, the computer began to record the absorbance at different times. The degradation rate (R) of methylene blue is shown in Eq. 1.

$$R = \frac{A_0 - A_t}{A_0} \times 100\% \quad \dots(1)$$

Where, A_t is the absorbance of wastewater solution when $t = t$ s and A_0 is the absorbance of wastewater solution when $t = 0$ s.

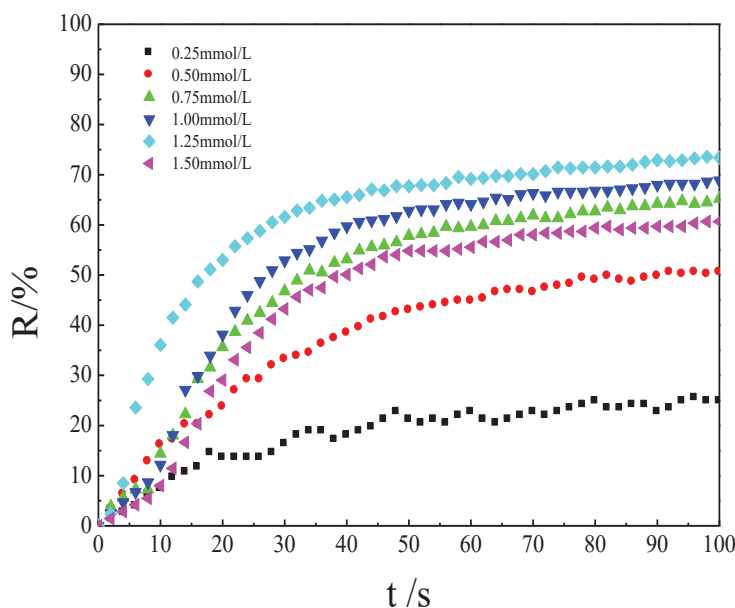
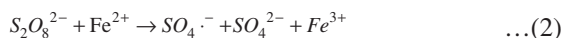


Fig. 3: Effect of sodium persulfate concentration on MB degradation system (MB = 7.5mg/L, Fe²⁺ = 0.2mmol/L, pH = 6.99, room temperature).

RESULTS AND DISCUSSION

Effect of Ferrous Ion Concentration

Sodium Persulphate is difficult to decompose by itself to produce sulphate radicals because of its stable ionic compound structure. Ferrous ion can catalyse Persulphate to produce sulphate radicals. The initial concentrations of methylene blue and sodium Persulphate were 7.5 mg/L and 2.0 mmol·L⁻¹, respectively. Fig. 2 showed the effect of the change of initial Fe²⁺ concentration in the range of 0.05 to 0.4 mmol/L for the MB removal at 100s at neutral medium. From Fig. 2, it could also be seen that the MB removal increased rapidly in the first 60s and increased slowly after 60s to 100s. With the addition of Fe²⁺, the sulphate radicals were produced with Persulphate (Shang et al. 2017). It is shown in Eq. 2. The MB in aqueous solution was decomposed by sulphate radicals because of its strong oxidizability. With the reaction proceeding, the Fe²⁺ in system was continuously consumed, resulting in the reduction of sulphate radicals, so the degradation efficiency of MB showed a gentle upward tendency (Wang et al. 2010).



The MB removal increased from 19.2% to 50.5% with the rise of initial Fe²⁺ dosage from 0.05 to 0.2 mmol/L after 100s. When Fe²⁺ dosage continuously added to 0.3 mmol/L,

the MB removal was decreased to 43.8% at 100s. The MB removal was only 31.1% with 0.4 mmol/L Fe²⁺ dosage. The optimal initial Fe²⁺ dosage was 0.2 mmol/L with 50.5% MB removal after 100s. This phenomenon suggested that appropriate concentration of ferrous ions could promote the degradation of MB, and when the concentration of ferrous ions was excessive, it would inhibit the degradation. This was because when the system contained excessive ferrous ions, it would react with sulphuric acid radical and result in consuming SO₄²⁻ in the system, thus inhibiting the degradation of methylene blue (Shao et al. 2017). The mechanism of SO₄²⁻ consumption is shown in Eq. 3. Taking ferrous ion dosage and degradation efficiency into consideration, ferrous ion concentration of 0.2 mmol·L⁻¹ was selected for the next experiment.

Effect of Sodium Persulphate Concentration

Sodium Persulphate is a strong oxidizing agent, which was the source of sulphate radical in this system. The initial Persulphate dosage was an important factor for affecting the MB removal. The effects of initial sodium Persulphate dosage from 0.25 to 1.5 mmol/L on MB removal was investigated at neutral medium and the results are shown in Fig. 3, when the initial concentration of methylene blue was 7.5 mg·L⁻¹, and the concentration of ferrous ions 0.2 mmol·L⁻¹. As could be seen from Fig. 3, when the concentration of sodium Persulphate increased from 0.25 to 1.25 mmol/L, the

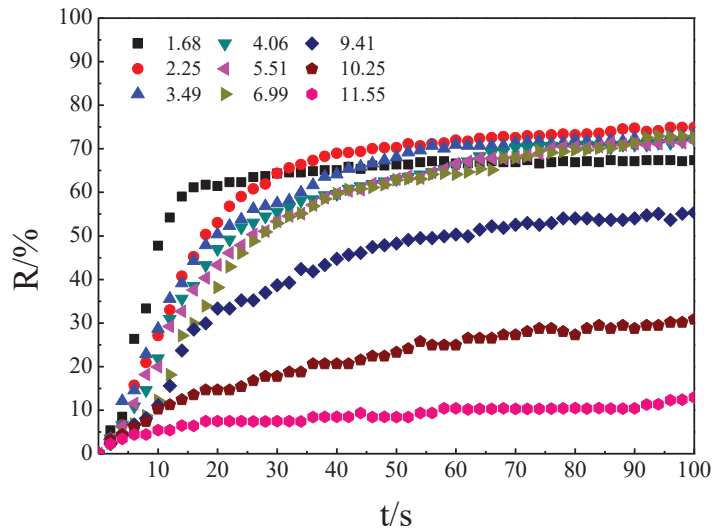


Fig. 4: Effect of pH value on MB degradation system (MB = 7.5mg/L, Fe^{2+} = 0.2mmol/L, SP = 1.25mmol/L, room temperature).

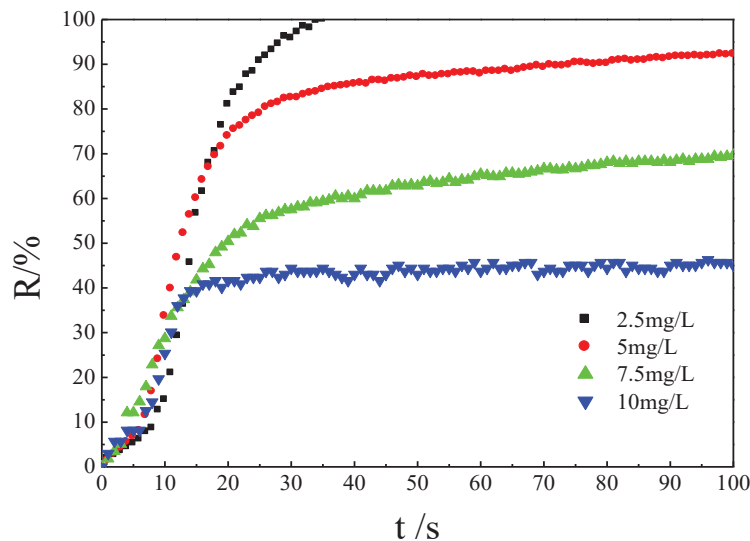
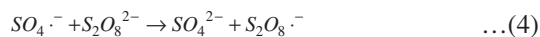


Fig. 5: Effect of different initial concentrations of MB on degradation system (Fe^{2+} = 0.2mmol/L, SP = 1.25mmol/L, pH = 6.99, room temperature).

MB removal increased from 24.8% to 73.6% at 100s. When sodium Persulphate continued to increase to 1.5 mmol/L, the MB removal decreased to 60.7%. The best sodium Persulphate dosage was 1.25 mmol/L with the 73.6% MB removal.



This was because the ferrous ion acted as an electron donor to catalyse the decomposition of Persulphate to produce sulphate radicals which could result in stability in the system removing MB (Liang et al. 2009). With the increase

of sodium Persulphate concentration, more sulphate radicals were generated to improve degradation efficiency of MB. When the sodium Persulphate concentration was excessive, $S_2O_8^{2-}$ would interact with sulphate radical in the system and consume sulphate radical in the system, thus inhibiting MB degradation (Xu et al. 2011). The reaction equation was shown in Eq.4. In addition, because there was a large number of sulphate radicals in the system, there would be a certain disproportionate reaction between them, and sulphate radical was also consumed. The reaction equation is shown as Eq. 5, thus reducing the concentration of sulphate radicals

in the system and affecting the degradation efficiency of MB. Considering the dosage and cost of the oxidant, sodium Persulphate concentration of 1.25 mmol·L⁻¹ was selected for the next experiment.

Effect of pH Value



The pH value in solution is one of the important factors to influence the reaction process in advanced oxidation technology (Ye et al. 2016). In this study, the effect of pH value on the MB degradation system was investigated in Fig. 4 when the initial concentrations of sodium Persulphate and ferrous ions were 1.25 mmol/L and 0.2 mmol/L, respectively at room temperature. It could be seen from Fig. 4 that the initial pH value significantly affected the MB degradation efficiency. When the pH values of the oxidizing environment ranged from 2.25 to 6.99, there were similar MB removal efficiencies which were over 70% after 100s. When the pH value of solution was 1.68, the MB removal was 67.7%, which exhibited a slight decline. When the pH value increased from 9.49 to 11.25, the MB removal significantly decreased from 55.7% to 9.3%. Fe²⁺/S₂O₈²⁻ system revealed an excellent oxidizing ability in weak acidic and neutral medium. The alkaline or strong acidic medium were disadvantage for degradation process. The reason for the decrease of MB removal in alkaline environment is that ferric divalent ions in solution changed to the ferric composite [Fe(OH)₂ or FeOH⁺] and mechanism is shown in Eq. 6 and Eq. 7. As the result, the amount of ferric divalent ions, which reacted with Persulphate in the system were reduced, thereby reducing the degradation efficiency of MB (Yuan et al. 2014). And Fe(OH)₂ and FeOH⁺ had no catalytic activity resulting in reduced number of sulphuric acid radical in the system, thus reducing the degradation efficiency of MB (Miao et al. 2018). The greatest advantage of Fe²⁺/S₂O₈²⁻ system was that it had a great degradation effect in acidic or neutral environment.

Effect of the Initial Concentration of Methylene Blue

The initial concentration of pollutant in printing and dyeing wastewater is an important factor influencing the reaction process. In this study, the effect of different initial methylene blue concentrations on MB degradation system were investigated when the sodium Persulphate and ferrous ion concentration were 1.25 mmol·L⁻¹ and 0.2 mmol·L⁻¹ at neutral environment. The experimental results are shown in Fig. 5. It could be seen that when the initial concentration of MB increased from 2.5 mg·L⁻¹ to 10.0 mg·L⁻¹, the degradation efficiency was 100%, 92.2%, 73.6% and 45.1%, respectively after 100s. As the initial concentration of MB increased, the

degradation efficiency of MB decreased. This was because the ferrous ion and concentration of sodium Persulphate were constant. Therefore, the number of sulphate radicals were constant. When the initial concentration of MB in the system increased, the molar ratio of sulphate radical to MB was lower, and the amount of degraded methylene blue was limited. Therefore, when the concentration of the ferrous ions and sodium Persulphate was constant, the degradation efficiency of low MB concentration was higher.

CONCLUSION

The oxidizing efficiency of ferrous/Persulphate system to degrade methylene blue in aqueous solution was investigated in this study using online monitoring technology. The ferrous ion coupling Persulphate exhibited a very fast MB degradation process. The online spectrophotometer showed a great advantage to measure the change of MB concentration in a quick, accurate and convenient way. It could minimize the systematic error caused by the termination of adding chemicals and manual operation. At room temperature, the optimal condition was acquired with 73.6% MB removal after 100s at neutral medium when initial ferrous dosage and sodium Persulphate were 1.25 mmol·L⁻¹ and 0.2 mmol·L⁻¹, respectively. Fe²⁺/S₂O₈²⁻ system exhibited a great degradation efficiency in acidic or neutral environment.

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