



Review

Oxidation of acidic dye Eosin Y by the solar photo-Fenton processesHuaili Zheng^{a,b,*}, Yunxia Pan^b, Xinyi Xiang^a^a College of Chemistry and Chemical Engineering, Chongqing University, 174 Shapingba Zhengjie, Chongqing 400044, PR China^b Key Laboratory of the Three Gorges Reservoir Region's Eco-Environment, State Ministry of Education, Chongqing University, Chongqing 400045, PR China

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Abstract

Oxidation of acidic dye Eosin Y has been investigated with Fenton process and photo-Fenton process (solar light or artificial light source). With UV-Fenton process and Fenton, 42.5% and 21.3% of dye could be removed from the water, respectively. However, 94.1% of dye was removed in solar-Fenton in 90 min. Based on solar-Fenton process, the effect of pH value and the concentration of dye, Fe²⁺, H₂O₂ as well as oxalic acid concentration on Eosin Y degradation efficiency were investigated. In 60 min, 96% of Eosin Y was degraded when the pH value was 3.5 and the concentration of Fe²⁺, H₂O₂ and oxalic acid was 10 mol/L, 600 mg/L and 300 mg/L, respectively. The Eosin Y degradation was dependent on the dye concentration. That is higher Eosin Y concentration resulted in lower degradation efficiency. Under the conditions of pH 3.5, the Eosin Y apparent kinetics equation was $-dC/dt = 0.000249[\text{Eosin Y}]^{0.78}[\text{Fe}^{2+}]^{1.14}[\text{H}_2\text{O}_2]^{1.26}$. Meanwhile, this research also proved that oxalic acid could improve the photocatalytic efficiency in the solar-Fenton process.

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Keywords: Acidic dye; Eosin Y; Solar-Fenton process; Fenton process; Decolorization**Contents**

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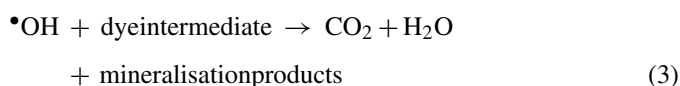
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1. Introduction

Eosin Y, a heterocyclic dye containing bromine atoms, is used in the fields of dyeing, printing, leather, printing ink and fluorescent pigment, etc. The direct release of wastewater containing Eosin Y will cause serious environmental problem due to its dark color and toxicity [1]. Traditional techniques, such as coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis) or absorption of activation carbon, are only based on a phase transfer of the pollutant. Biological methods are also ineffective to decolorization of Eosin Y for its stability and complex aromatic structure [2–5]. Recently, advanced oxidation processes (AOPs) were developed to oxidize organic compound into CO₂, H₂O and inorganic ions, or biodegradable compounds [6]. These methods are environmentally friendly. Therefore, AOPs are considered as promising treatment methods to wastewater.

Among AOPs, homogeneous Fenton reaction, the Fe²⁺/H₂O₂ system, is one of the most important processes to generate •OH radicals [7]. This reaction is easy and no sludge generation. Thus, it has been widely used to degrade pollutants [8,9]. Hydroxyl radical is a powerful oxidant that can rapidly and non-selectively oxidize organic contaminants into carbon dioxide and water [10,11], so it is able to degrade pollutants effectively [12–14]. Photo-Fenton is another effective method to degrade pollution. Xu reported that dyes decolorization could be accelerated by the combination of UV and Fenton's process because it produced •OH radical directly (Eqs. (1–3)) [15].



UV is the most commonly employed light source in photo-assisted oxidation processes, but the cost is high to generate UV for artificial light. Therefore, sunlight is considered as economical light source. However, H₂O₂ has low molar extinction coefficient and partly absorbs UV above 320 nm, so photo-Fenton process can only use photons of wavelength up to 400 nm, which only represent minority of total solar radiation [16]. Ferrioxalate was found to be able to expand the usage of solar spectrum range in solar-Fenton process, which resulting in the oxidation efficiency improvement of organic contaminants [17,18]. Ferrioxalate has been widely used as a chemical actinometer for decades. In recent years, it was also applied in the degradation of contaminants [6,18,19]. Arslan et al. [19] reported that decolorization of the ferrioxalate-photo-Fenton process was three times faster than the photocatalytic process. Nogueira et al. [6] also found that the degradation of DCA and the herbicides diuron and tebuthiuron is most efficient when ferrioxalate was used. Despite of the ferrioxalate beneficial effect in photo-Fenton process, the addition of oxalate has been considered as disadvantageous due to the increase of carbon load in the system. However, due to the complete conversion of oxalate

to CO₂ no net increase of carbon is expected [6]. Hence, ferrioxalate is expected to play important role in degradation of contaminants in photo-Fenton process.

Eosin Y is used in the dyeing industries because of its vivid color. The effective treatment of this effluent is eco-friendly to aqueous environment. But there is no report on the degradation of this dye which using Fenton or (and) photo-Fenton processes up to now. In practical use of these processes in wastewater treatment, there is a need to determine the optimal experimental parameters for color removal. Here, we investigated the influences of various factors (pH, H₂O₂ and Fe²⁺ dosage, dye and oxalic acid concentration) on the Eosin Y degradation based on solar-Fenton process. Furthermore, we compared the effect of light sources on the Eosin Y decolorization by Fenton process and photo-Fenton process (solar light or artificial light source). The degradation of Eosin Y in a Fe²⁺/C₂O₄²⁻/H₂O₂ system was also examined to reveal some details on interaction of Eosin Y with Fe²⁺.

2. Experimental

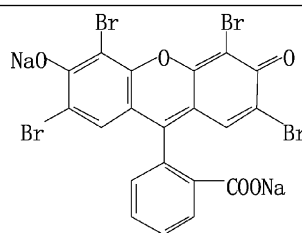
2.1. Materials

Eosin Y was purchased from the Third Reagent Ltd., Shanghai, PR China. Its chemical characteristic is illustrated in Table 1. H₂O₂ (30% w/w), FeSO₄·7H₂O, Na₂SO₃ and H₂C₂O₄ were also from the Third Reagent Ltd., Shanghai, PR China. All solutions were prepared with distilled water. The pH of the dye solution was adjusted with HCl (0.1 mol/L) or NaOH (0.1 mol/L).

2.2. Irradiation experiments

In solar-Fenton process, all photocatalytic experiments were carried out under similar conditions on July or August sunny days between 11 a.m. and 16 p.m. in Chongqing, China. Solar irradiation was carried out under the open-air condition. Solar light intensity was measured for every 60 min and the average light intensity over the duration of each experiment was calculated. The sensor was always set in the position of maximum intensity. The intensity of solar light was measured using TES-1332A Digital illuminance meter (Fig. 1). It was nearly constant during the experiments. In UV-Fenton process, all

Table 1
Characteristics of Eosin Y

Name	λ (nm)	Molecular weight (g/mol)	Chemical structure
Eosin Y	515	560.0	

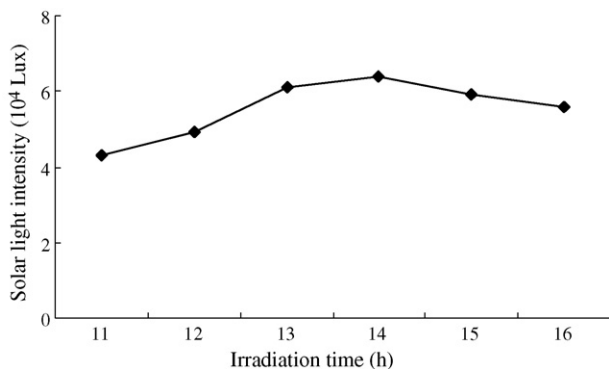


Fig. 1. Change of solar light intensity with time in Chongqing (between 11 a.m. and 16 p.m. on July or August sunny days).

experiments were conducted using 500 mL of reaction solution in 600 mL Pyrex Erlenmeyer flask reactors open to atmosphere. The reactor was inserted into a chamber equipped with a 450 W high-pressure mercury lamp (365 nm). Its light intensity was 5.61×10^4 lx. UV–Fenton process and Fenton process were performed in thermostat water bath of 45 °C. The reaction time was recorded when the UV lamp was turned on.

2.3. Analysis

$\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{Eosin Y}$ solution with different concentration was freshly prepared with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2O_2 and dye stock solution. The initial pH of the dye solutions was adjusted to 5.0 with 0.1 mol/L HCl or NaOH. During periodic intervals, samples of reacting dye solution were withdrawn, and analyzed in a UV–vis scanning spectrum 200–800 nm, using a UV/Vis spectrophotometer, Model GBC Cintra 10e, manufactured by Australia. Na_2SO_3 solution was used to quench the oxidation of Fenton reaction before the spectrophotometer analyzed. Initial COD (before oxidation) and the COD after one hour of oxidation were measured according to an EPA approved reactor digestion method (for a COD range of 0–1500 mg/L) using HACHDR2000. Concentration of dye solution at different times were obtained by surveying the absorbance at maximum wavelength ($\lambda_{\text{max}} = 515$ nm) and computing from calibration curve (Fig. 2).

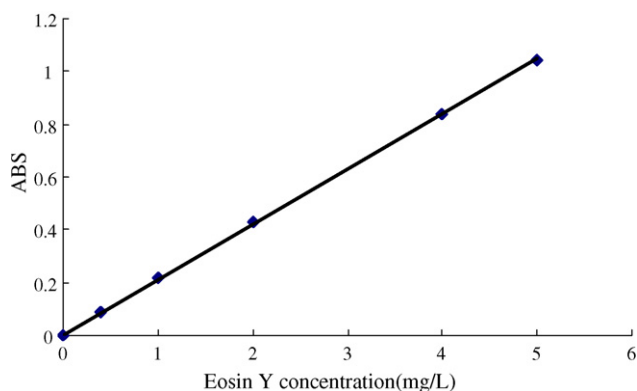


Fig. 2. Standard work curve of Eosin Y at wavelength of 515 nm.

Dye decolorization was analyzed as follows:

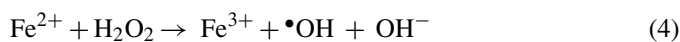
$$\text{dye decolorization (\%)} = \frac{1 - C_{\text{dye},t}}{C_{\text{dye},0}} \times 100$$

where $C_{\text{dye},t}$ and $C_{\text{dye},0}$ are the concentrations of dye at reaction time t and 0, respectively. Toxicity tests were carried out using cabbage seed germination.

3. Results and discussion

3.1. Effect of different light source

The purpose of the experiment was to investigate the effect of light sources on the Eosin Y decolorization by Fenton process and photo-Fenton process (solar light or artificial light source). Fig. 3 showed that color removal was 21.3% in Fenton and 95.3% or 50% in photo-Fenton process (solar light or artificial light source) at 120 min. This indicated that photo-Fenton process is more efficient than Fenton process. This result was consistent with as previously described [1,20]. However, lower decolorization rate in Fenton shared much lower similarity with as reported previously [11,21]. This may be due to the elimination of adjacent aromatic ring structure is much more difficult than that of N=N bonds. As [22] pointed out, $\bullet\text{OH}$ radicals can react with most organic compounds by hydrogen abstraction or addition to double bonds. Thus, in case of Eosin Y, $\bullet\text{OH}$ radicals destruct the long conjugated π systems, and consequently causing decolorization. The high efficiency of photo-Fenton process is due to the production of more hydroxyl radicals than the Fenton process. The generation of hydroxyl radical in the Fenton process is due to ferrous ion catalyses decomposition of H_2O_2 (Eq. (4)) [23].



Whereas in photo-Fenton processes, the major reactions of the formation of $\bullet\text{OH}$ radical include Fenton reaction (Eq. (4)), photolysis of hydrogen peroxide (Eq. (1)) and photoreduction of ferric ion (Eq. (5)).

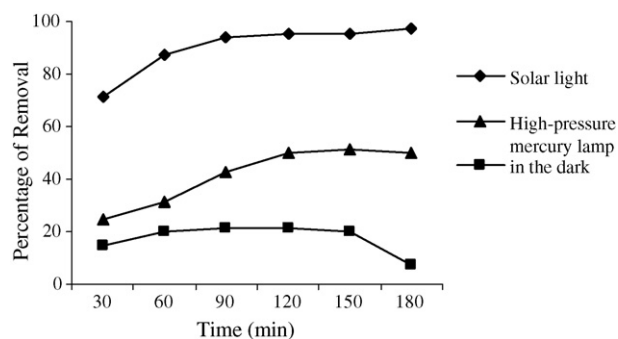
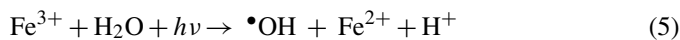
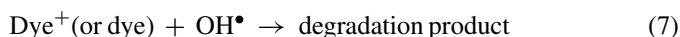
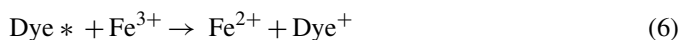


Fig. 3. Removal of Eosin Y under different conditions. (◆) Fenton process with solar light, (■) Fenton process, (▲) Fenton process with 450 W high-pressure mercury lamp (Eosin Y: 20 mg/L; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 5 mg/L; H_2O_2 : 600 mg/L; pH 5.0).

In addition, Fe(III)-peroxy complexes formed by photolysis of Fe(III) + H₂O₂ may also directly attack dye molecule, and accelerate decolorization of Eosin Y (Eqs. (6) and (7)) [4].



Initially, rapid decolorization of photo-Fenton processes is due to the fast reaction of Fe²⁺ with H₂O₂ producing hydroxyl radicals. While in Fenton process, the decrease of color removal rate in 180 min may be due to the color resurgence.

In solar-Fenton process, the color removal rates were 71.2%, 87.5% and 94.1% at 30, 60 and 90 min, respectively. In UV-Fenton process, 25%, 31.3% and 42.5% of decolorization were obtained, respectively. This suggested that solar-Fenton process is more efficient than UV-assisted Fenton process. Because photocatalytic wavelength arranges from 310 to 550 nm [3], and that solar-Fenton reaction makes use of ultraviolet and visible spectrum (200–800 nm). While UV-Fenton process (365 nm) only uses a little part of the UV-vis spectrum. Hence, solar-Fenton reaction can take full advantage of photons to produce more hydroxyl radical. Therefore, compared to UV-Fenton, the decolorization rate of solar-Fenton process obviously increased.

Solar energy is an abundant natural energy source. Solar-Fenton process can make use of sunlight instead of artificial light, which accordingly reduces the operating costs and is eco-friendly to the environment. Therefore, solar-Fenton process is a promising process.

3.2. Effect of H₂O₂ dosage

In solar-Fenton reaction, H₂O₂ concentration affects the decolorization of Eosin Y, and its optimal concentration may also reduce the operating cost. Fig. 4 showed that the color removal increased from 87% to 94.1% at 90 min with the addition of H₂O₂ from 300 mg/L to 600 mg/L, which resulted from more •OH radicals produced with the addition of more H₂O₂. However, as H₂O₂ concentration was exceeded 600 mg/L, the decolorization of Eosin Y had no significant change (only elevated 1.8%), which was similar to those reported by many researchers [7,8]. This is due to the fact that scavenging of •OH

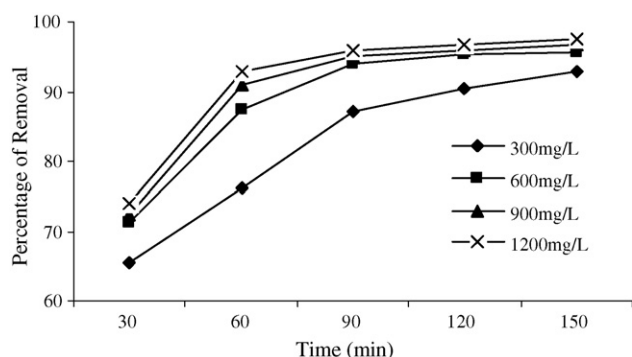
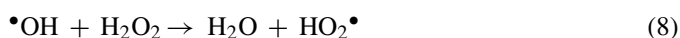


Fig. 4. Effect of the addition of H₂O₂ on the removal of Eosin Y (Eosin Y: 20 mg/L; FeSO₄·7H₂O: 5 mg/L; pH 5.0; under solar light).

radicals will occur at a higher H₂O₂ concentration as expressed by the following equation [24]:



The scavenging effect occurred decreases the number of •OH radicals in the reaction system. As a result, color removal rate was not significantly increased.

All of decolorization efficiency was close to 96% after reaction terminated (Fig. 4). This suggested that overall decolorization rate had no difference after 150 min in spite of the different initial color removal rate each other. Hence, 600 mg/L of H₂O₂ dosage is an optimal dosage.

3.3. Effect of ferrous dosage

The effect of different Fe²⁺ concentration on the decolorization of Eosin Y has been investigated. The results are shown in Fig. 5. Decolorization was faster in the early stage of the reaction than that in the later stage, since ferrous ion catalyses H₂O₂ to form hydroxyl radical quickly in initial stage of the reaction. Color removal increased from 87.5% to 96.5% with the addition of Fe²⁺ from 5 mg/L to 10 mg/L at 60 min. This indicated that Fe²⁺ as a catalyst can significantly accelerate the decomposition of H₂O₂. The increase in decolorization is due to production of more •OH radicals. However, color removal decreased as Fe²⁺ concentration increased from 10 mg/L to 20 mg/L. This suggested that excessive Fe²⁺ has a negative effect on decolorization of Eosin Y. The decrease in decolorization at high Fe²⁺ dosage is due to Fe²⁺ competing •OH with dye molecules, which can be expressed by the Eqs. (7) and (11):



In addition, color resurgence caused by Fe²⁺ intermediate may also lead to the decrease of decolorization. Meanwhile, high Fe²⁺ dosage increased additional flocculation treatment in practice. Therefore, Fe²⁺ concentration should be controlled properly to gain desired decolorization during reaction period.

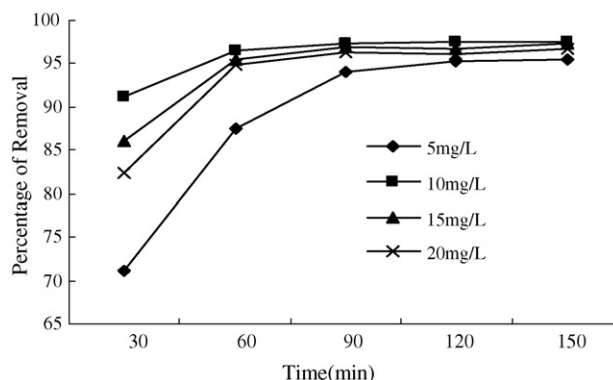


Fig. 5. Effect of the addition of Fe²⁺ on the removal of Eosin Y (Eosin Y: 20 mg/L; H₂O₂: 600 mg/L; pH 5.0; under solar light).

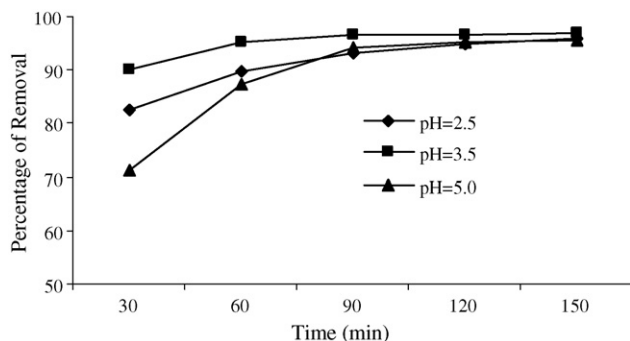


Fig. 6. Effect of pH on the removal of Eosin Y (Eosin Y: 20 mg/L; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 5 mg/L; H_2O_2 : 600 mg/L; under solar light).

10 mol/L of Fe^{2+} can be used as an optimum dosage for solar-Fenton process.

3.4. Effect of initial pH value

The pH is an important parameter for decolorization of Eosin Y. It affects the formation of $\bullet\text{OH}$ and the concentration of Fe^{2+} . Kang et al. [25] reported that photo-Fenton process could remove pollutants under acidic condition. A similar trend was found in the decolorization of Eosin Y. Fig. 6 showed that maximum decolorization efficiency in 30 min was up to 90% at pH 3.5. But color removal rate were only 82.4% and 71.2% at pH 2.5 and 5.0, respectively. Hence, pH 3.5 was found to be the optimum pH in the solar-Fenton process. The decrease in decolorization at pH 5.0 is owing to the fact that the coagulation of Fe^{3+} complex formed in the reaction reduced the catalysis of Fe^{2+} . The low removal rate at pH 2.5 is due to the hydroxyl radical scavenging effects of H^+ ions (Eq. (12)) [11].



In addition, the low pH will produce higher neutral treatment cost. Therefore, pH 3.5 is the optimum pH in the solar-Fenton process.

3.5. Effect of dye concentration

Fig. 7 showed that decolorization of Eosin Y significantly decreased as dye concentration increased from 10 mg/L to

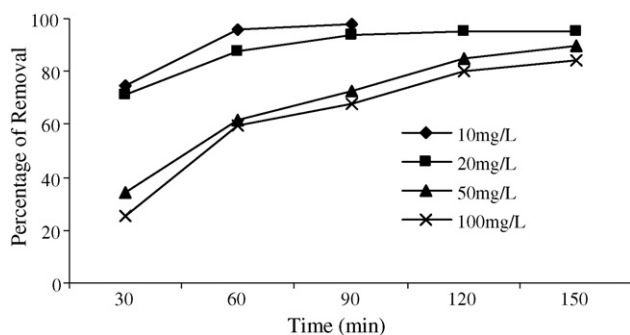
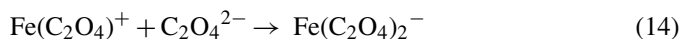
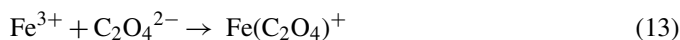


Fig. 7. Effect of dye concentration on the removal of Eosin Y ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 5 mg/L; H_2O_2 : 600 mg/L; pH 5.0; under solar light).

100 mg/L. Decolorization of 10 mg/L Eosin Y was almost complete at 90 min and color removal rate was up to 98%. However, as dye concentration were 20 mg/L, 50 mg/L and 100 mg/L, only 94.1%, 72.6% and 68% of decolorization, respectively, were obtained. This is because that dye concentration increases, but $\bullet\text{OH}$ does not increase accordingly, which caused the decreased removal rate. In addition, in solar-Fenton process, high dye concentration also reduces the penetrability of photons into dye solution, decreasing $\bullet\text{OH}$ radical production. In the case of high concentration dye solution, although coagulation of Fe^{3+} complex could accelerate color removal, it also shielded Fe^{3+} ion, resulting in the termination of photoredox reaction. Hence, photo-Fenton process degrades dyes more efficiently at a lower dye concentration.

3.6. Effect of oxalic acid dosage

Kositzia et al. and Arslan et al. reported that ferrioxalate complex could expand a broad range of wavelengths and increase absorption of solar UV–vis fraction [19,26]. In order to investigate its effect on photocatalytic degradation of Eosin Y, different concentrations of oxalic acid were added into the reaction system, respectively. The results were shown in Fig. 8. When oxalic acid increased from 0 mg/L to 600 mg/L, color removal increased from 71.2% to 89.7% at 30 min. The result was agreed with early reports [19,26,27]. This is due to the fact that the increased oxalic acid results in a faster ferrioxalate formation. As Wu et al. reported [28], in the presence of oxalate, and pH ranges from 3 to 5, Fe(III)-oxalate complexes are the predominant dissolved species as follows:



The complexation of oxalate not only increases the quantum yield for the photoreduction of Fe^{3+} from 0.14 to 1.2 at 313 nm but also extends the absorption band into the visible region to some extent and increases the absorption coefficient. As a sequence, the absorption of UV light increases. Under UV light irradiation, $\text{Fe}(\text{C}_2\text{O}_4)_3^{2-}$ could effectively convert Fe^{3+} ion into Fe^{2+} ion (Eq. (16)), and the generated Fe^{2+} ion reacts with

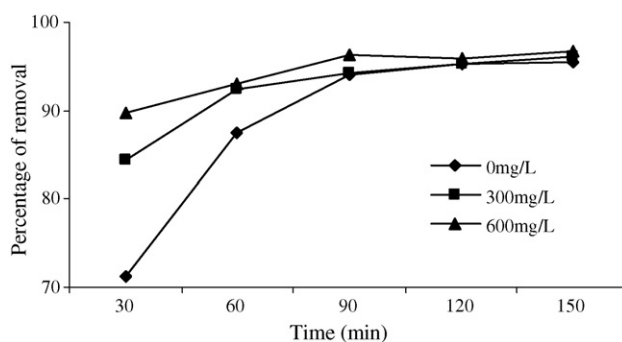
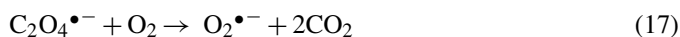
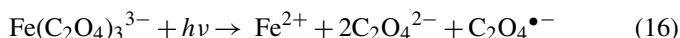


Fig. 8. Effect of the addition of oxalic acid on the removal of Eosin Y (Eosin Y: 20 mg/L; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 5 mg/L; H_2O_2 : 600 mg/L; pH 5.0; under solar light).

H₂O₂ as Eq. (4) to form •OH radicals. As a result, the number of •OH radicals formed increases substantially, giving rise to a higher color removal. In addition, under UV irradiation, main Fe(C₂O₄)₃³⁻ could also produce H₂O₂ ((Eqs. (16)–(18)) [29], providing a continuous source for photo-Fenton process. Meanwhile, oxalic acid may also adjust the pH of dye solution [30].

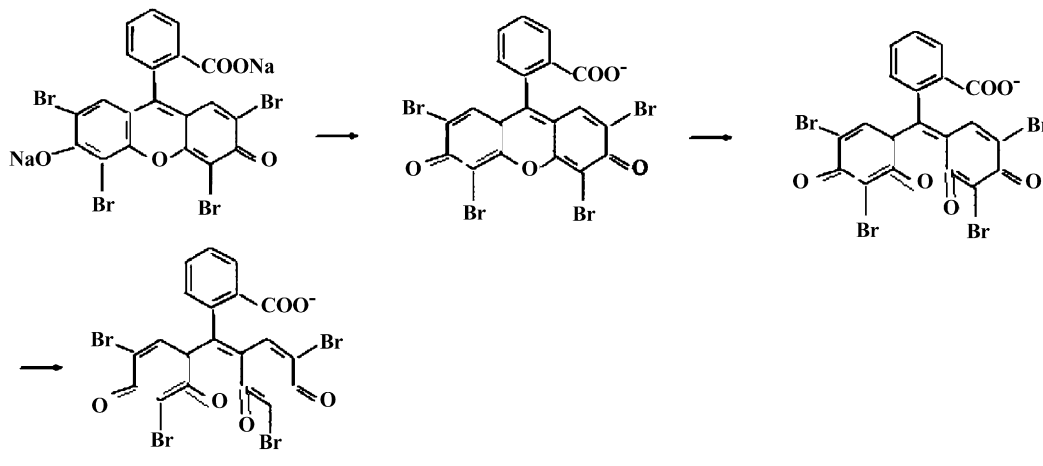


Hence, the addition of oxalic acid can not only promote the degradation of dye, but also reduce treatment cost.

However, excessive oxalic acid has negative effect on the decolorization of Eosin Y. Because CO₂ produced in Eq. (17) can be converted to CO₃²⁻ or HCO₃⁻ in acidic solution. They may scavenge hydroxyl radical and color removal was decreased accordingly. So, the decolorization of Eosin Y did not increase significantly after 90 min. Therefore, the optimum concentration of oxalic acid was 300 mg/L for lower operation cost and higher color removal.

3.7. Oxidation of Eosin Y

To study the oxidation of Eosin Y, UV–vis absorption spectra of 20 mg/L Eosin Y solution were considered before and



after the treatment with solar-Fenton process (Fe²⁺ = 10 mg/L, H₂O₂ = 600 mg/L, oxalic acid = 300 mg/L, pH 3.5). As it could be observed in Fig. 9, the UV band at 515 nm became smaller as the irradiation time increased until no signal was detected. No additional UV–vis signals were detected in the sample analysis, meaning that no radiation absorbing intermediates at this wavelength was generated. Nevertheless, a generation of intermediates could be detected by COD. Removal rate of COD was 82.7% after the reaction ended. This indicated that the majority of dye was mineralized by the Fenton's reagent. In the earlier stages of the solar-Fenton process, •OH radicals firstly attack the C=C conjugated bond of Eosin Y, then break ether linkage, as the process runs, macromolecular Eosin Y is oxidized to micromolecule up to almost complete mineralization at the

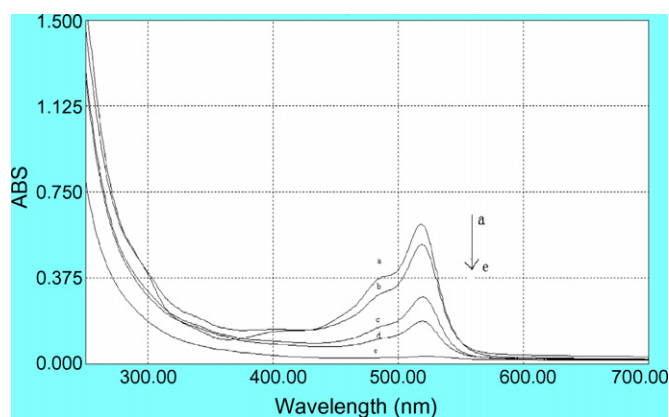


Fig. 9. Change of UV–vis spectra of Eosin Y in solar-Fenton process (Eosin Y: 20 mg/L; FeSO₄·7H₂O: 10 mg/L; H₂O₂: 600 mg/L; oxalic acid: 300 mg/L; reaction time = 1 h; pH 3.5. a = 0 min, b = 15 min, c = 30 min, d = 45 min, e = 60 min).

end of the experiment. The advanced oxidation process can be justified if the generated intermediates are easily biodegradable. Chacón et al. [31] have studied the relation between color and toxicity, they thought that the trend of toxicity was agreed with colorant degradation. Once the color had been depleted and the toxicity reduced. Our toxicity tests result is consistent with their description. The ratio of seed germination after dye treatment is almost the same as the control. This indicates that coupling photocatalysis with biological degradation could be an interesting issue to the treatment of dye wastewater.

3.8. Analysis of photodegradation kinetics

The initial concentrations of various factors and corresponding v_0 could be described as the equation $v_0 = -dC/dt = kC_0^a$. The apparent kinetics equations were obtained under the experimental conditions (Table 2). The results showed that the initial rate of Eosin Y photodegradation increased with increasing the concentrations of each component, respectively. The initial rates v_0 obtained was fitted against corresponding [Eosin Y]^{0.78}[Fe²⁺]^{1.14}[H₂O₂]^{1.26} according to linear equation (5 mg/L [Fe²⁺] < 20 mg/L, 300 mg/L < [H₂O₂] < 1200 mg/L), the apparent kinetics equation $-dC/dt = 0.000249[\text{Eosin Y}]^{0.78}[\text{Fe}^{2+}]^{1.14}[\text{H}_2\text{O}_2]^{1.26}$ was obtained. To verify the proposed model, the experimental data and modeled curves are

Table 2
Kinetics analysis of the photodegradation of Eosin Y

Parameters	Concentration (mg/L)	Initial rate v_0 (mg/L min)	Kinetics equation
H_2O_2 ([Eosin Y] = 20 mg/L, $[\text{Fe}^{2+}]$ = 10 mg/L, pH 3.5)	300	13.567	$-\text{dC}/\text{dt} = 1.192[\text{H}_2\text{O}_2]^{1.26}$
	600	16.367	
	900	33.333	
	1200	63.367	
Fe^{2+} ([Eosin Y] = 20 mg/L, $[\text{H}_2\text{O}_2]$ = 600 mg/L, pH 3.5)	5	11.767	$-\text{dC}/\text{dt} = 1.573[\text{Fe}^{2+}]^{1.14}$
	10	16.367	
	15	28.033	
	20	64.1	
Eosin Y ([H_2O_2] = 600 mg/L, $[\text{Fe}^{2+}]$ = 10 mg/L, pH 3.5)	10	11.067	$-\text{dC}/\text{dt} = 1.698[\text{Eosin Y}]^{0.78}$
	20	16.7	
	50	33.3	
	100	68.5	

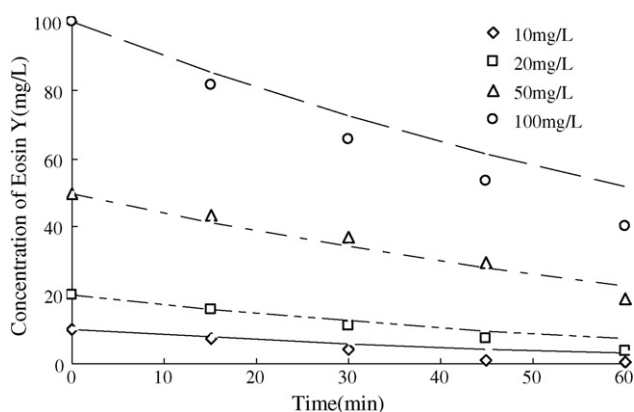


Fig. 10. Comparison of the experimental data (symbols) with the model calculation (dashed lines) at the different Eosin Y concentration ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 10 mg/L; H_2O_2 : 600 mg/L, pH 3.5).

compared in Fig. 10, where the curves show a good fit to the experimental data. Comparing the reaction orders in the kinetics equation, H_2O_2 had the largest power (1.26) and Eosin Y had the lowest power (0.78), which implied that H_2O_2 was the dominant factor in determining the removal efficiency of Eosin Y by the solar-Fenton process. Therefore, an efficient way to improve the decolorization of Eosin Y in practice is to increase the concentration of H_2O_2 , as a smaller $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio leads to a higher overall oxidation of Eosin Y.

4. Conclusion

In this study, the decolorization of Eosin Y has been studied by applying homogeneous Fenton process and photo-Fenton processes. Based on the above-mentioned results, the following conclusions can be drawn.

1. Photo-Fenton processes were more efficient than Fenton process for color removal. In photo-Fenton processes, solar-Fenton reaction could significantly increase color removal

and reduce the operating cost. Decolorization rate of solar-Fenton process was increased by 40% over that of artificial light source.

2. In solar-Fenton process, the H_2O_2 dosage dominated the overall efficiency of color removal. 600 mg/L of H_2O_2 showed satisfactory color removal rate.
3. The ferrous as catalyst accelerated the color removal during the initial reaction period. Fe^{2+} concentration of 10 mg/L could be used as an optimum dosage for solar-Fenton process.
4. The optimum pH for both the formation of $\bullet\text{OH}$ and color removal was 3.5.
5. The degradation of Eosin Y decreased with the increasing of dye concentration.
6. Oxalic acid played dual roles in photo-Fenton reaction. It not only increased the absorption of UV light but also enhanced the color removal. In addition, oxalic acid could adjust the pH of dye solution and reduced operation cost. The optimum concentration of oxalic acid was 300 mg/L in the experiment.
7. Under the above conditions, the apparent kinetics equation $-\text{dC}/\text{dt} = 0.000249[\text{Eosin Y}]^{0.78}[\text{Fe}^{2+}]^{1.14}[\text{H}_2\text{O}_2]^{1.26}$ was obtained.

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References

- [1] M. Muruganandham, M. Swaminathan, Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology, *Dyes Pigments* 63 (2004) 315–321.
- [2] M. Kositz, A. Antoniadis, I. Poulios, I. Kiridis, S. Malato, Solar photocatalytic treatment of simulated dyestuff effluents, *Solar Energy* 77 (2004) 591–600.
- [3] M. Pérez, F. Torrades, X. Domènech, J. Peral, Fenton and photo-Fenton oxidation of textile effluents, *Water Res.* 36 (2002) 2703–2710.

- [4] Y. Xie, F. Chen, J. He, Z. Jincai, H. Wang, Photoassisted degradation of dyes in the presence of Fe^{3+} and H_2O_2 under visible irradiation, *J. Photochem. Photobiol. A* 136 (2000) 235–240.
- [5] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigments* 71 (2006) 235–243.
- [6] R.F.P. Nogueira, M.R.A. Silva, A.G. Trovó, Influence of the iron source on the solar photo-Fenton degradation of different classes of organic compounds, *Solar Energy* 79 (2005) 384–392.
- [7] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, Discoloration and mineralization of Reactive Red HE-3B by heterogeneous photo-Fenton reaction, *Water Res.* 37 (2003) 3776–3784.
- [8] M. Muruganandham, M. Swaminathan, Advanced oxidative decolourisation of Reactive Yellow 14 azo dye by UV/ TiO_2 , UV/ H_2O_2 , UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ processes—a comparative study, *Sep. Purif. Technol.* 48 (2006) 297–303.
- [9] P.K. Malik, S.K. Saha, Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Sep. Purif. Technol.* 31 (2003) 241–250.
- [10] M. Muruganandham, M. Swaminathan, Solar driven decolourisation of Reactive Yellow 14 by advanced oxidation processes in heterogeneous and homogeneous media, *Dyes Pigments* 72 (2007) 137–143.
- [11] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigments* 71 (2006) 235–243.
- [12] I.B.S. Will, J.E.F. Moraes, A.C.S.C., photo-Fenton degradation of wastewater containing organic compounds in solar reactors, *Sep. Purif. Technol.* 34 (2004) 51–57.
- [13] H. Zheng, X. Xiang, Photo-Fenton oxidation processes used in the degradation of Rhodamine B, *Spectrosc. Spectral Anal.* 24 (2004) 726–729.
- [14] X. Xiang, H. Zheng, A review of Fenton oxidation used in degradation of dyes, *Chongqing Jianzhu Univ.* 26 (2004) 126–130.
- [15] Y. Xu, Comparative studies of the $\text{Fe}^{3+/2+}$ -UV, H_2O_2 -UV, TiO_2 /UV/VIS systems for the decolourization of a textile dye X-3B in water, *Chemosphere* 43 (2001) 1103–1107.
- [16] P.L. Huston, J.J. Pignatello, Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction, *Water Res.* 33 (1999) 1238–1246.
- [17] R.F.P. Nogueira, J.R. Guimarães, Photodegradation of dichloroacetic acid and 2,4-dichlorophenol by ferrioxalate/ H_2O_2 system, *Water Res.* 34 (2000) 895–901.
- [18] C.A. Emilio, W.F. Jardim, M.L. Litter, H.D. Mansilla, EDTA destruction using the solar ferrioxalate advanced oxidation technology (AOT): comparison with solar photo-Fenton treatment, *J. Photochem. Photobiol. A* 151 (2002) 121–127.
- [19] I. Arslan, I.A. Balcioglu, D.W. Bahnemann, Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate-Fenton/UV-A and TiO_2 /UV-A processes, *Dyes Pigments* 47 (2000) 207–218.
- [20] M. Neamtu, A. Yediler, I. Siminiceanu, M. Macoveanu, A. Kettrup, Decolorization of disperse red 354 azo dye in water by several oxidation processes—a comparative study, *Dyes Pigments* 60 (2004) 61–68.
- [21] R. Liu, H.M. Chiu, C.-S. Shiau, R. Yu-Li Yeh, Y.-T. Hung, Degradation and sludge production of textile dyes by Fenton and photo-Fenton processes, *Dyes Pigments* 73 (2007) 1–6.
- [22] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}^-$) in aqueous solutions, *J. Phys. Chem. Ref. Data* 17 (1988) 513–586.
- [23] H.J.H. Fenton, Oxidation of tartaric acid in the presence of iron, *J. Chem. Soc. Lond.* 65 (1894) 899–910.
- [24] C.-L. Hsueh, Y.-H. Huang, C.-C. Wang, C.-Y. Chen, Photoassisted fenton degradation of nonbiodegradable azo-dye (Reactive Black 5) over a novel supported iron oxide catalyst at neutral pH, *J. Mol. Catal. A Chem.* 245 (2006) 78–86.
- [25] S.-F. Kang, C.-H. Liao, S.-T. Po, Decolorization of textile wastewater by photo-Fenton oxidation technology, *Chemosphere* 41 (2000) 1287–1294.
- [26] M. Kositzia, I. Poullos, S. Malato, J. Caceres, A. Campos, Solar photocatalytic treatment of synthetic municipal wastewater, *Water Res.* 38 (2004) 1147–1154.
- [27] A. Safarzadeh-Amiri, J. Bolton, S. Catter, Ferrioxalate-mediated photo-degradation of organic pollutants in contaminated water, *Water Res.* 31 (1997) 787–798.
- [28] K. Wu, Y. Xie, J. Zhao, H. Hidaka, Photo-Fenton degradation of a dye under visible light irradiation, *J. Mol. Catal. A Chem.* 144 (1999) 77–84.
- [29] X. Yinde, C. Feng, H. Jianjun, J. Zhao, Recent advance in photo-Fenton reaction, *Photogr. Sci. Photochem.* 18 (2000) 357–365.
- [30] Y. Zuo, J. Holgne, Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of Iron(III)-oxalate complexes, *Environ. Sci. Technol.* 26 (1992) 1014–1022.
- [31] J.M. Chacón, Ma.T. Leal, M. Sánchez, E.R. Bandala, Solar photocatalytic degradation of azo-dyes by photo-Fenton process, *Dyes Pigments* 69 (2006) 144–150.