

## Oxidation of Fast Green FCF by the Solar Photo-Fenton Process

A. Kumar, M. Paliwal, R. Ameta and S.C. Ameta\*

*Photochemistry and Solar Energy Laboratory, Department of Chemistry,  
University College of Science, M.L. Sukhadia University, Udaipur, India*

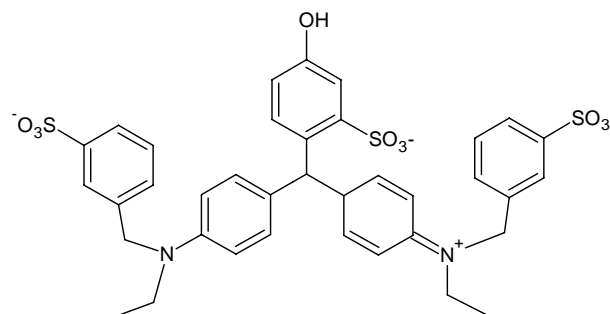
*(Received 3 September 2007, Accepted 14 October 2007)*

This study was conducted to assess the removal efficiency of fast green FCF (a dye) from aqueous medium using the photo-Fenton process. Fenton's reagent, a mixture of hydrogen peroxide ( $H_2O_2$ ) and ferric ions ( $Fe^{3+}$ ), used to generate hydroxyl radicals ( $\cdot OH$ ), was used to attack the target contaminant and degrade it. A visible light source was used to provide the radiation needed in the photo-Fenton method (*i.e.*  $H_2O_2/Fe^{3+}$ ). The effects of varying the parameters of ferric ion, fast green FCF and hydrogen peroxide concentrations, as well as pH, and light intensity on the reaction rate were determined. More effective and faster than Fenton's reagent in removing fast green FCF, the results show that the photo-Fenton method completely oxidizes and degrades fast green FCF into  $CO_2$  and  $H_2O$ . A tentative mechanism for photobleaching of the dye is proposed.

**Keywords:** Photochemical degradation, Solar photo-Fenton, Fast green FCF, AOPs, Photobleaching

### INTRODUCTION

The heterocyclic dye fast green FCF (Scheme 1) is used in dyeing, printing, leather processing, fluorescent pigments and widely used as a colorant in the cosmetics and drug industries. The direct release of wastewater containing fast green FCF causes serious environmental problems due to its dark color and toxicity [1]. Traditional removal techniques, such as coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis) or adsorption by activated carbon, are based only on a phase transfer of the pollutant. Recently, advanced oxidation processes (AOPs) have been developed to oxidize the organic compound into  $CO_2$ ,  $H_2O$  and inorganic ions, or biodegradable compounds [2]. These environmentally friendly AOPs are considered as promising wastewater treatment methods. Among AOPs, the homogeneous Fenton reaction, the  $Fe^{3+}/H_2O_2$  system, is one of the most important processes,

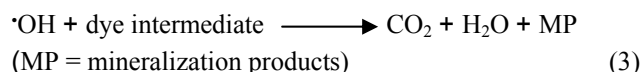


Scheme 1. Molecular structure of fast green FCF.

which generate  $\cdot OH$  radicals [3]. Since this reaction is easy and does not generate sludge, it has been widely used to degrade pollutants [4,5]. The hydroxyl radical is a powerful oxidant that can rapidly and non-selectively oxidize organic contaminants into carbon dioxide and water [6,7], so it is able to degrade pollutants effectively [8-9]. The photo-Fenton method is also effective in the degradation of pollutants. Xiang

\*Corresponding author. E-mail: ameta\_sc@yahoo.com

[10] reported that dye decolorization is accelerated by the combination of UV irradiation and Fenton's process because it produced  $\cdot\text{OH}$  radicals directly (Eqs. 1-3).



UV is the most commonly employed light source in photoassisted oxidation processes, but the high cost of generating artificial UV light leads researchers to the economical light source of the sun. However,  $\text{H}_2\text{O}_2$  has a low molar extinction coefficient and partly absorbs UV above 320 nm, so the solar photo-Fenton process can only use photons of wavelengths up to 400 nm, which only represent a minority of total solar radiation [11].

The treatment of effluent by the photo-Fenton method is eco-friendly to aqueous environments. Mogra *et al.* [12-13] reported the photochemical degradation of *p*-dichlorobenzene and chlorobenzene by the photo-Fenton reagent. Walling [14] studied intermediates in the reaction of Fenton's type reagents. However, there is no report on the degradation of this dye using Fenton and/or photo-Fenton processes. In the practical application of these processes to wastewater treatment, there is a need to determine the optimal experimental parameters for color removal. Here, we investigated the influences of various factors (pH,  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}$  and dye concentrations and light intensity) on the degradation of fast green FCF based on the solar-Fenton process.

## EXPERIMENTAL

### Materials and Methods

Fast green FCF (Central Drug House, CDH),  $\text{FeCl}_3$  (CDH) and  $\text{H}_2\text{O}_2$  (30%, Merck), were used in the present investigations. The dye solution of fast green FCF was prepared in doubly distilled water. The photochemical degradation of fast green FCF was studied in the presence of  $\text{Fe}^{3+}$  ion,  $\text{H}_2\text{O}_2$  and visible light. Stock solutions of fast green FCF (0.0808 g,  $1.0 \times 10^{-4}$  M) and  $\text{FeCl}_3$  (anhydrous, 0.4055 g,

$5.0 \times 10^{-3}$  M) were prepared in doubly distilled water (100 and 500 ml, respectively). For the photochemical degradation of fast green FCF, 30 ml of diluted stock dye solution ( $5.0 \times 10^{-6}$  M) and 2.0 ml of diluted stock  $\text{FeCl}_3$  solution ( $1.0 \times 10^{-3}$  M) was exposed to light (intensity  $70.0 \text{ mW cm}^{-2}$ ) from a 200-watt tungsten lamp (Sylvania Laxman). Sunlight was used for higher intensity light, measured by a lux meter (Model SM 201, Suryamapi Central Electronics Ltd., India). A water filter was used to cut off thermal radiations. The pH of the solution was measured with a digital pH meter (Systronics Model 106) and adjusted within a range of 3-4 by the addition of previously standardized hydrochloric acid and sodium hydroxide solutions. A G-3 sintered glass crucible was used for filtration during the measurement of the optical density at different time intervals. The  $\lambda_{\text{max}}$  of the dye was determined using a Shimadzu UV 240 spectrophotometer.

## RESULTS AND DISCUSSION

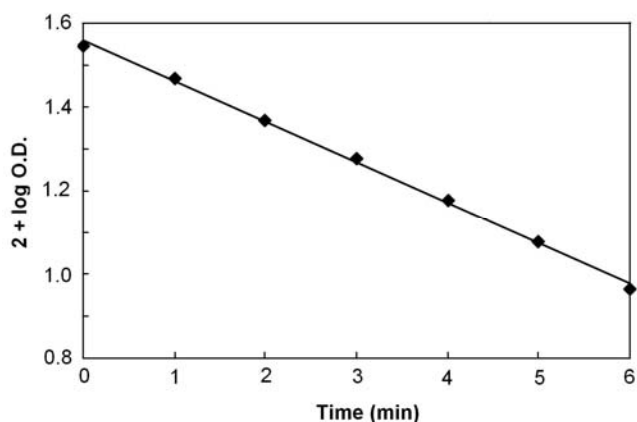
The photochemical degradation of fast green FCF was observed at  $\lambda_{\text{max}} = 625 \text{ nm}$ . The results for a typical run are given in Table 1 and graphically represented in Fig. 1.

The optical density of fast green FCF solution decreases with an increase in the time of irradiation, indicating that fast green FCF is consumed on irradiation. The plot of  $2 + \log\text{OD}$  against time (Fig. 1) was linear, following pseudo-first order

**Table 1.** Results of a Typical Fast Green FCF Degradation Run by the Photo-Fenton Method<sup>a</sup>

Time (min)	Optical density (OD)	2 + logOD
0	0.352	1.5465
1	0.294	1.4683
2	0.233	1.3674
3	0.190	1.2788
4	0.151	1.1790
5	0.131	1.0755
6	0.092	0.9638

<sup>a</sup>[Fast green FCF] =  $5.0 \times 10^{-6}$  M;  $\text{H}_2\text{O}_2 = 1.0 \text{ ml}$ ;  $[\text{Fe}^{3+}] = 1.67 \times 10^{-4}$  M; light intensity =  $70.0 \text{ mW cm}^{-2}$ ; pH = 3.2;  $k = 3.71 \pm 0.092 \times 10^{-3} \text{ s}^{-1}$ .



**Fig. 1.** Typical photochemical degradation of fast green FCF observed at  $\lambda_{\max} = 625$  nm under the optimized conditions of [fast green FCF] =  $5.0 \times 10^{-6}$  M,  $\text{H}_2\text{O}_2 = 1.0$  ml,  $[\text{Fe}^{3+}] = 1.67 \times 10^{-4}$  M, light intensity =  $70.0 \text{ mWcm}^{-2}$  and pH = 3.2.

kinetics. The rate constant was determined using the expression  $k = 2.303 \times \text{slope}$ , with an optimum rate constant of  $k = 3.71 \pm 0.092 \times 10^{-3} \text{ sec}^{-1}$ .

### Effect of pH

The rate of degradation of fast green FCF, reported in Table 2, increases with an increase in pH up to 3.2, after which it decreases with increasing pH. The hydroxyl radicals are generated by two steps: (i) the reaction between ferrous ions and hydrogen peroxide, and (ii) the photochemical reaction of ferric ions and water.

The increase in the pH of the medium favors the formation of  $\text{OH}^-$  ions and hydroxyl radicals in step (i), rather than the generation of protons in step (ii); thus, it may be concluded that step (i) dominates over step (ii) in the pH range below 3.2. However, retardation of the reaction above pH 3.2 suggests the dominance of step (ii) over step (i).

### Effect of Fast Green FCF Concentration

As shown in Table 3, the rate of photochemical degradation was found to increase with the increase in fast green FCF concentration up to  $5.0 \times 10^{-6}$  M. A further increase in concentration brought a sudden decrease in the rate of degradation, perhaps because more molecules of fast green

**Table 2.** Effect of pH on the Efficiency of the Degradation of Fast Green FCF by the Photo-Fenton Method<sup>a</sup>

pH	$k (\times 10^3 \text{ s}^{-1})$
3.0	$1.73 \pm 0.043$
3.1	$3.51 \pm 0.087$
3.2	$3.71 \pm 0.092$
3.3	$3.51 \pm 0.087$
3.4	$3.28 \pm 0.082$
3.5	$2.34 \pm 0.058$
3.6	$1.57 \pm 0.039$
3.7	$0.88 \pm 0.022$
3.8	$0.35 \pm 0.008$
3.9	$0.23 \pm 0.006$
4.0	$0.20 \pm 0.005$

<sup>a</sup>[Fast green FCF] =  $5.0 \times 10^{-6}$  M;  $\text{H}_2\text{O}_2 = 1.0$  ml;  $[\text{Fe}^{3+}] = 1.67 \times 10^{-4}$  M; light intensity =  $70.0 \text{ mW cm}^{-2}$ .

**Table 3.** Effect of Fast Green FCF Concentration on the Efficiency of the Degradation of Fast Green FCF by the Photo-Fenton Method<sup>a</sup>

[Fast Green FCF] $\times 10^6$ M	$k (\times 10^3 \text{ s}^{-1})$
1.67	$2.81 \pm 0.070$
3.33	$3.12 \pm 0.078$
5.00	$3.71 \pm 0.092$
6.67	$3.51 \pm 0.087$
8.33	$3.12 \pm 0.078$
10.0	$2.65 \pm 0.066$
11.67	$2.24 \pm 0.056$
13.33	$2.24 \pm 0.056$

<sup>a</sup> $[\text{Fe}^{3+}] = 1.67 \times 10^{-4}$  M; light intensity =  $70.0 \text{ mW cm}^{-2}$ ; pH = 3.2.  $\text{H}_2\text{O}_2 = 1.0$  ml.

FCF were available for degradation, or because the glut of fast green FCF may act as a filter for the incident light, preventing a sufficient intensity of light from reaching the dye molecule in the bulk of the solution.

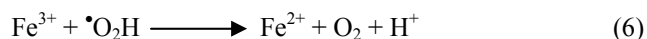
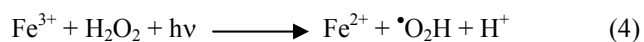
### Effect of Ferric Ion Concentration

Keeping all other factors identical, the effect of the

concentration of  $\text{Fe}^{3+}$  ions on the rate of photochemical degradation of fast green FCF was observed. As summarized in the Table 4, the rate of photodegradation increases with the increase in the concentration of  $\text{Fe}^{3+}$  ions up to  $1.67 \times 10^{-4}$  M. The increase in ferric ions in the reaction mixture also increases the concentration of  $\text{Fe}^{2+}$  ions, which is accompanied by enhanced generation of  $\bullet\text{OH}$  radicals, consequently increasing the rate of photodegradation.

### Effect of Hydrogen Peroxide Concentration

As seen in Table 5, by increasing the amount of  $\text{H}_2\text{O}_2$ , the rate of reaction increases, with an optimum rate at 1.0 ml  $\text{H}_2\text{O}_2$ . Thereafter, the rate of degradation decreases as the amount of the hydrogen peroxide increases. We postulate that more  $\text{H}_2\text{O}_2$  molecules are available to react with the  $\text{Fe}^{2+}$  ions, thereby increasing the number of  $\bullet\text{OH}$  radicals and the reaction rate. However, above 1.0 ml  $\text{H}_2\text{O}_2$ , the rates of reactions in Eqs. 4 and 5 become fast, and, according to Eq. 5,  $\bullet\text{OH}$  radicals are consumed rapidly due to the greater availability of  $\text{H}_2\text{O}_2$  molecules. Also from Eqs. 4 and 5, the greater amounts of generated  $\bullet\text{OOH}$  radicals produce  $\text{H}^+$  ions (Eq. 6), slightly decreasing the pH at the end of the reaction. As a consequence, the rate of photodegradation decreases.



### Effect of Light Intensity

A linear relationship was observed between the rate constant and light intensity (Table 6), which indicates that an increase in the light intensity increases the rate of reaction. This may be attributed to the increased number of photons reacting with  $\text{Fe}^{3+}$  ions and, as a result, there is an increase in the number of hydroxyl radicals and a corresponding increase in the rate of reaction.

## MECHANISM

On the basis of experimental observations, which corroborate the existing literature, a tentative mechanism has

**Table 4.** Effect of Ferric Ion Concentration on the Efficiency of the Degradation of Fast Green FCF by the Photo-Fenton Method<sup>a</sup>

$[\text{Fe}^{3+}] \times 10^4$ M	$k (\times 10^3 \text{ s}^{-1})$
0.17	$0.21 \pm 0.005$
0.33	$0.74 \pm 0.018$
0.50	$0.83 \pm 0.021$
0.67	$0.97 \pm 0.024$
0.83	$1.84 \pm 0.046$
1.00	$1.94 \pm 0.048$
1.17	$2.39 \pm 0.059$
1.33	$2.43 \pm 0.061$
1.50	$3.47 \pm 0.087$
1.67	$3.71 \pm 0.092$

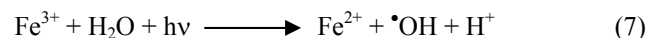
<sup>a</sup> $[\text{Fast green FCF}] = 5.0 \times 10^{-6}$  M;  $\text{H}_2\text{O}_2 = 1.0$  ml; light intensity =  $70.0 \text{ mW cm}^{-2}$ ; pH = 3.2.

**Table 5.** Effect of Hydrogen Peroxide Concentration on the Efficiency of Degradation of Fast Green FCF by the Photo-Fenton Method<sup>a</sup>

$\text{H}_2\text{O}_2$ (ml)	$k (\times 10^3 \text{ s}^{-1})$
0.5	$1.99 \pm 0.049$
0.7	$2.55 \pm 0.063$
0.8	$2.84 \pm 0.071$
1.0	$3.71 \pm 0.092$
1.5	$2.16 \pm 0.054$
2.0	$1.85 \pm 0.046$
2.5	$1.62 \pm 0.041$
3.0	$1.39 \pm 0.034$
3.5	$1.24 \pm 0.031$

<sup>a</sup> $[\text{Fast green FCF}] = 5.0 \times 10^{-6}$  M;  $[\text{Fe}^{3+}] = 1.67 \times 10^{-4}$  M; light intensity =  $70.0 \text{ mW cm}^{-2}$ ; pH = 3.2.

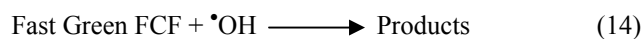
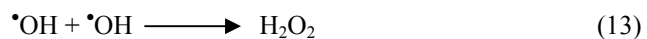
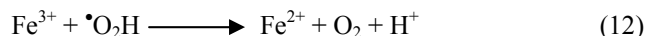
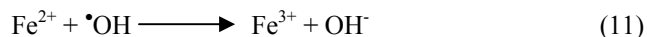
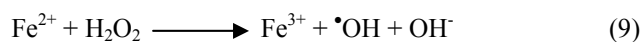
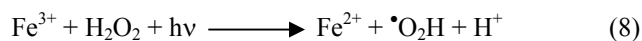
been proposed for photodegradation of fast green FCF with the photo-Fenton reagent.



**Table 6.** Effect of Light Intensity on the Efficiency of Fast Green FCF Degradation by the Photo-Fenton Method<sup>a</sup>

Light intensity (mW cm <sup>-2</sup> )	k (× 10 <sup>3</sup> s <sup>-1</sup> )
10.0	1.88 ± 0.047
20.0	1.90 ± 0.048
30.0	2.03 ± 0.051
40.0	2.26 ± 0.056
50.0	2.67 ± 0.066
60.0	3.13 ± 0.078
70.0	3.71 ± 0.092

<sup>a</sup>[Fast green FCF] = 5.0 × 10<sup>-6</sup> M; H<sub>2</sub>O<sub>2</sub> = 1.0 ml; [Fe<sup>3+</sup>] = 1.67 × 10<sup>-4</sup> M; pH = 3.2.



The aqueous solution of ferric ions on exposure to light dissociates water into a proton and  $\cdot\text{OH}$  radical and ferric ions are reduced to ferrous ions. These ferrous ions will decompose H<sub>2</sub>O<sub>2</sub> into a hydroxyl ion and a hydroxyl radical, while ferrous ions undergo oxidation to ferric ions. Ferric ions generate  $\cdot\text{OOH}$  radicals due to dissociation of H<sub>2</sub>O<sub>2</sub> in the presence of light. The incorporation of  $\cdot\text{OH}$  with H<sub>2</sub>O<sub>2</sub> also produces  $\cdot\text{OOH}$  radicals. Ferrous ions will undergo oxidation to ferric ions by the addition of  $\cdot\text{OH}$  radicals, while ferric ions are reduced to ferrous ions by the incorporation of  $\cdot\text{OOH}$  radicals, producing H<sup>+</sup> ions.  $\cdot\text{OOH}$  radicals are highly unstable in water and undergo facile disproportionation rather than reacting

slowly with the dye molecules. The participation of the hydroxyl radical as an active oxidizing species was confirmed using the hydroxyl radical scavenger 2-propanol, which drastically reduced rate of photodegradation (data not shown).

The two possibilities for the consumption of  $\cdot\text{OH}$  radicals include, firstly, the dissociation of H<sub>2</sub>O<sub>2</sub> into  $\cdot\text{OOH}$  and water or combining to form H<sub>2</sub>O<sub>2</sub> molecules, and, secondly, a reaction with fast green FCF to give the colorless degradation products.

The main advantage of using the photo-Fenton reagent is the cyclic regeneration of the consumed Fe<sup>2+</sup> ions on illumination. The amount of ferrous salt required in photo-Fenton process is small as compared to that when using the Fenton reagent, where ferrous ions must be added; otherwise the reaction will stop after conversion of ferrous ions to ferric ions. This is an important advantage of the photo-Fenton process for industrial use, as further separation of the ferric ions is not required after wastewater treatment [15-20].

## ACKNOWLEDGEMENTS

One of the authors (Anil Kumar) wishes to thank the Council of Scientific and Industrial Research (CSIR) for the JRF award.

## REFERENCES

- [1] M.A. Ali, S.A. Bashier, Food Add. Contam. 23 (2006) 452.
- [2] R.F.P. Nogueira, M.R.A. Silva, A.G. Trov'ó, Solar Energy 79 (2005) 384.
- [3] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, Water Res. 37 (2003) 3776.
- [4] M. Muruganandham, M. Swaminathan, Sep. Purif. Technol. 48 (2006) 297.
- [5] P.K. Malik, S.K. Saha, Sep. Purif. Technol. 31 (2003) 241.
- [6] M. Muruganandham, M. Swaminathan, Dyes Pigments 72 (2007) 137.
- [7] M.S. Lucas, J.A. Peres, Dyes Pigments 71 (2006) 235.
- [8] I.B.S. Will, J.E.F. Moraes, Sep. Purif. Technol. 34 (2004) 51.
- [9] H. Zheng, X. Xiang, Spectrosc. Spectr. Anal. 24

- (2004) 726.
- [10] X. Xiang, H. Zheng, Chongqing Jianzhu Univ. 26 (2004) 126.
- [11] Y. Xu, Chemosphere 43 (2001) 1103.
- [12] D. Mogra, M. Mehta, R. Ameta, S.C. Ameta, J. Indian. Chem. Soc. 79 (2002) 593.
- [13] D. Mogra, R. Ameta, N. Chhabra, S.C. Ameta, Intl. J. Chem. Sci. 1 (2003) 211.
- [14] C. Walling, Acc. Chem. Res. 31 (1998) 155.
- [15] B. Anna, Y. Tatiana, M. Jerzy, J. Kiwi, New J. Chem. 28 (2004) 519.
- [16] X. Tao, J. Su, J. Chen, J. Zhao, Chem. Commun. (2005) 4607.
- [17] W. Ma, Y. Huang, J. Li, C. Cheng, W. Song, J. Zhao, Chem. Commun. 1582 (2003)
- [18] F. Chen, W. Ma, J. He, J. Zhao, J. Phys. Chem. A 106 (2002) 9485
- [19] T.J. Collins, Acc. Chem. Res. 35 (2002) 782.
- [20] R.G. Zepp, B.C. Faust, J. Hoingne, Environ. Sci. Techno. 26 (1992) 313.