



DEGRADATION OF FAST GREEN FCF USING IMMOBILIZED PHOTO-FENTON REAGENT

GARGI SHARMA^a, DIPTI SONI^a, SURBHI BENJAMIN^a, RAKSHIT AMETA^a and
SANYOGITA SHARMA^{*,b}

^aDepartment of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA

^bDepartment of Chemistry, Faculty of Engineering, PAHER University, UDAIPUR – 313003 (Raj.) INDIA

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ABSTRACT

Degradation of fast green FCF by Fe-pillared bentonite clay in presence of light has been carried out. The progress of the reaction was monitored spectrophotometrically. The effect of some parameters affecting the rate of reaction, such as pH, dye concentration, amount of Fe-pillared clay, amount of iron concentration, H₂O₂, light intensity, etc. has been studied. Kinetic studies show that this reaction follows pseudo-first order kinetics. A tentative mechanism for photo-Fenton degradation of fast green FCF has also been proposed.

Key words: Photo-Fenton degradation, fast green FCF, Fe-pillared bentonite clay.

INTRODUCTION

The entire world is facing a burning problem in the form of water pollution. Organic synthetic dyes represent relatively large group of organic chemicals, which are present in practically all spheres of mankind daily life. Dyes are all around us, they make out our world beautiful but they also bring pollution and therefore the community has to be focused on possible solutions environmental problems caused by dye industries. The manufacturing and the processing of dye involve the handling and the production of many organic compounds that are toxic and hazardous to human health.

Now-a-days, due to increasing presence of refractory molecules in the waste water streams, it is important to develop new technologies to degrade such recalcitrant pollutant molecules into smaller innocuous ones. Thus wastewater treatment attracted the attention of many researchers. They have developed some methods for wastewater treatment like chemical oxidation, incineration, wet oxidation, air stripping, adsorbents, electrolyte decomposition, ion exchange method, biological methods etc. These treatment methods are not suitable at large scale due to high cost and therefore, some alternative methods are required, which are reliable as well as low cost and easy to handle. Photo-Fenton provides an eco-friendly pathway for degradation of many organic pollutants. This technique is considered as a promising technology for wastewater treatment.

Lina and Wang¹ have studied the use of anion-cation organobentonite for the treatment of wastewater generated during a textile dyeing and printing process. Li et al.² have prepared both Fe-pillared bentonite (Fe-Ben) and Al-Fe-pillared bentonite (Al/Fe-Ben) and used as heterogeneous catalysts for the photo-Fenton discoloration of azo dye X-3B under UV irradiation. Cao et al.³ have used Fe-pillared bentonite (Fe-Ben) ion exchange as heterogeneous catalyst for degradation of organic contaminants in petroleum refinery wastewater. Kumar et al.⁴ have removed fast green FCF (a dye) from aqueous medium using the photo-Fenton process.

Sahoo et al.⁵ have carried out the photocatalytic degradation of crystal violet, a triphenyl methane dye in aqueous solutions. Segura et al.⁶ determined the pre-treatment of a pharmaceutical wastewater by Fenton oxidation with zero-valent iron and hydrogen peroxide to improve the degradation of the complex-mixture of organic compounds present in the wastewater.

Elmori et al.⁷ have reported the decolorization of the mordant red 73 (MR73) azo dye in water using UV/H₂O₂ and photo-Fenton treatments. Saquib et al.⁸ have carried out the photocatalytic degradation of two selected dye derivatives, fast green FCF and acid blue 1 in aqueous suspensions of titanium dioxide under a variety of conditions.

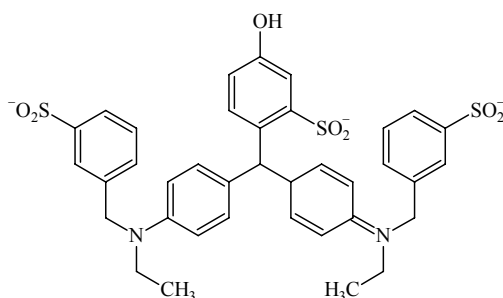
Bhandari et al.⁹ have studied the photocatalytic bleaching of some dyes (erythrosin-B, fast green FCF and eosin Y) in the presence of semiconducting zinc oxide while Bhati et al.¹⁰ synthesized CeCr₂O₅ nanoparticles by microwave method for the decolorization of yellowish orange and fast green dyes, the common water effluents of textile industries. Tamimi et al.¹¹ have investigated the chemical degradation of pesticide methomyl in water by Fenton (H₂O₂/Fe²⁺) and photo-Fenton (H₂O₂/Fe²⁺/UV) process.

EXPERIMENTAL

Preparation of bentonite supported photo-Fenton reagent

Solutions A, B, C, D and E were prepared separately in a beaker. 6.950 g, 13.90 g, 20.85 g, 27.80 g and 34.75 g of FeSO₄ were taken, respectively and then in each beaker 500 mL of distilled water and 50 g bentonite clay and few drops of dilute H₂SO₄ were added to it. Solutions A, B, C, D, E, were separately put on magnetic stirrer for 5-6 hours. The product was filtered and washed with distilled water 6-7 times. It was dried in an oven at 100°C for 4-5 hrs.

Stock solution of fast green FCF dye (1.0 x 10⁻³ M) was prepared in doubly distilled water. It was further diluted as and when required. The photo-Fenton degradation of fast green FCF dye was studied after addition of 0.11 g of Fe-pillared clay in 50 mL dye solution (1 x 10⁻⁵ M) and (0.2 N Fe²⁺) was added to it. Then 1.1 mL amount of H₂O₂ was added. The pH of the reaction mixture was adjusted to 3.0 and this solution was exposed to a 200 W tungsten lamp at 50.0 mWcm⁻². Irradiation was carried out in glass vessel (Pyrex. 100 mL). A solarimeter (Suryamapi CEL 201) was used for the measurement of light intensities.



Structure of Fast Green FCF

Water filter was used to cut thermal effect. A digital pH meter (Systronic Model 335) was used to measure pH of the dye solutions. pH of the dye solutions were adjusted by addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solution. UV-Visible spectrometer (Systronic Model 106) was used to measure absorbance (A) of the dye solution at regular time intervals. Controlled experiments were also carried out to confirm that the degradation of fast green FCF by Fe-pillared bentonite clay and by using H₂O₂ was photo-Fenton in nature.

RESULTS AND DISCUSSION

Degradation of fast green FCF was observed at $\lambda_{\text{max}} = 625 \text{ nm}$. A graph plotted between $\log v/s$ time was a straight line, which shows that photo-Fenton degradation of fast green FeF follows pseudo-first order kinetics. The rate constant for degradation of dye was calculated by the following expression –

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

A typical run has been presented in Table 1 and graphically represented in Fig. 1.

Table 1: A typical run

pH = 3.0	[Fe ²⁺] = 0.20 N	
[Fast green FCF] = $1.10 \times 10^{-5} \text{ M}$	Amount of clay = 0.11 g	
H ₂ O ₂ = 1.10 mL	Light intensity = 50.0 mWcm ⁻²	
Time (min.)	Absorbance (A)	1 + log A
1.0	0.240	0.3802
2.0	0.210	0.3222
3.0	0.199	0.2789
4.0	0.178	0.2504
5.0	0.158	0.1986
6.0	0.135	0.0969
7.0	0.120	0.0792
8.0	0.113	0.0531
Rate constant (k) = $8.75 \times 10^{-4} \text{ sec}^{-1}$		

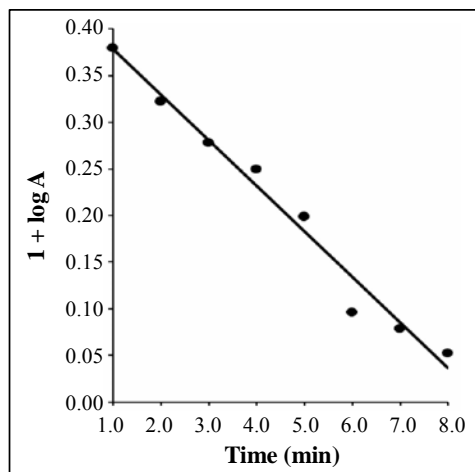


Fig. 1: A typical run

Effect of pH

The effect of pH on the rate of degradation of Fast green FCF was investigated in the pH range 3.0 to 10.0. The results are reported in Table 2.

Table 2: Effect of pH

[Fast green FCF] = 1.10×10^{-5} M	[Fe ²⁺] = 0.20 N
H ₂ O ₂ = 1.10 mL	Light intensity = 50.0 mWcm ⁻²
Amount of clay = 0.11 g	
pH	Rate constant (k) × 10 ⁴ (sec ⁻¹)
3.0	8.75
4.0	5.01
5.0	3.96
6.0	1.23
7.0	1.17
8.0	1.00
9.0	0.79
10	0.66

It is evident from the data given in the Table 2 that the photochemical degradation of fast green FCF is very sensitive to pH of the reaction medium. The rate of reaction was found to be optimum at pH = 3.0 and after that, it decreases. It may be attributed to the fact that at high pH, the generation of •OH radicals get slower because of the formation of the ferric hydroxo complex.

Effect of dye concentration

Effect of variation of dye concentration on the rate of reaction was also studied by taking different concentrations of fast green FCF solution. The results are tabulated in Table 3.

Table 3: Effect of fast green FCF concentration

pH = 3.0	[Fe ²⁺] = 0.20 N
H ₂ O ₂ = 1.10 mL	Light intensity = 50.0 mWcm ⁻²
Amount of clay = 0.11 g	
[Fast green FCF] × 10 ⁵ M	Rate constant (k) × 10 ⁴ (sec ⁻¹)
0.60	3.96
0.70	4.59
0.80	5.65
0.90	5.72
1.10	8.75
1.20	5.39
1.30	3.59

The rate of photochemical degradation was found to increase with increasing concentration of fast green FCF upto 1.10×10^{-5} M. Further increase in its concentration, resulted in a sudden decrease in the rate of degradation. This may be explained on the basis that initially on increasing the concentration of fast green FCF, more molecules of fast green FCF were available for degradation. However, on increasing the concentration above 1.10×10^{-5} M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of fast green FCF was increased above 1.10×10^{-5} M, it started acting like a filter for the incident light and therefore, its larger concentration will not permit the desired light intensity to reach the dye molecules in the bulk of the solution; Thus, a decrease in the rate of photochemical degradation of fast green FCF was observed.

Effect of amount of clay

The effect of amount of clay on the rate of photodegradation of fast green FCF was observed by keeping all other factor identical. The results are tabulated in Table 4.

Table 4: Effect of amount of clay

Amount of clay (g)	Rate constant (k) $\times 10^4$ (sec ⁻¹)
0.05	5.93
0.07	8.18
0.09	8.31
0.11	8.75
0.13	6.93
0.17	4.62
0.19	2.85
0.21	1.80

It was observed that as the amount of Fe-pillared clay was increased, there was a corresponding increase in rate of photodegradation of dye. It may be explained on the basis that on increasing the amount of clay, the amount of loaded iron also increases, generating more $\bullet\text{OH}$ radicals resulting with increased rate of photodegradation. There was a decreasing in the rate of reaction as increases the amount of Fe-pillared clay was increased above 0.11 g. This may be due to the role of iron present in clay as a scavenger of $\bullet\text{OH}$ radicals. As a result, the rate of photodegradation of the dye decreases.

Effect of ferrous ion concentration

The effect of concentration of Fe^{2+} ions on the rate of photodegradation of fast green FCF was observed by keeping all other factors identical. The results are summarized in the Table 5.

It is clear from the data that the rate of photodegradation increases on increasing the concentration of Fe^{2+} ions upto 0.20 N, while a reverse trend was observed beyond this limit. This may be explained on the basis that increase in the Fe^{2+} ions concentration in the reaction mixture is accompanied by enhanced generation of $\bullet\text{OH}$ radicals. Consequently increasing the rate of photodegradation. After the optimal Fe^{2+} ions, the higher concentrations of Fe^{2+} resulted in a brown turbidity that causes the recombination of $\bullet\text{OH}$ radicals. Fe^{2+} also reacts with $\bullet\text{OH}$ as a scavenger and therefore, the rate decreases.

Table 5: Effect of ferrous ion concentration

pH = 3.0		Amount of Clay = 0.11 g
[Fast green FCF] = 1.10×10^{-5} M		Light Intensity = 50.0 mWcm^{-2}
H ₂ O ₂ = 1.10 mL		
[Fe ²⁺] N	Rate constant (k) $\times 10^4$ (sec ⁻¹)	
0.05	1.90	
0.10	6.82	
0.15	7.43	
0.20	8.75	
0.25	4.23	

Effect of amount of hydrogen peroxide

The effect of amount of hydrogen peroxide on the photodegradation of fast green FCF was also investigated. The results are recorded in Table 6.

Table 6: Effect of amount of hydrogen peroxide

pH = 3.0		[Fe ²⁺] = 0.20 N
[Fast green FCF] = 1.10×10^{-5} M		Light Intensity = 50.0 mWcm^{-2}
Amount of Clay = 0.11 g		
H ₂ O ₂ (mL)	Rate Constant (k) $\times 10^4$ (sec ⁻¹)	
0.10	4.99	
0.30	5.62	
0.50	5.82	
0.70	6.01	
0.90	6.23	
1.10	8.75	
1.03	6.86	
1.50	6.16	

It was observed that the rate of reaction increases on increasing the amount of H₂O₂ upto 1.10 mL. On further increase, a decrease in the rate of degradation was observed. This can be explained on the basis that at optimum concentration of H₂O₂, more hydroxyl radicals were produced by Fe²⁺ ions, which degrade more dye molecules. On further increasing the amount of H₂O₂, the rate of reaction was found to decrease. It is because of the fact that as the amount of H₂O₂ was increased along its optimum condition (1.10 mL), the rate of the reaction [Eq. 5 and 6] becomes fast and •OH radicals are consumed rapidly due to more availability of H₂O₂ molecule. The peroxide radicals formed were utilized [Eq. 7] and H⁺ ions produced. The production of H⁺ ions were confirmed by a slight decrease in pH of the reaction mixture at the end of reaction. As a consequence, the rate of photodegradation decreases.

Effect of light intensity

The effect of light intensity on the photodegradation of fast green FCF was also observed. The results obtained are reported in Table 7.

Table 7: Effect of light intensity

pH = 3.0		[Fe ²⁺] = 0.20 N
[Fast green FCF] = 1.10 × 10 ⁻⁵ M		H ₂ O ₂ = 1.10 mL
Amount of Clay = 0.11 g		
Light intensity (mWcm ⁻²)	Rate constant (k) × 10 ⁴ (sec ⁻¹)	
20.0	4.97	
30.0	5.19	
40.0	6.84	
50.0	8.75	
60.0	6.60	
70.0	4.75	

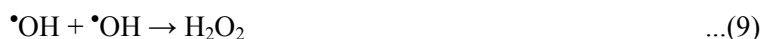
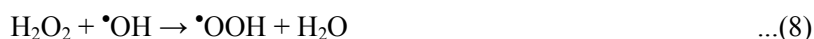
A linear plot was obtained between the rate constant and light intensity. It is evident from the data that an increase in the light intensity, increases the rate of reaction because an increase in the intensity of light will increase the number of photons striking catalyst particles per unit time per square cm. As a result, more photons will react with Fe³⁺ ions and generate more number of active species (hydroxyl radical) and hence, resulting in an increase in the rate of reaction.

Mechanism

On the basis of the experimental observations and corroborating the existing literature, the mechanism of Fenton oxidation is based on the generation of •OH radicals by the catalytic decomposition of H₂O₂ in acidic media. In presence of Fe²⁺, the peroxide breaks down to •OH and ⁻OH, according to the following reaction.



Consumption of •OH radicals



The ferrous ions decomposed H_2O_2 into hydroxyl ions and hydroxyl radical, while ferrous ions undergo oxidation to ferric ions. The ferric ion generates HO_2^\bullet radical due to dissociation of H_2O_2 in presence of light. The aqueous solution of ferric ions on exposure to light dissociates water into a proton and $^\bullet\text{OH}$ radicals and ferric ions are reduced to ferrous ions. The incorporation of $^\bullet\text{OH}$ with H_2O_2 also produces HO_2^\bullet radicals. Ferric ions get reduced to ferrous ions by incorporation of HO_2^\bullet radicals and producing O_2 and H^+ ions. $^\bullet\text{OOH}$ radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules.

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