

Monitoring of decolorization kinetics of Reactive Brilliant Blue X-BR by online spectrophotometric method in Fenton oxidation process

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Abstract

Online spectrophotometry method is employed to monitor simulated Reactive Brilliant Blue X-BR (RBB X-BR) in aqueous solution in Fenton oxidation process. The effects of initial dosage of FeSO₄ and H₂O₂, pH value, initial concentration of dye and temperature have been studied. The results show that online spectrophotometric method is a quick, feasible and convenient technique to monitor color removal of RBB X-BR in Fenton process. The optimal dosage of H₂O₂ and pH is 3.529 mM and 3, respectively. The optimal dosage of Fe²⁺ for color removal is 0.1618 mM. The concentration of initial FeSO₄ against the reaction rate constant (*k*_{ap}) for decolorizing is linear correlation as: *k*_{ap} = 0.1354[Fe²⁺]₀ (*R*² > 0.99). The apparent activation energies of reaction is 25.21 kJ mol⁻¹ (*R*² > 0.99). The intrinsic reaction rate constant of •OH with RBB X-BR in aqueous solution is 7.396 × 10¹⁰ M⁻¹ s⁻¹. The molecule structure of RBB X-BR is decomposed and not mineralized by Fenton's reagent. The main intermediate products are 1,2-diacetylene and 2,5-dinitrobenzoic acid. The probable mechanism of the decoloration of RBB X-BR is also discussed.

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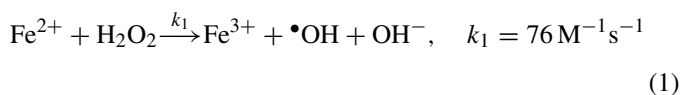
Keywords: Spectrophotometry; Fenton; Reactive Brilliant Blue X-BR; Kinetics; Wastewater

1. Introduction

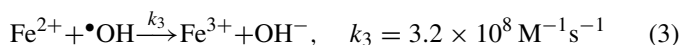
Synthetic dyes (D) that bring color to the world with polluting our living environment seriously have been utilized broadly in the textile industry [1,2]. Around 12% of synthetic dye flows away during processes every year [3,4]. In general cases, wastewater was directly discharged without any primary treatment that has strong chroma, high value of COD and a relatively low BOD/COD ratio [5]. Therefore, one of the vital problems in dye industry is the colored effluent containing visible pollutants [6].

Nowadays, there are many approaches to deal with dyes wastewater, such as biodegradation [7], activated carbon adsorption [8], membrane separation [9], ultrasonic synergistic degradation [10], chemical coagulation [11], electrical chemistry [12], TiO₂ photocatalytic oxidation [13], Fenton oxidation [14] and so on. Fenton oxidation is a popular method to dispose off colored effluents. The solution of hydrogen peroxide and

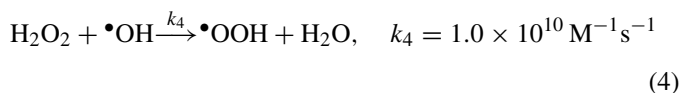
iron catalyst can effectively oxidize organic contaminant. In a weak acid medium, Fe²⁺ is oxidized by H₂O₂ to generate Fe³⁺, hydroxyl radical (•OH) and OH⁻ [15]. Then high active •OH attacks and destroys molecule structure of organic dye (D). The overall reactions can be expressed as follow:



Meanwhile, the •OH created from Reaction (1) can also oxidize Fe²⁺ to Fe³⁺ in aqueous solution [16]:

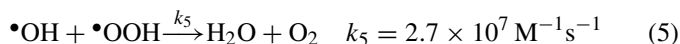


Moreover, some other reactions between •OH and H₂O₂ [17], and •OH peroxide radicals (•OOH) exist in the process [18]:

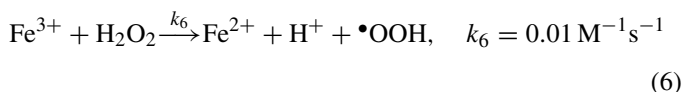


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In Fenton oxidation process, the auto-regenerative reaction of Fe^{2+} takes place because of the redox reaction between Fe^{3+} and H_2O_2 [19].



Previous studies have shown that the concentration of dyestuff can be analyzed by spectrophotometer [20,21]. NaOH or Na_2SO_4 solution could be used to decompose H_2O_2 and end off the reaction before measurement. Fe^{2+} , a popular inorganic coagulating ion, can remove a part of dye in alkaline medium. Furthermore, this process consumed time when samples of dye solution were withdrawn during the course of the oxidation process. Online spectrophotometric method can be used to monitor the instant dye in aqueous solution during Fenton process. The early study reported that Coque et al. had successfully used the online spectrophotometry method to investigate dyes of Red Remazol and Trypan Blue removal processes [22]. It was proved that online spectrophotometry is a simple monitoring method for fast color removal.

There are various types of dye such as acidic, reactive, disperse, metal complex, direct, sulphur, vat dye and so on. Nonetheless, the reactive type is the most popular utility in textile industry and more than 15% of it runs off in wastewater stream [23]. A typical dye pollutant of textile wastewater, Reactive Brilliant Blue X-BR (RBB X-BR), was investigated in this study.

In this paper, online spectrophotometry system was set up to monitor instant absorbance of dye. The feasibility analysis of Fenton oxidation process of RBB X-BR degradation was done with this method. The effects of initial dosage of FeSO_4 and H_2O_2 , pH value, initial concentration of dye in aqueous solution and temperature on RBB X-BR degradation were investigated in detail. The decolorizing kinetics of Fenton oxidation was researched based on experimental data. According to the Fenton oxidation mechanism mentioned in the previous literatures, the kinetic model of dye degradation in Fenton system was established. The intermediate products of RBB X-BR degradation were analyzed by ultraviolet visible spectrum (UV–vis), gas chromatography–mass spectrometry (GC–MS) and ion chromatography (IC), respectively. The possible degradation mechanism of RBB X-BR was predicted.

2. Experimental

2.1. Materials

The chemical structure of RBB X-BR ($\text{C}_{23}\text{H}_{12}\text{O}_8\text{N}_6\text{S}_2\text{C}_{12}\text{Na}_2$, 681 g mol^{-1}) is shown in Fig. 1. Dye was obtained from Jiangsu Shenxin Dyestuffs Company (China) without further purification. Wastewater of RBB X-BR was prepared by dissolving a requisite quantity of dyestuffs in double-distilled water. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2SO_4 and H_2O_2 (30% in H_2O) were of

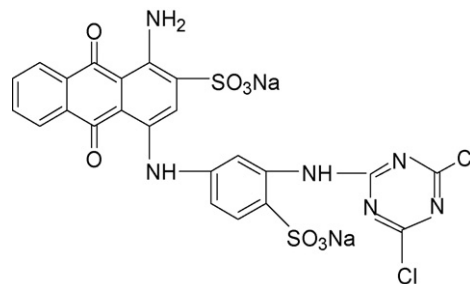


Fig. 1. The chemical structure of RBB X-BR.

analytical grade and purchased from Beijing Chemical Reagent Company.

2.2. Apparatus

Fig. 2 shows online spectrophotometric system. This system consists of three parts: reaction unit, optical measuring unit and recording unit. Reaction unit contains a magnetic stirrer apparatus (Rongsheng Instrument company, China), thermometer, 250 mL beaker and temperature controller. Magnetic stirrer apparatus is used to heat the solution at the same time. Optical measuring unit includes UV–vis spectrometer, peristaltic pump and current colorimetric container (UNICO 2012PC, Shanghai, China). General velocity of wastewater in system was 18.5 mL min^{-1} . Recording unit was a computer and the monitoring frequency was 6 min^{-1} during the reaction process.

2.3. Procedures

Fenton oxidation process was performed in a beaker with 200 mL solution, in which the specified concentration of selected dyestuff was remained. FeSO_4 and H_2SO_4 of the calculated concentrations were added into wastewater and pH adjustment of the wastewater was done by adding H_2SO_4 . At the same time, stir and pump were applied. The wastewater was pressed into the current colorimetric container in UV–vis spectrophotometer by peristaltic pump. Absorbance was determined at maximal absorption peak of dye by UV–vis spectrophotometer. When H_2O_2 at the calculated concentrations was added into the wastewater the computer that was linked with spectrophotometer began to record experimental absorbance results.

2.4. IC analysis

Inorganic ions (Cl^- , NO_3^- and SO_4^{2-}) in aqueous solution were measured by a Dionex Series DX 600 Ion Chromatography (IC) with conductivity detector, IonPac AS11 ($4 \times 250 \text{ mm}$) column and PEAKNET software. The eluent was a mixture of Na_2CO_3 (2.0 mmol L^{-1}) and NaHCO_3 (0.75 mmol L^{-1}). The eluent flow rate was 1.0 mL min^{-1} .

2.5. GC–MS analysis

Organic substance in sample was measured by GC–MS testing. The chromatographic analysis was performed in a Finningan

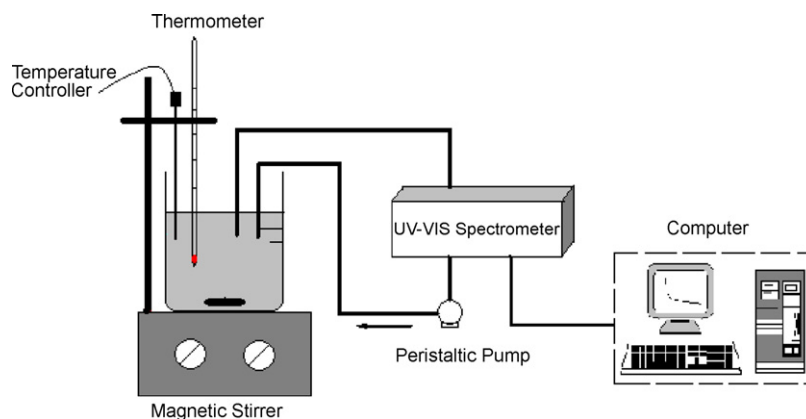


Fig. 2. Online spectrophotometric system.

Trace GC 2000 chromatography. Chromatographic separations were carried out using a DB-5 MS fused quartz capillary chromatographic column (J&W Scientific, Folsom, CA, USA) of $30\text{ m} \times 0.25\text{ mm}$ i.d. and $0.25\text{ }\mu\text{m}$ phase thickness. The analytes were observed by mass spectrometry, using a Trace MS 2000 mass spectrometer (Thermo-Quest, Finnigan, USA) working in EI+ mode, coupled to the chromatography. The working conditions were as follows: the injector temperature was $250\text{ }^\circ\text{C}$; the initial temperature of the oven heating program was $100\text{ }^\circ\text{C}$ for 5 min; the temperature was then raised to $280\text{ }^\circ\text{C}$ at $30\text{ }^\circ\text{C min}^{-1}$; the temperatures of the interface and ion source were 250 and $150\text{ }^\circ\text{C}$, respectively; the carrier gas was helium at a flow of 1 mL min^{-1} in constant-flow mode.

3. Results and discussion

3.1. Feasibility analysis of online spectrophotometric method

Online spectrophotometry method was applied to analyze RBB X-BR in Fenton oxidation process. The UV-vis spectra of RBB X-BR, H_2SO_4 , Fe^{2+} , Fe^{3+} , H_2O_2 are showed in Fig. 3. Only spectra of RBB X-BR in 500–700 nm spectral range has a

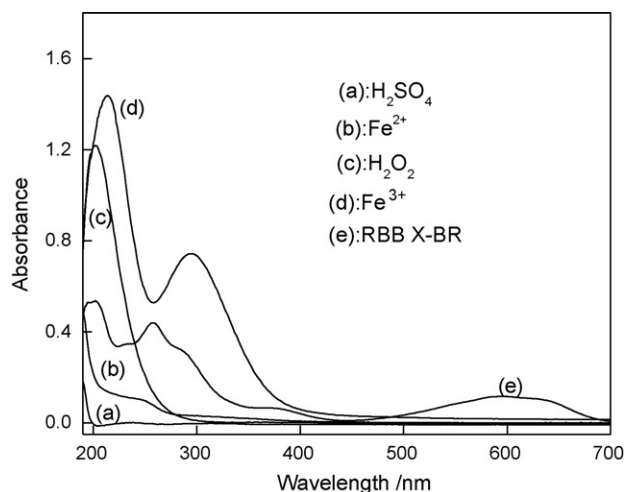
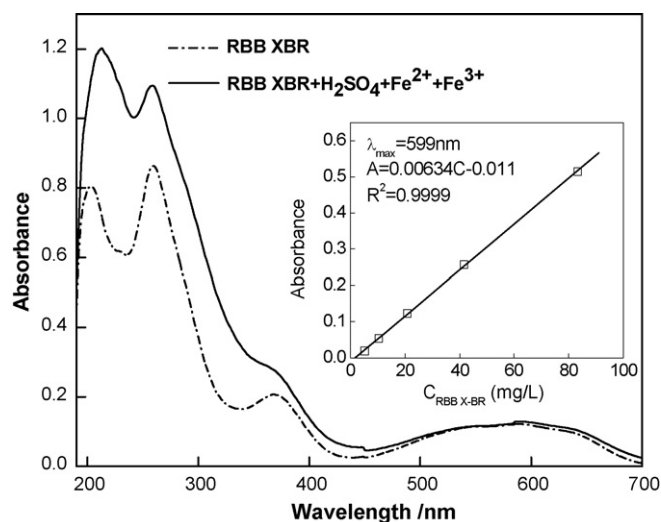


Fig. 3. UV-vis spectrum of materials.

great absorption, and the maximum adsorption peak is 599 nm. The criterion equation of RBB X-BR and absorbance (A) at 599 nm against RBB X-BR concentration (C) at neutral pH value are shown in Fig. 4 ($A = 0.00634C - 0.011$, $R^2 = 0.9999$). In the experiments, instant absorbance results recorded by computer were transferred to concentrations of dyes on the basis of the criterion equation. Fig. 4 depicts the shift of UV-vis spectra of RBB X-BR when Fe^{2+} , Fe^{3+} and H_2SO_4 are added to the solutions. But the spectra of dyes solution in 500–700 nm does not display any variation with addition Fe^{2+} , Fe^{3+} and H_2SO_4 , which mean that UV-vis spectra of dyes solution are influenced by Fe^{2+} , Fe^{3+} and H_2SO_4 in visible spectral range. Therefore, 599 nm is taken as monitoring wavelength in this research.

3.2. Time-dependent degradation of RBB X-BR

The change in C/C_0 value of dyes versus irradiation time is shown in Fig. 5. C represents the concentration of dye with time and C_0 is the initial concentration. Fenton oxidation process for the treatment of RBB X-BR consists two stages. The decolorization is very fast at the first stage. In the second stage

Fig. 4. Comparison of dye UV-vis spectrum between dye and dye ($+\text{H}_2\text{SO}_4 + \text{Fe}^{2+} + \text{Fe}^{3+}$).

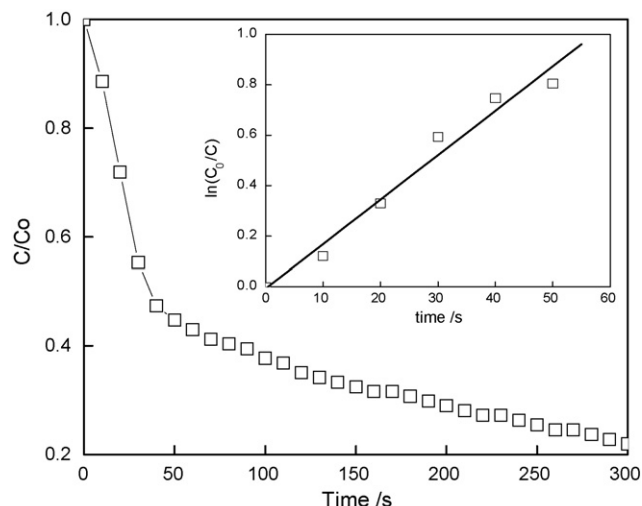


Fig. 5. Time-dependent degradation of RBB X-BR. $[\text{RBB X-BR}]_0 = 17 \text{ mg/L}$, $[\text{Fe}^{2+}]_0 = 0.1618 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 3.529 \text{ mM}$, $\text{pH} 3$, $T = 15^\circ\text{C}$.

($\geq 50 \text{ s}$), decolorizing rate is significantly retarded with the reaction time extending. These experimental phenomena can be explained from two aspects. First, the concentration of Fe^{2+} and H_2O_2 in aqueous is consumed during Fenton process. Second, intermediate products engaged in the reaction can reduce apparent rate of dye degradation. Fenton oxidation process apparently followed first-order kinetics in the first stage [24,25], $\ln(C_0/C) = k_{\text{ap}}t$. The slope (k_{ap}) of the best-fit line through the data points represents the first-order rate constants. From Fig. 5, the results of current study can be suitable to the simple first-order rate law ($t \leq 50 \text{ s}$).

3.3. Effect of different factors

Five factors of initial dosage of FeSO_4 , H_2O_2 , pH value, initial concentration of RBB X-BR and temperature were investigated in this paper. The decolorizing reaction rate constant (k_{ap}) and removal of dye ($R = (C_0 - C/C_0) \times 100\%$) at 300 s were used for comparison under different experimental conditions.

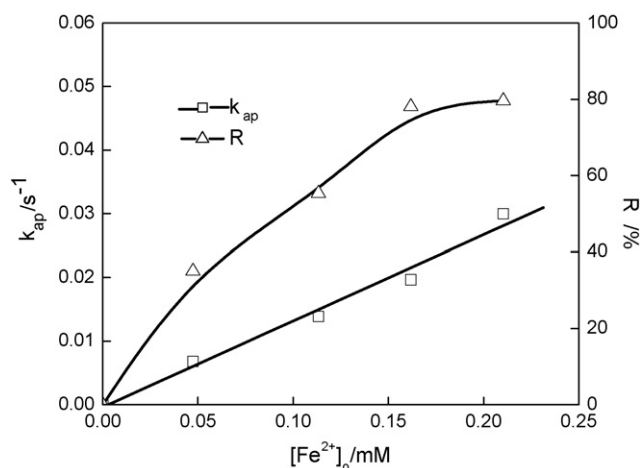


Fig. 6. Influence of initial Fe^{2+} concentration. $[\text{RBB X-BR}]_0 = 17 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 3.529 \text{ mM}$, $\text{pH} 3$, $T = 15^\circ\text{C}$.

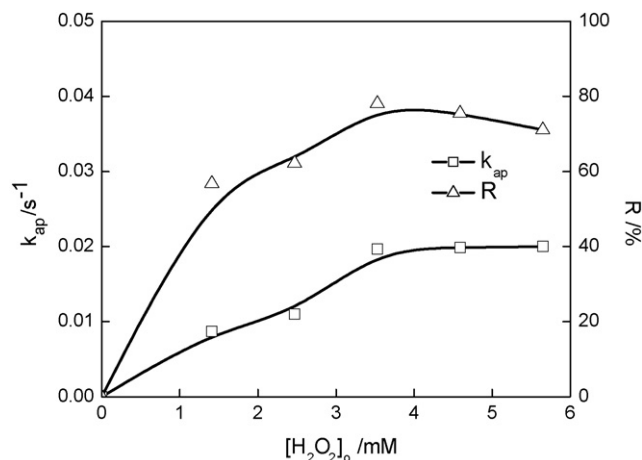


Fig. 7. Influence of initial H_2O_2 concentration. $[\text{RBB X-BR}]_0 = 17 \text{ mg/L}$, $[\text{Fe}^{2+}]_0 = 0.1618 \text{ mM}$, $\text{pH} = 3$, $T = 15^\circ\text{C}$.

3.3.1. Effect of initial Fe^{2+} concentration

A series of Fe^{2+} concentrations on the constant k_{ap} and the removal of RBB X-BR have been observed in Fig. 6. From this figure, the color removal of RBB X-BR increases from 35.04% to 78.07% with the addition of Fe^{2+} dosage from 0.04737 to 0.1618 mM. But color removal is only 79.65% when Fe^{2+} catalyst improves to 0.2104 mM. This experimental phenomenon suggests that high Fe^{2+} dosage does not effect decolorization of RBB X-BR in the Fenton oxidation process due to Fe^{2+} ion competing for $\bullet\text{OH}$ with dye molecules [26], which can be expressed in Reaction (3). Therefore, 0.1618 mM of initial Fe^{2+} can be used as an optimum dosage. The k_{ap} of RBB X-BR have a great raise from 0.00681 to 0.02999 s^{-1} with increasing Fe^{2+} dosage from 0.04737 to 0.2104 mM, and initial Fe^{2+} dosage against k_{ap} shows a linear correlation [27], $k_{\text{ap}} = 0.1354[\text{Fe}^{2+}]_0$, $R^2 = 0.9917$. Here, $[\text{Fe}^{2+}]_0$ is the initial Fe^{2+} dosage. Thus, it indicates that the decomposition of H_2O_2 and production of $\bullet\text{OH}$ can be obviously accelerated by Fe^{2+} catalyst.

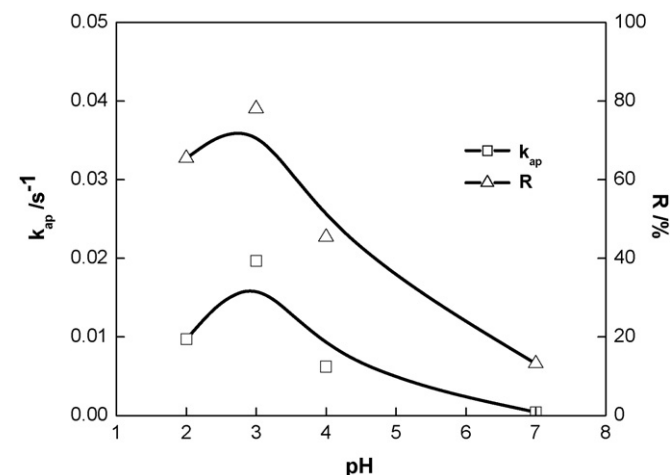


Fig. 8. Influence of pH. $[\text{RBB X-BR}]_0 = 17 \text{ mg/L}$, $[\text{Fe}^{2+}]_0 = 0.1618 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 3.529 \text{ mM}$, $T = 15^\circ\text{C}$.

3.3.2. Effect of initial H_2O_2 concentration

Another important point to be considered in Fenton oxidation was the amount of hydrogen peroxide [28]. Fig. 7 shows the decolorizing kinetics constant k_{ap} and color removal of RBB X-BR in a fixed initial Fe^{2+} dosage and various amounts of initial H_2O_2 concentration. The color removal of RBB X-BR increases from 58.78% to 78.07% with the dosage of H_2O_2 rising from 1.412 to 3.529 mM. On the contrary, Fig. 7 exhibits that the removal value is only 71.45% when H_2O_2 dosage rises to 5.647 mM. The k_{ap} varies from 0.00873 to 0.01966 with increasing H_2O_2 dosage from 1.412 to 3.529 mM. When H_2O_2 dosage increases from 3.529 to 5.647 mM, the k_{ap} greatly fluctuates between 0.01966 and 0.02000 s^{-1} . The increase of H_2O_2 dosage accelerates the generation of $\bullet OH$. However, as a result of reaction of H_2O_2 and $\bullet OH$ [29] higher concentration of H_2O_2 can consume $\bullet OH$ (Reactions (4) and (5)). Thus, 3.529 mM of initial H_2O_2 dosage can be used as an optimum dosage for Fenton process to treat with RBB X-BR.

3.3.3. Effect of initial pH value

The pH value of the solution plays an important role on decolorizing dyes in Fenton process [30]. The influence of pH value on decomposition of RBB X-BR by Fenton oxidation is shown in Fig. 8. It can be seen clearly from Fig. 8 that the addition of pH value in aqueous solution from 2 to 3 increases the color removal from 65.46% to 78.07% and k_{ap} of RBB X-BR from 0.00975 to 0.01966 s^{-1} , respectively. But the color removal and k_{ap} decrease sharply from 78.07% to 13.24% and 0.01966 to 0.00045 s^{-1} , respectively, with the further rise of pH from 3 to 7. Therefore, pH value 3 is considered as the optimum pH in Fenton process to treat with RBB X-BR. The color removal and reaction rate are limited at low pH ($pH < 3$) [30,31] because the hydroxyl radical is consumed by the excessive hydrogen ion as Reaction (7). When pH value is higher than 3 in this reaction, Fenton oxidizing ability is decreased due to the decomposition of hydrogen peroxide and deactivation of the ferrous catalysts with the formation of ferric hydroxo complexes. Therefore, Fenton process is sensitive to the pH value of the solution in the treatment process of RBB X-BR.



3.3.4. Effect of initial dye concentration

To study the influence of initial dye concentration on color removal and the decolorizing reaction constant k_{ap} , the initial dye concentrations ranging from 9 to 35 $mg L^{-1}$ were investigated in Fig. 9. It is observed that the lower the dye concentrations were, the higher the color removal and k_{ap} for degradation of RBB X-BR are. The rise of dye concentration in aqueous solution increases the number of dye molecules in the water but the hydroxyl radical, so the color removal and the decolorizing constant (k_{ap}) decreases.

3.3.5. Effect of temperature

Temperature is a key parameter impacting the reaction rate. In order to define the influence of reaction temperature on the

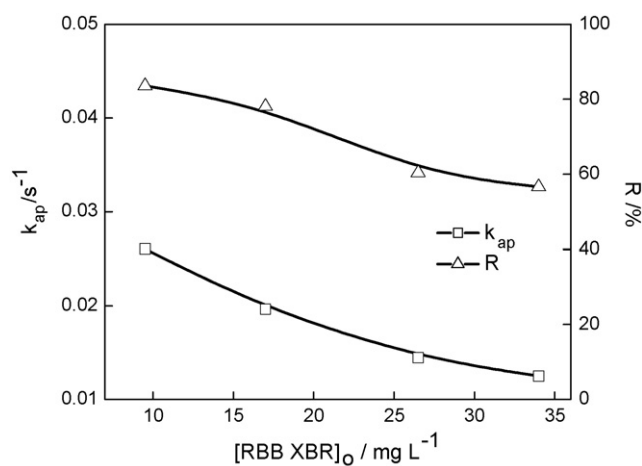


Fig. 9. Influence of initial dye concentrations. $[Fe^{2+}]_0 = 0.1618$ mM, $[H_2O_2]_0 = 3.529$ mM, pH 3, $T = 15^\circ C$.

degradation of RBB X-BR, a series of experiments were put into practice by varying temperature. The results are exhibited in Fig. 10. It is shown that decolorizing reaction rate constant (k_{ap}) of degradation of RBB X-BR increase from 0.01966 to 0.03869 s^{-1} with rising of reaction temperature from 15 to 51 $^\circ C$ in Fenton oxidation. However, the color removal presents a little bit decrease from 78.07% to 71.94%. The production rate of oxidizing species such as $\bullet OH$ or high-valence iron species can possibly be improved because of increased reaction rate constant, which is caused by higher temperature. However, the quantity of oxidizing agent (H_2O_2) does not increase with temperature, and ferrous ion is easily hydrolyzed when H_2O_2 is very instable and thereafter decomposed by itself. The color removal therefore does not increase with the rise of temperature. According to Arrhenius formula ($\ln k_{ap} = (-E_a/RT + \ln A)$), the dependence of $\ln k_{ap}$ on $-1/T$ [32] can be linear fit to calculate the activation energy (E_a) in the similar temperature range. The activation energy of Fenton oxidation is 25.21 $kJ mol^{-1}$ ($R^2 > 0.99$).

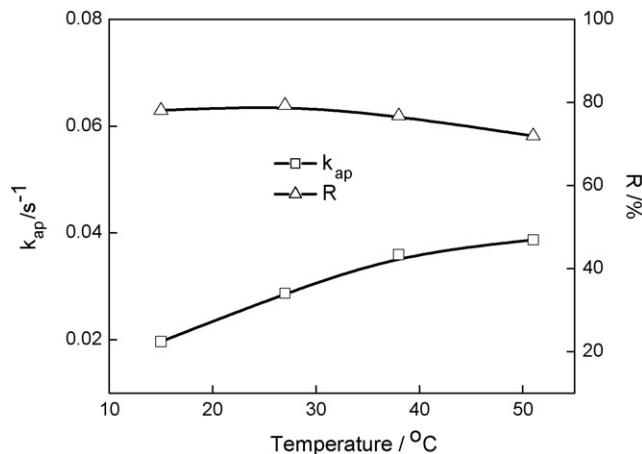


Fig. 10. Influence of temperature. $[RBB X-BR]_0 = 17$ mg/L, $[Fe^{2+}]_0 = 0.1618$ mM, $[H_2O_2]_0 = 3.529$ mM, pH 3.

3.4. Kinetics study

Eqs. (1)–(5) are the main reactions in the early stage. It can be clearly concluded from the reactions that the rate of disappearance of dye may be represented by:

$$-\frac{d[D]}{dt} = k_2[\bullet\text{OH}][D] \quad (8)$$

The concentration of $\bullet\text{OH}$ can be obtained by applying steady-state assumption.

$$\begin{aligned} \frac{d[\bullet\text{OH}]}{dt} &= k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_2[\bullet\text{OH}][D] \\ &\quad - k_3[\text{Fe}^{2+}][\bullet\text{OH}] - k_4[\text{H}_2\text{O}_2][\bullet\text{OH}] - k_5 \\ &\quad [\bullet\text{OOH}][\bullet\text{OH}] = 0 \end{aligned} \quad (9)$$

$$\frac{d[\bullet\text{OOH}]}{dt} = k_4[\text{H}_2\text{O}_2][\bullet\text{OH}] - k_5[\bullet\text{OOH}][\bullet\text{OH}] = 0 \quad (10)$$

$$[\bullet\text{OH}] = \frac{k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{k_2[D] + k_3[\text{Fe}^{2+}] + 2k_4[\text{H}_2\text{O}_2]} \quad (11)$$

Combining Eqs. (8) and (11) yields:

$$-\frac{d[D]}{dt} = \frac{k_1 k_2 [\text{Fe}^{2+}][\text{H}_2\text{O}_2][D]}{k_2[D] + k_3[\text{Fe}^{2+}] + 2k_4[\text{H}_2\text{O}_2]} \quad (12)$$

Therefore, Eq. (12) deduces to

$$\frac{[\text{H}_2\text{O}_2][D]}{(-d[D]/dt)} = \frac{k_3}{k_1 k_2} + \frac{2k_4[\text{H}_2\text{O}_2]}{k_1 k_2 [\text{Fe}^{2+}]} + \frac{[D]}{k_1 [\text{Fe}^{2+}]} \quad (13)$$

Fenton oxidation process apparently follows first-order kinetics, it can be obtained:

$$-\frac{d[D]}{dt} = k_{\text{ap}}[D] \quad (14)$$

In initial reaction condition of Fenton process, conjoining Eqs. (13) and (14) gains:

$$\frac{[\text{H}_2\text{O}_2]_0}{k_{\text{ap}}} = K[D]_0 + B \quad (15)$$

$$B = \frac{k_3}{k_1 k_2} + \frac{2k_4[\text{H}_2\text{O}_2]_0}{k_1 k_2 [\text{Fe}^{2+}]_0} \quad (16)$$

The experimental results in Fig. 11 show the linear relationship between $[\text{H}_2\text{O}_2]_0/k_{\text{ap}}$ and $[\text{RBB X-BR}]_0$ ($R^2 > 0.99$). According to the intercept (B), the calculated intrinsic rate constant (k_2) of RBB X-BR with $\bullet\text{OH}$ in aqueous solution is $7.396 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

3.5. Analysis of products after Fenton oxidation

In order to estimate chemical structure of RBB X-BR after Fenton oxidation experiment, UV-vis, GC-MS and IC were used to study intermediates. The probable mechanism for the decoloration of RBB X-BR was also discussed. The reaction conditions were fixed as follows: dosage of Fe^{2+} was 0.1618 mM; initial H_2O_2 dosage was 3.529 mM; RBB X-BR

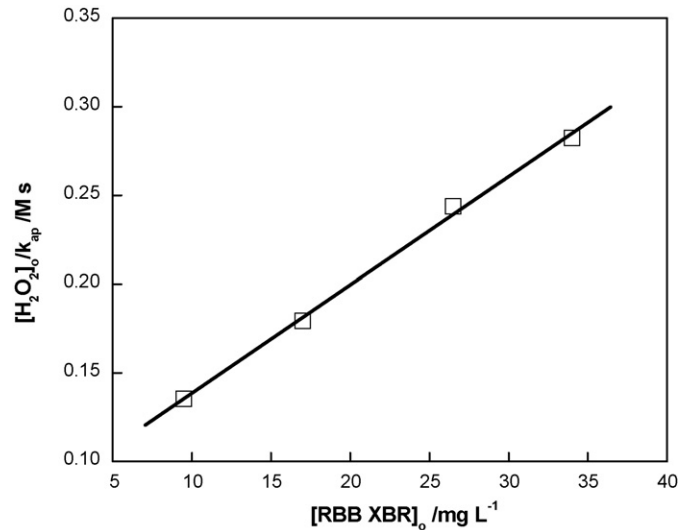


Fig. 11. The relationship between $[\text{H}_2\text{O}_2]_0/k_{\text{ap}}$ and $[\text{RBB X-BR}]_0$. $[\text{Fe}^{2+}]_0 = 0.1618 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 3.529 \text{ mM}$, pH 3, $T = 15^\circ \text{C}$.

concentration was 17 mg L^{-1} ; pH was 3; temperature was 15°C ; reaction time was 300 s.

3.5.1. UV-vis spectrum

As shown in the Fig. 12 about UV-vis spectral changes of dyes during Fenton oxidation, RBB X-BR displays a maximum absorbability ($\lambda_{\text{max}} = 599 \text{ nm}$) in visible spectral range before reaction and there is a great absorbance from 500 to 700 nm. There is no absorbability in visible region but only in ultraviolet area after Fenton oxidation in 300 s. Therefore, decolorization of RBB X-BR wastewater can effectively be achieved. This result that molecule structure of RBB X-BR is totally damaged in Fenton oxidation is revealed. However, strong absorbance in ultraviolet area means that some intermediates and byproducts exist after Fenton oxidation. So, RBB X-BR is not mineralized by Fenton oxidation.

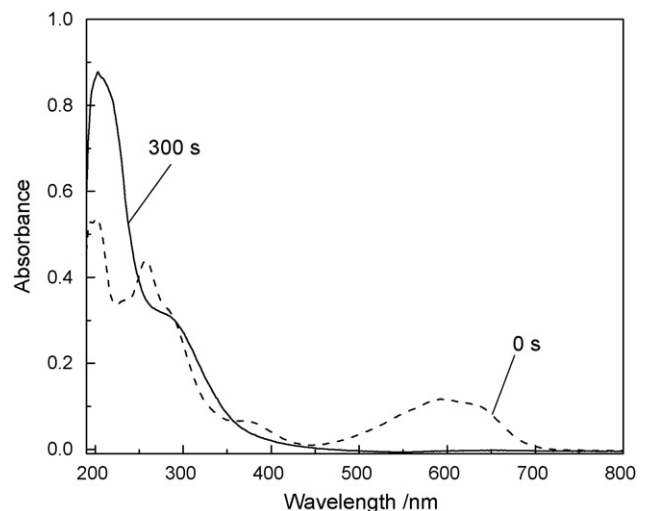


Fig. 12. UV-vis spectral changes of dyes during Fenton oxidation (1: 0 s, 2: 300 s).

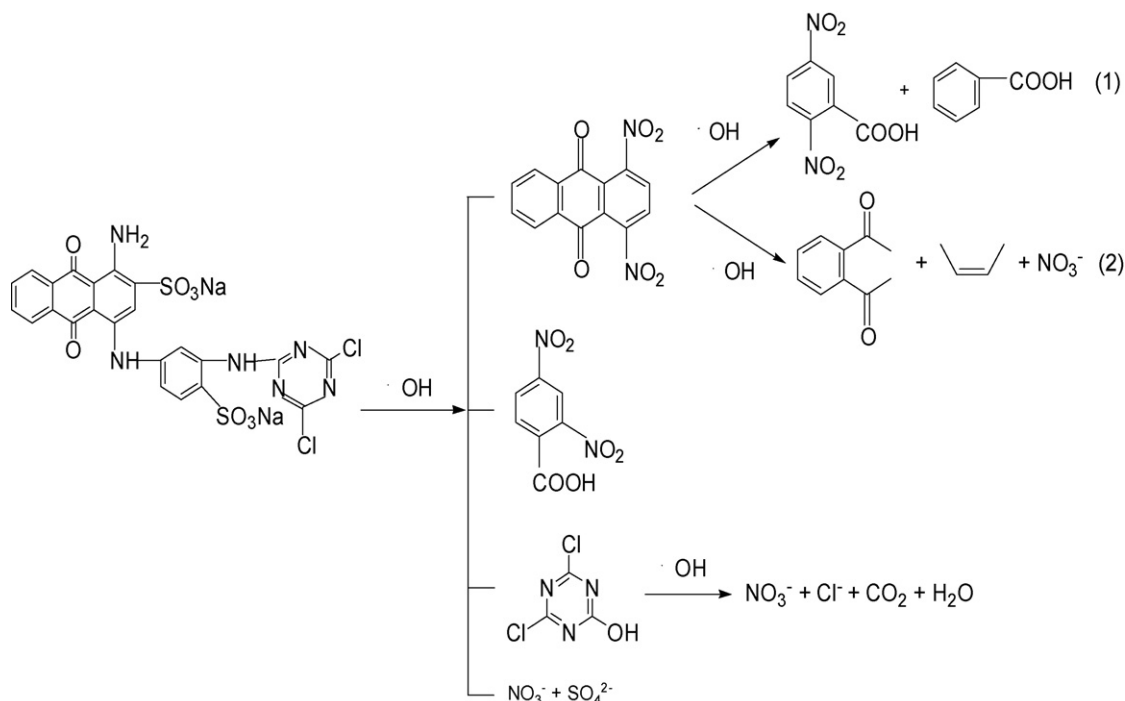


Fig. 13. The possible reaction degradation pathway of RBB X-BR.

3.5.2. Analysis of IC

Inorganic products were analyzed by IC. There are a lot of SO_4^{2-} ions in aqueous solution. It embodies that the chemical structure of RBB X-BR is destructed by Fenton oxidation. However, the result that a little of NO_3^- and Cl^- ions exist in aqueous solution in this process exhibits that the reaction is not thorough in a period shorter than 300 s. If the reaction is fully sufficient, plenty of NO_3^- and Cl^- ions exist in aqueous solution. Therefore, RBB X-BR is not mineralized in short period by Fenton process.

3.5.3. Analysis of GC–MS

In order to study the intermediates and byproducts after Fenton oxidation, analysis of GC–MS about wastewater after Fenton oxidation is showed in Table 1. The result shows that RBB X-BR molecule structure can be effectively damaged. However, there are a lot of colorless intermediate products. The main intermediates are 1,2-diacetylene (retention time: 6.81) and 2,5-dinitrobenzoic acid (retention time: 17.45). According to the GC–MS analysis, the concentrations

of other byproducts are so little that they are ignored. RBB X-BR is not mineralized by Fenton oxidation according to the GC–MS.

3.5.4. The possible reaction degradation pathway of RBB X-BR

According to the GC–MS, the possible reaction pathway for degradation of RBB X-BR is predicted in Fig. 13. The chemical structure of RBB X-BR contains some chemical bonds, C–N and C–S, which are easily destroyed because of low bond energy. Therefore, high active hydroxyl radical firstly attacks and oxidizes these bonds and decomposes the chemical structure. Some primary intermediates can be produced, such as 1,4-dinitroanthracene-9,10-dione, 2,4-dinitrobenzoic acid, 4,6-dichloro-[1,3,5]triazin-2-ol and some inorganic ions. The 1,4-dinitroanthracene-9,10-dione can be oxidized according to two degradation processes. Firstly, the 1,4-dinitroanthracene-9,10-dione can be oxidized to 2,5-dinitrobenzoic acid and benzoic acid. Secondly, it can be decomposed to 1,2-diacetylene, but-2-ene and NO_3^- . The 1,2-diacetylene and 2,5-dinitrobenzoic acid was detected by GC–MS analysis. Although only 2,5-dinitrobenzoic acid was detected by GC–MS, 2,4-dinitrobenzoic acid existed in aqueous after Fenton oxidation because the 2,4-dinitrobenzoic acid and 2,5-dinitrobenzoic acid are isomer. The 4,6-dichloro-[1,3,5]triazin-2-ol was not checked by GC–MS. Maybe it was mineralized by hydroxyl radical. The structure of benzene ring was difficultly decomposed by Fenton oxidation at short 300 s. From the possible degradation mechanism, the chemical structure of RBB X-BR can be decomposed by Fenton's reagent and there are plenty of byproducts yielded after oxidation in limited 300 s.

Table 1
Identified intermediates of degradation of RBB X-BR by Fenton process

RT (min)	Authentic chemical formula
6.81	1,2-Diacetylene ^a
7.40	3,5,5-Trimethylhexanoic acid
14.13	4βH,5α-eremophila-1(10),11-diene
16.53	Phthaic acid, diisobutylester
17.45	2,5-Dinitrobenzoic acid ^a
19.23	<i>trans</i> -8(sup-9)-Octabecenoic acid

^a Main products.

4. Conclusions

Based on the research of RBB X-BR model compound of textile wastewater using Fenton oxidation, the following conclusions can be obtained:

- (1) This study demonstrates that the online spectrophotometric method is a feasible and convenient monitoring technique for investigating color removal of RBB X-BR in Fenton oxidation process. RBB X-BR degradation follows a first-order kinetic law in the early 50 s. The decolorization process can be classified into two periods: faster decolorizing reaction rate is exhibited with high decolorization efficiency in the first period, while the decolorizing reaction rate slows down in the second period.
- (2) The color removal (R) and decolorizing rate constant (k_{ap}) are investigated in Fenton oxidation process. The optimum initial H_2O_2 dosage of RBB X-BR is 3.529 mM. The optimal dosage of Fe^{2+} for color removal is 0.1618 mM. The best pH value is 3. The initial concentration of $FeSO_4$ against k_{ap} presents a linear correlation: $k_{ap} = 0.1354[Fe^{2+}]_0$. The lower the dye concentration, the higher the color removal and k_{ap} . The apparent activation energy of RBB X-BR is 25.21 kJ mol⁻¹ ($R^2 > 0.99$). According to the mechanism of Fenton oxidation, a kinetic modeling has been established to calculate intrinsic reaction rates of $\bullet OH$ and different dyes. The intrinsic rate constant of RBB X-BR in aqueous solution during Fenton oxidation is $7.396 \times 10^{10} M^{-1} s^{-1}$.
- (3) Fenton oxidation can rapidly decompose the chemical structures of RBB X-BR after 300 s, and decolorization of dye wastewater is effectively achieved according to the UV-vis, GC-MS and IC analysis. Nevertheless, there are some intermediates and byproducts existing during the Fenton process. The main intermediate products are 1,2-diacetylene and 2,5-dinitrobenzoic acid. The possible degradation mechanism is predicted. So, mineralization process is not fully performed in limited 300 s.

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