

# Degradation of the dye X-3B by UV/Fe(III)-generated hydroxyl radicals in aqueous solution

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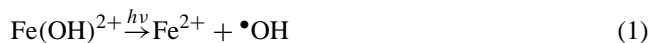
## Abstract

Bleaching of the dye, Reactive Brilliant Red X-3B, by irradiation with light at  $\lambda \geq 320$  nm in an air-saturated aqueous solution of Fe(III) species was investigated under various conditions. It was observed that the dye, quite stable to the UV light, could be degraded efficiently when it was irradiated in the ferric solution. The initial rate degradation was almost independent of the initial [X-3B], but was greatly influenced by the initial [Fe(III)], pH, light intensity, and the anions of chloride or sulfate added to the solution. A further analysis showed that the degradation began with a simultaneous formation of ferrous ions. When all the ferric ions were transferred into Fe(II), the dye disappearance terminated no matter how much of the dye was left in the solution. The molar ratio of the Fe(II) formed to the X-3B disappeared was evaluated to be over 3, depending on the yield of the dye degradation. The result suggests that the process is initiated by the photolysis of Fe(III)-hydroxy species, from which the hydroxyl radicals are generated to oxidize the dye substrate subsequently. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Ferric ions; Reactive Brilliant Red X-3B; Photolysis; Bleaching; Hydroxyl radicals

## 1. Introduction

It has been known that the irradiation of aqueous ferric ions in charge transfer band results in the formation of Fe(II) and hydroxyl radicals (Eq. (1)) [1,2]. Since the hydroxyl radical is a powerful oxidant ( $E^0 = 2.80$  V) that can oxidize most of organic compounds [3], this system may be used as an alternative method for the photochemical treatment of organic pollutants in a homogeneous solution. The quantum yield for the  $\bullet\text{OH}$  formation has been determined to be 0.182 at 300 nm, but it declines to 0.060 [4] or 0.017 [2] at 360 nm. However, the UV/Fe<sup>3+</sup> system seems competitive with the mostly studied technology of TiO<sub>2</sub> photocatalysis [2,3], in which the  $\bullet\text{OH}$  quantum yield has been carefully measured to be 0.040 at 365 nm in the aqueous suspension [5]. The  $\bullet\text{OH}$  yield can be improved by addition of H<sub>2</sub>O<sub>2</sub>, and the photo-Fenton (i.e. UV/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>) reaction has been shown to be efficient for the complete mineralization of chlorophenol [7], herbicides [8], and a dye of Malachite green [9] in water.



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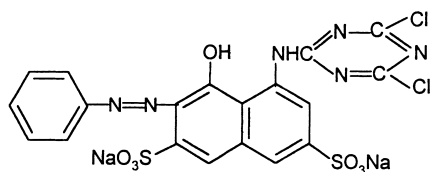
This report is to examine the kinetic details of UV/Fe<sup>3+</sup> system for the degradation of a common textile dye, named commercially as Reactive Brilliant Red X-3B. Understanding the fundamentals of this system would be helpful to the photo-Fenton reaction. Secondly, this class of the dye has strong absorption in the visible range, and the mechanism for its photo-assisted degradation may be different from those of the organic compounds cited above [7–9]. The experiment was carried out in an aqueous solution of ferric sulfate with irradiation at  $\lambda \geq 320$  nm. The kinetics was examined under different conditions, such as initial [X-3B], [Fe<sup>3+</sup>], pH, anions, and light intensity as to determine the controlling factors for this reaction.

## 2. Experimental details

### 2.1. Materials

The dye of Reactive Brilliant Red X-3B (98%) was from Jining dye manufacture of Shengdong, China, and used directly without further purification. Ammonium iron(II) sulfate hexahydrate (99%), ammonium iron(III) sulfate dodecahydrate (99%), and perchloric acid (70% w/w in water) were from Shanghai Chemicals. All other chemicals were

of reagent grade, and used as received. Except the Fe(II) solution that was freshly prepared, all other stock solutions were prepared by aqueous solution of perchloric acid at pH 2.22. The pH was adjusted with a very small amount of sodium hydroxide solution.



Reactive Brilliant Red X-3B

## 2.2. Photochemical experiments

The light source was a 75 W Xenon lamp (USHIO Inc. Japan) enclosed in a A1010 lamp housing (PTI, USA) and powered generally to 5.00 A by an LPS-200 lamp power supply from PTI. The reactor was made of a common glass that cut off the light at  $\lambda=320$  nm. The beam was passed through a water cell (10 cm path length) before entering into the reactor. The Xenon lamp emits light of continuous band from UV to visible range. When a visible light was interested, the water cell was replaced by a chromate solution ( $1 \times 10^{-3}$  mol dm $^{-3}$  K $_2$ CrO $_4$  in aqueous solution of 23 g dm $^{-3}$  Na $_2$ CO $_3$ ). Different light intensity was obtained simply by operating the lamp at different output under other fixed conditions.

In each experiment, 100 cm $^3$  of the air-saturated solution was used, and the temperature was maintained at 25°C. At certain reaction interval, a 2 ml of sample was withdrawn, analyzed with a 722 spectrophotometer (Shanghai Analytical Instrument Factory) or a Bio 40 UV-VIS-NIR spectrophotometer (Perkin-Elmer), and returned quickly back to the reactor. In the experiment for a simultaneous determination of X-3B and Fe $^{2+}$ , the solution was irradiated separately for certain time, and then subjected in total to the analysis.

## 2.3. Analysis method

The X-3B concentration was determined by its absorbance at 540 nm (the molar absorption coefficient  $\epsilon=1.36 \times 10^4$ ), and the interference from either ferric or ferrous ions was negligible in the concentration range used in the present study. The Fe $^{2+}$  was analyzed at 510 nm ( $\epsilon=1.11 \times 10^4$ ) via its complex with 1,10-phenanthroline, and the interference from the undegraded dye was subtracted by the absorbance at 510 nm ( $\epsilon=1.34 \times 10^4$  for X-3B) measured before the addition of the phenanthroline ligand. All the samples were analyzed immediately to avoid any further reactions.

## 3. Results and discussion

### 3.1. Effect of X-3B concentration

The dye X-3B was quite stable to the irradiation of light at  $\lambda \geq 320$  nm (Fig. 1A-a), but it degraded efficiently when ferric sulfate was added (Fig. 1A-c). The bands centered at 540, 510,  $\sim 320$ , 280 and 234 nm decreased, respectively, with the irradiation time (Fig. 1B), while the absorbance in the region of 380–460 and 600–800 nm increased. After 40 min, however, the absorbance did not change considerably with the irradiation time, even though there was still more than 60% of the undegraded dye left in the solution. Several additional runs were then performed by using only different initial concentration of the X-3B to examine whether or not this reaction is dependent of the dye concentration. Again, no further changes in the absorbance after 40 min was observed for all the cases (Fig. 1A). Moreover, it was seen that the decreased absorbance ( $\Delta A$ ) increased only slightly with

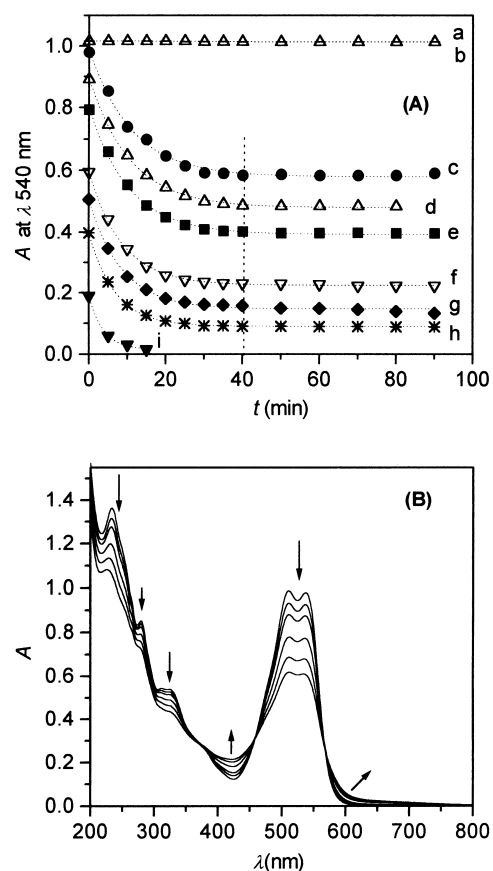


Fig. 1. Effect of the dye initial concentration (A) and the spectrum changes with irradiation time  $t$  (B). Conditions: initial  $[\text{Fe}^{3+}]$  at  $1.08 \times 10^{-4}$  mol dm $^{-3}$ , initial pH at 2.3, and  $\lambda \geq 320$  nm (the lamp was operated at 5.00 A). For comparison, the sample (a) was performed in the absence of Fe $^{3+}$ , while the sample (b) was performed in the dark. The spectra (B) was recorded for sample (c) at  $t=0, 2, 5, 10, 15,$  and 30 min, respectively (where the arrow presents the direction of the change in absorbance  $A$  with irradiation time).

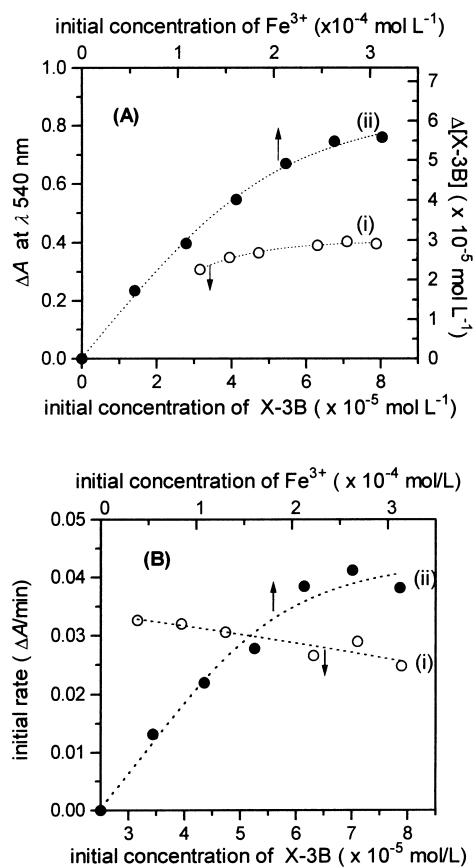


Fig. 2. The decreased absorbance ( $\Delta A$ ) (A) and the initial bleaching rate (B) as a function of initial [X-3B] or initial [Fe(III)]. The  $\Delta A$  and the initial rate were collected at 40 min from Fig. 1 for curve (i) or at 80 min from Fig. 3 for curve (ii). Here the initial rate was expressed by the decreased absorbance per minute, while the right axis in Fig. 2A is the corresponding change in X-3B concentration ( $\Delta[X-3B]$ ).

the initial [X-3B] (Fig. 2A-(i)), and while the initial rate became slightly decreased (Fig. 2B-(i)). Since the same initial [Fe(III)] was employed for each run, this result points out that the yield of the dye degradation is determined by the amount of the ferric species present in the solution, while the slight decrease in the initial rate might be due to the gradual increase in the effect of solution filter because of the increase in the dye concentration.

However, the ferric ions are not the direct oxidant for the obvious degradation of the dye. The initial [Fe(III)] employed for Fig. 2A-(i) was  $1.08 \times 10^{-4} \text{ mol dm}^{-3}$ , which was larger than the initial [X-3B] of  $7.20 \times 10^{-5} \text{ mol dm}^{-3}$ . But the maximum yield of the dye disappearance counted only about 38% of the expected value. Obviously, the yield of the dye photo-bleaching is determined not only by the amount of Fe(III) present, but is also limited by the efficiency of the Fe(III) species that generates the hydroxyl radicals as shown by Eq. (1). The result may also imply that the reaction between the  $\bullet\text{OH}$  radicals and the X-3B is very fast so that the yield of the degraded dye is influenced only slightly by the dye initial concentration.

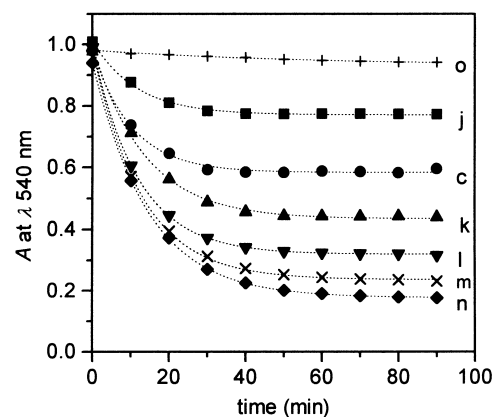


Fig. 3. Effect of initial [Fe(III)] on the X-3B degradation. Conditions: initial  $[\text{Fe}^{3+}]$  at (j)  $0.547$ , (k)  $1.61$ , (l)  $2.12$ , (m)  $2.63$  and (n, o)  $3.13 \times 10^{-4} \text{ mol dm}^{-3}$ , respectively. For all the samples the initial [X-3B] was  $7.89 \times 10^{-5} \text{ mol dm}^{-3}$ , initial pH at  $2.3$ , and the irradiation lamp operated at  $5.00 \text{ A}$ , but the sample (o) was performed in the dark.

### 3.2. Effect of Fe(III) concentration

The role of the Fe(III) species was further studied by employing different initial concentration of ferric sulfate under same conditions. As seen from the Fig. 3, the initial [Fe(III)] does show great effect on the photo-degradation of X-3B in the aerated aqueous solution. The initial rate increased with the initial [Fe(III)] (Fig. 2B-(ii)), while the yield of the degraded dye also increased (Fig. 2A-(ii)). For comparison, the dark oxidation by the Fe(III) was quite slow (Fig. 1A-b and Fig. 3o). In addition, the nonlinear response of the degradation yield or the initial rate to the increase of the initial [Fe(III)] (Fig. 2) suggests that the reactive  $\bullet\text{OH}$  radicals were also consumed by other components such as the anions of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  released from the X-3B photo-degradation, or from the ferric sulfate initially added to the solution (chloride and sulfate ions are known as the effective scavengers of  $\bullet\text{OH}$  radicals [2,3]).  $\text{Cl}^-$  was detected in the irradiated solution by a test of silver nitrate ( $0.01 \text{ mol dm}^{-3}$ ).

Following the mechanism discussed above, the ferrous ions must be detected in the irradiated solution as well. Fe(II) was analyzed by the complex of  $\text{Fe}^{2+}$  with 1,10-phenanthroline at different reaction time, and the sample (c) and (n) were taken as examples (Fig. 4). It was observed that in both the irradiated samples the Fe(II) accumulated gradually with the irradiation, but it approached a plateau at the time that corresponded exactly to the time at which the dye degradation was terminated (Fig. 3). Moreover, the formation yield, calculated at the plateau for both cases, was about 97% over the total Fe(III) that was initially added to the solution. This suggests that the dye degradation terminated at the time when all the Fe(III) was transferred into Fe(II).

It was also found that the molar ratio of the formed Fe(II) to the disappeared X-3B varied at different reaction stage.

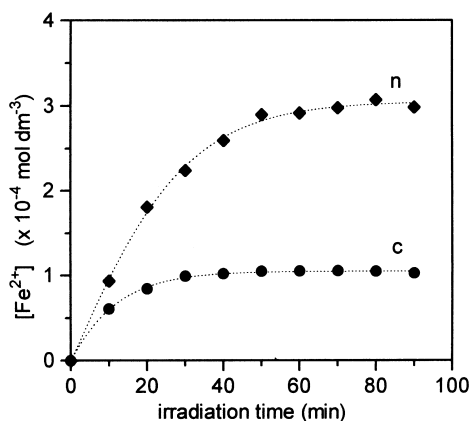


Fig. 4. Concentration of Fe(II) measured at different irradiation time for the samples (c) and (n), respectively.

For sample (c) the ratio was 3.43 at  $t=10$  min, but increased to 3.66 at  $t=60$  min, while for the sample (n) the ratio increased from 3.34 at  $t=10$  min to 5.30 at  $t=60$  min. Since the initial [Fe(III)] used in each study was fixed, the regular changes in this ratio is likely to be the reflection, that the amount of the  $\bullet\text{OH}$  radicals consumed by the target dye at longer reaction time is less than that at earlier stage. The concentration of the anions formed from the dye degradation is expected to increase with the irradiation time. We will see below that both the chloride and sulfate anions are efficient scavengers in this reaction.

If the dye degradation was via the reaction between the Fe(III) and the excited dye [9], the percentage of the X-3B degradation should approach the case of UV irradiation, since the band area in the region of 450–650 nm occupied 70% over the total area in the 320–650 nm region of the X-3B absorption spectrum. When the sample was illuminated by visible light at  $\lambda \geq 450$  nm for 60 min, however, the dye disappeared only by about 4%, which is much less than expected value of 38% from the same solution irradiated by UV light (the dark reaction was quite slow, and only 0.3% of the dye was disappeared under these conditions, as presented by Fig. 1A-o). The formed  $\text{Fe}^{2+}$ , on the other hand, counted only by 12%, that was also smaller than the expected value of 97% in UV irradiation. This observation supports the mechanism that the dye degradation is initiated by the photolysis of Fe(III)-hydroxy species, other than through the excited dye reacted with the Fe(III) species. The little observed degradation upon visible light irradiation was caused by the photolysis of ferric species which has a tailing band (rather weak) around 450 nm in its absorption spectrum [10]. Alternatively, the dye degradation may be initiated via the electron transfer from the ligand X-3B to the Fe(III) centers in their complex upon the light irradiation. But, neither new band nor band shift was observed when the X-3B was mixed with ferric sulfate, and the pathway via the electron transfer in the complex would be less possible.

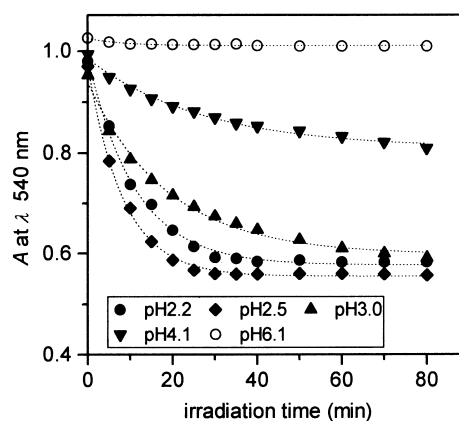


Fig. 5. Effect of initial pH on the degradation of X-3B in water. The other conditions were the same as in Fig. 1.

### 3.3. pH effect

The pH has a great effect on the photo-assisted degradation of X-3B in the aqueous solution of ferric ions (Fig. 5). The optimal pH was found to be about 2.5, and the degradation rate above pH 3 decreased with increasing pH. This result is similar to the photo-Fenton reaction that has been observed for the degradation of several organic compounds [6–9]. It has been known that the quantum yield of Fe(II) and/or free radical formation decreases with increasing polymerization of Fe(III) species [2]. At more acidic solution, the  $\text{Fe}(\text{OH})^{2+}$  is predominant species, but the precipitation of  $\text{Fe}^{3+}$  to amorphous oxyhydroxides becomes rapid at pH higher than 3 [8,9].

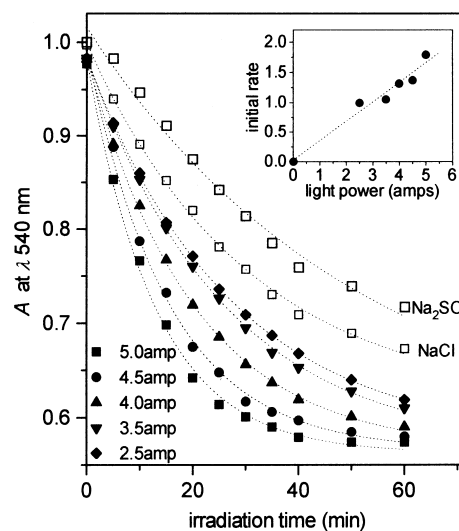


Fig. 6. Effect of light intensity and anions on the degradation of X-3B in water. Conditions for anion study: initial  $[\text{Cl}^-]$  or  $[\text{SO}_4^{2-}]$  at  $0.01 \text{ mol dm}^{-3}$ , the lamp was operated at 5.00 A, and the others were the same as in Fig. 1. The insert is the plot of the lamp output (A) vs. initial rate ( $10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$ ).

### 3.4. Effect of light intensity and added anions

As expected, the dye degradation was also influenced by the light intensity and by the presence of additional scavenging anions (Fig. 6). The initial rate increased linearly with the light intensity (the insert in Fig. 6), but decreased when additional anions of chloride or sulfate were added. In the latter case, the  $\text{SO}_4^{2-}$  as the deactivator was more efficient than the  $\text{Cl}^-$  (the same initial [anion] was employed in the study at  $0.010 \text{ mol dm}^{-3}$ ). This observation seems contradictory to the common realization that, as  $\bullet\text{OH}$  scavenger the chloride ion is more efficient than the sulfate [8]. The reason for this contradiction may be related to the difference in the anion complexation in which the percentage of the dominant  $\text{Fe}(\text{OH})^{2+}$  species in chloride solution has been reported to be much higher than that in sulfate solution at pH 2.7 and ionic strength of 0.1 M [8].

## 4. Conclusion

This report has shown that the textile dye of X-3B in an aqueous solution can be degraded by the irradiation at  $\lambda \geq 320 \text{ nm}$  only when ferric salt is present. The degradation rate increases with the concentration of Fe(III) and light intensity, but obviously decreases at  $\text{pH} > 3$  and/or when the anions ( $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ ) were added. Though there is lack of direct evidence for the radical participation in the dye degradation, several indirect observation can lead to the conclusion that the dye is oxidized by the  $\bullet\text{OH}$  radicals which are generated from the direct photolysis of ferric species, mainly the  $\text{Fe}(\text{OH})^{2+}$ . The result also suggests that the excited state of the dye X-3B is quite less efficient to have itself degraded

even in the aerated ferric solution. It is expected that addition of  $\text{H}_2\text{O}_2$  to this system will increase the degradation rate of the dye, at least due to the Fe(III) recycling via the Fenton reaction of  $\text{H}_2\text{O}_2$  with Fe(II).

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