



*Dedicated to the memory of
Professor Dumitru OANCEA (1941–2020)*

DEGRADATION OF BRILLIANT BLUE FCF THROUGH PHOTOLYSIS, IRRADIATION AND PHOTO-FENTON PROCESSES: A COMPARATIVE STUDY

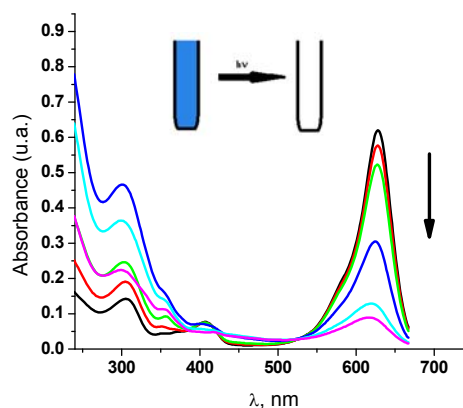
Daniela NEGOESCU,^a Petruța OANCEA,^{b,*} Adina RĂDUCAN^b and Mihaela PUIU^b

^a “Ilie Murgulescu” Institute of Physical Chemistry, Roumanian Academy, 202 Splaiul Independentei, 060021 Bucharest, Roumania

^b Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd. Regina Elisabeta, 4-12, Bucharest 030018, Roumania

Received September 30, 2020

In this work we performed a comparative study regarding the performance characteristics of three photochemical treatments for Brilliant Blue degradation: photolysis (only UV radiation), irradiation in the presence of H₂O₂ (H₂O₂ /UV), photo-Fenton reaction (Fe²⁺/H₂O₂ /UV). The kinetic analysis revealed that BB degradation follows an apparent first order kinetics. The examination of the estimated rate constants and the degradation efficiencies revealed the superior performance of the photo-Fenton oxidation, which may be due an increased gain of reactive oxygen species species comparative to the UV or UV/H₂O₂ treatment.



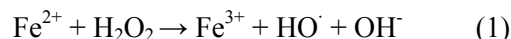
INTRODUCTION

Dyes are complex aromatic compounds that are overly used in many industries such as food, textiles, and printing. However, they also cause environmental issues, being life- and health threatening of living organisms due to their complex structure and enhanced chemical stability.^{1,2} Therefore, dye removal or at least dye degradation to non-harmful compounds, is a topic of major concern. Brilliant Blue FCF (BB), a triarylmethane dye, is used in food industry, rubber, paper, plastics, medications, and cosmetics.³ There are

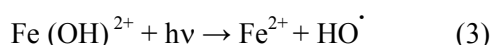
several conventional methods dedicated to the removal of synthetic dyes from waste: electrochemical oxidation,⁴ physical adsorption, chemical oxidation, and chemical coagulation/precipitation.⁵⁻⁷ These methods are not destructive, they only transfer the pollutant from one phase to another. Mineralization of dyes by industrial effluents can be achieved in advanced oxidation processes (AOPs).⁸⁻¹¹ UV/H₂O₂ photolysis is an efficient treatment for pollutants' removal displaying significant advantages such as no sludge production, simplicity of operation and low cost; besides all that, H₂O₂ is an environmental-friendly

* Corresponding author: petrutaoancea73@yahoo.com

oxidant. Even if the discovery of the Fenton reagent, a mixture of hydrogen peroxide and ferrous ions, traces back to the late 19th century, its application in oxidative destruction of toxic compounds did not begin until the late 1960s.¹²⁻¹⁴ Reactive oxygen species (ROS) are generated during the Fenton process through the chemical reactions (eqs. 1-2):¹⁵



In addition to the above reactions the photo-Fenton ensures the formation of hydroxyl radicals according to the photochemical reactions (eqs. 3-5):



There are not many studies reporting photodegradation of Brilliant Blue. Gosetti *et al.*¹⁶ evaluated the oxidative degradation of BB by addition of potassium persulfate at different persulfate to dye molar ratios under natural sunlight irradiation. Parvin *et al.*¹⁷ studied photocatalytic degradation of Brilliant Blue FCF using silver-doped ZnO designed particles. It is worth mentioning several fast and effective degradation of Brilliant Blue in aqueous medium such as ozonation¹⁸ and photolytic oxidation with H₂O₂.¹⁹ The aim of our work was the perform and to optimize the photodegradation degradation of BB either through UV induced H₂O₂ photolysis, or by photo-Fenton oxidation at pH 3. The method was based on the monitoring the decrease of

absorbance during the irradiation time. In this context we explored the decay kinetics of BB and the decolourization degree at settled experimental conditions. We evaluated the effect of the initial concentration of hydrogen peroxide and irradiation time on the decolourization rate.

RESULTS AND DISCUSSION

As previously mentioned, the photodegradation of BB was followed under different experimental condition: photolysis (only UV radiation), irradiation in the presence of H₂O₂ (H₂O₂ /UV), photo-Fenton reaction (Fe²⁺/H₂O₂ /UV) (Fig. 1). The normalized form of the exponential decay equation was fitted onto the experimental data absorbance *vs.* time aiming the estimation of the decolourization kinetic constants *k* (eq. 6).

$$\frac{A}{A_0} = \exp(-kt) \quad (6)$$

Here A₀ is the absorbance at the beginning of the experiment and A is the instantaneous absorbance (at a certain time value). Absorbances were recorded at specific wavelength λ = 630 nm.

The fastest decolourization was observed in the case of the photo-Fenton system, while the simple irradiation produced low decolourization degrees within an hour. The preliminary examination of the extended kinetic curves indicate that 1) the decolourization kinetic constants decrease in the order $k_{\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}} > k_{\text{H}_2\text{O}_2/\text{UV}} > k_{\text{UV}}$ and 2) H₂O₂ plays an important role as a source of •OH both in H₂O₂/UV and photo-Fenton reaction.

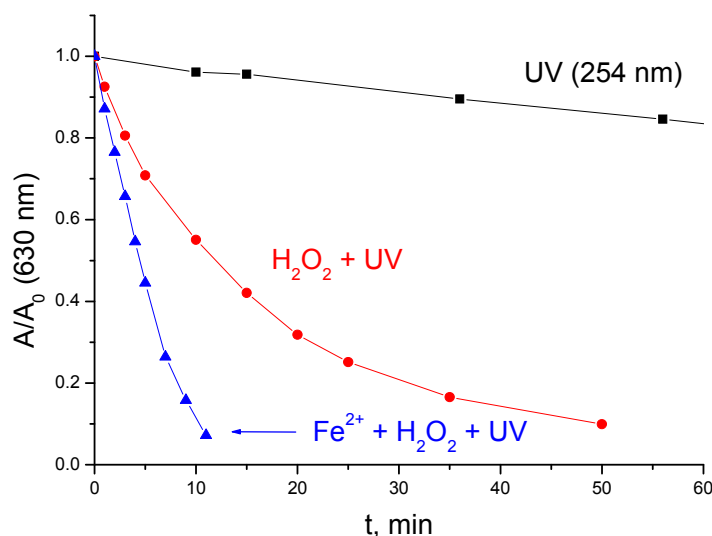


Fig. 1 – Comparative study on the efficiency of three photodegradation methods based on the extended kinetic curves absorbance *vs.* time. [BB]₀ = 1.0 × 10⁻⁵ M, [H₂O₂]₀ = 4.0 × 10⁻⁴ M [Fe²⁺]₀ = 1 × 10⁻³ M.

Influence of H₂O₂ in irradiation experiments

The simple preliminary assay started from 1.0×10^{-5} M BB and a ten-fold excess of H₂O₂. At settled times, 3 mL from the reaction mixture were extracted and analysed through UV-VIS measurements. After 20 minutes only 10% BB was degraded in the absence of H₂O₂, while around 70% dye faded using the UV/H₂O₂ system. As shown in Fig. 2, a plot of $\ln(A_0/A_t)$ vs. irradiation time led to a linear dependence, characteristic to a pseudo-first order kinetics. Here, the slopes

represent the decolourization kinetic constants: $k = 2.93 \times 10^{-3} \text{ min}^{-1}$ (with a determination coefficient, $R^2 = 0.9997$) for the BB/UV system and $k = 51.0 \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.9943$) for the BB/UV/H₂O₂ system.

The increase of the rate constant in the case of the BB/UV/H₂O₂ system can be explained by the enhanced production of hydroxyl radicals ($\cdot\text{OH}$) during the UV irradiation of hydrogen peroxide in aqueous solution, according to the sequence of eqs. 7–9:



Next, the UV/H₂O₂ oxidation was performed by varying H₂O₂ concentration within $1 - 5 \times 10^{-4}$ M, at constant Brilliant Blue concentration (1×10^{-5} M). The estimated pseudo-first-rate constants,

together with the percentage degradation efficiency ($\eta\%$, defined in eq. 10) after 20 min, are summarized Table 1.

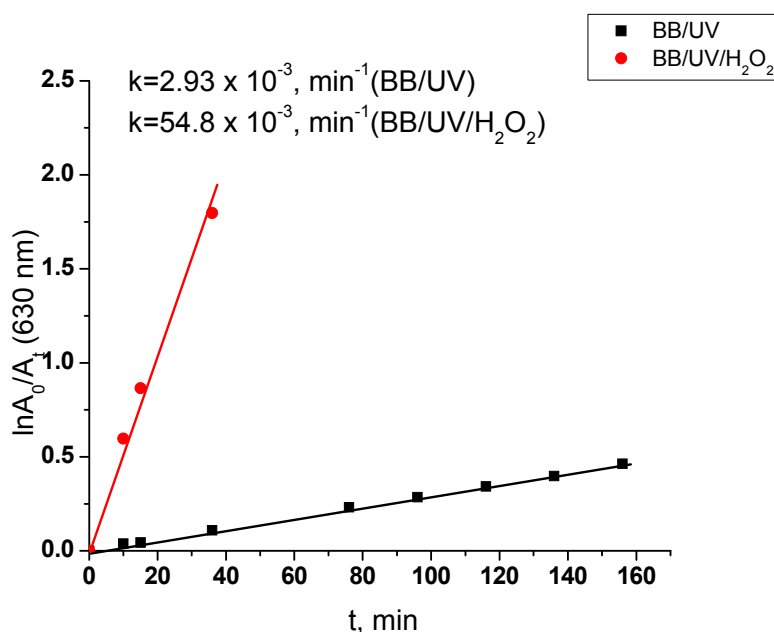


Fig. 2 – Evidence of the striking influence of H₂O₂ on the kinetics of Brilliant Blue photodegradation [BB]₀ = 1.0×10^{-5} M, [H₂O₂]₀ = 1.0×10^{-4} M.

Table 1

Performance parameters of Brilliant Blue photodegradation using UV/H₂O₂ system

[H ₂ O ₂] ₀ × 10 ⁴ (M)	k (min ⁻¹) × 10 ²	t _{1/2} (min)	η %
1	5.48 ± 0.019	12.64	69
2	11.18 ± 0.085	6.19	89
4	14.6 ± 0.062	4.74	93
5	13.2 ± 0.074	5.25	90

t_{1/2} – half-life

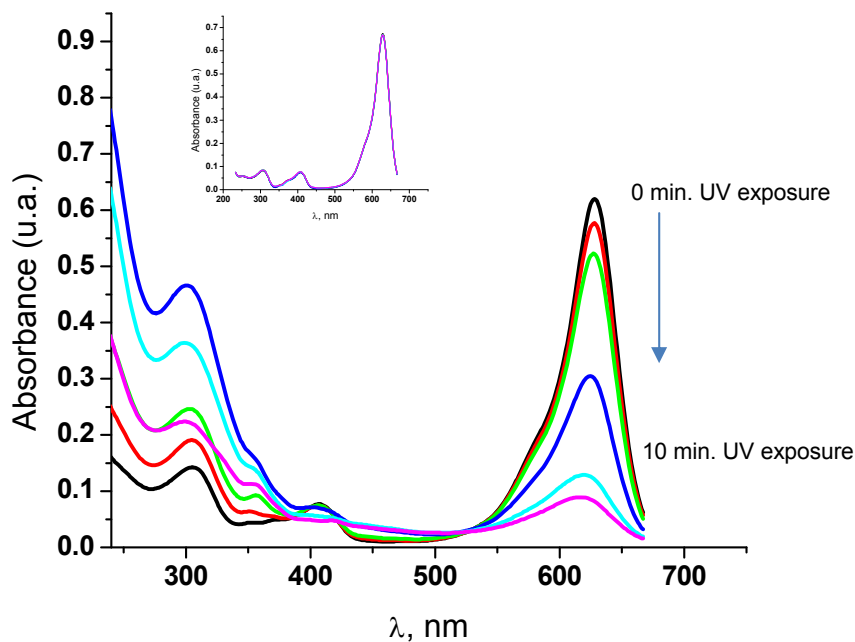


Fig. 3 – UV-Vis absorption spectra of an aqueous Brilliant Blue solution during degradation with the Photo-Fenton process: $[BB] = 1.0 \times 10^{-5} \text{ M}$, $[H_2O_2] = 1.0 \times 10^{-4} \text{ M}$ $[Fe^{2+}] = 1 \times 10^{-3} \text{ M}$. Insert: Fenton degradation of BB.

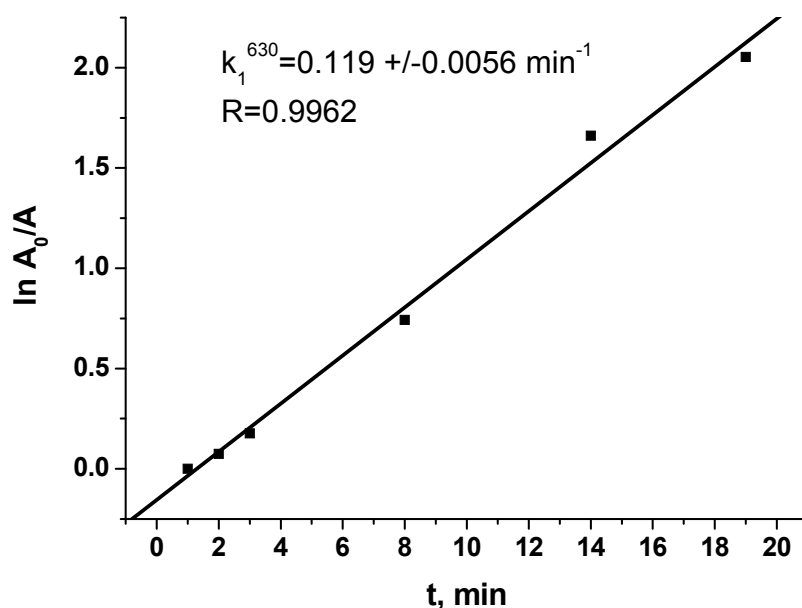


Fig. 4 – First-order reaction kinetics for the degradation of Brilliant Blue the Photo-Fenton process: $[BB] = 1.0 \times 10^{-5} \text{ M}$, $[H_2O_2] = 1.0 \times 10^{-4} \text{ M}$ $[Fe^{2+}] = 1 \times 10^{-3} \text{ M}$.

The rate constant increases with the increase of H_2O_2 concentration up to $4 \times 10^{-4} \text{ M}$, but decreases at $5 \times 10^{-4} \text{ M}$. Similar effects were reported by other authors²⁰⁻²¹ for the degradation of different dyes.

The increasing of H_2O_2 concentration and keeping constant $FeSO_4$ and BB concentrations lead to a rapid discoloration of the solution. In this case the reaction rate constant could not be calculated due to the very short degradation times.

The effect of UV irradiation on BB degradation with the photo-Fenton system

The experiments were carried out in the absence and the presence of light employing the Fe^{2+}/H_2O_2 (Fenton reagent). According to the literature,²² the optimum pH is 3. At pH = 3, Fe^{3+} and $Fe(OH)^{2+}$ complex ions co-exist in equal proportion, which grant enhanced light absorption

and high quantum yield for hydroxyl radical generation. The increase of pH lead to a decrease of the concentration of $\cdot\text{OH}$ in solution, due to the coagulation of Fe^{3+} and Fe^{2+} complexes. Moreover, at higher pH value precipitation of ferrous ions as oxyhydroxide may occur, reducing the concentration of hydroxyl radicals and thus affecting the degradation rate.²³ The examination of UV-VIS spectra of BB during the degradation with Fenton and photo-Fenton system are presented in Fig. 3.

It was noticed that in the absence of UV light, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system is not able to degrade the dye, probably due to the small amount of $\cdot\text{OH}$ radicals generated in the "classic" Fenton reaction (eqs. 1 and 2). After 60 min no noticeable change in the BB spectra was observed. Then, after 10 min UV exposure, an 88% percent of dye faded, due to the contribution of the steps 3–5, which increase $\cdot\text{OH}$ concentration. The rate constant was estimated by the pseudo-first order model onto data $\ln(A_0/A)$ vs. time (Fig. 4).

EXPERIMENTAL

Materials

All other reagents (Brilliant Blue FCF, FeSO_4 , H_2O_2) obtained from Sigma were of analytical grade and were used as received without further purification. H_2O_2 30% was diluted and the concentration was measured spectrophotometrically with $\epsilon_{240\text{nm}} = 39.4 \text{ M}^{-1}\text{cm}^{-1}$.²⁴

Photodegradation experiments

Brilliant Blue FCF samples (3 mL) was exposed to an artificial source, the low-pressure Hg lamp of 150W. The incident photonic flow was determined by ferrioxalate actinometry.²⁵ We found a value of $1.92 \times 10^{-6} \text{ einstein s}^{-1}$. The UV-vis spectra of dye were recorded from 200 to 700 nm using a UV-vis spectrophotometer (Pye Unicam α Helios) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of brilliant is 630 nm. The pH of the solution was measured with a Radiometer pH-meter with glass electrode E11M001. Data were processed using the ORIGIN 8.0 software.

CONCLUSIONS

In this work, we performed and optimized the oxidative treatments for Brilliant Blue FCF decolourization using UV/ H_2O_2 and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ /UV systems. It was noticed that the degradation of BB with both systems follow apparent first-order

kinetics. The examination of the estimated rate constants and the degradation efficiencies revealed the superior performance of the photo-Fenton oxidation, which may be due an increased gain of ROS species comparative to the UV/ H_2O_2 treatment. The increase of the H_2O_2 concentration caused a significant augmentation of the rate constant, but only up to $4.0 \times 10^{-4} \text{ M}$. Above this value, the rate constant dropped, probably due to the scavenging effect of excess H_2O_2 and $\cdot\text{OH}$ radicals.

REFERENCES

1. X. Zhang, Z. Geng, J. Jian, Y. He, Z. Lu, X. Liu and H. Yuan, *Catalysts*, **2020**, *10*, 293–298.
2. S. A. Phaltane, S. A. Vanalakar, T. S. Bhat, P. S. Patil, S. D. Sartale and L. D. Kadam, *J. Mater. Sci. Mater. Electron.*, **2017**, *28*, 8186–8191.
3. V. K. Gupta, R. Jain and S. Vorshney, *J. Colloid Interface Sci.*, **2007**, *312*, 292–296.
4. N. Daneshvar, D. Salari and D. Aber, *J. Hazard. Mater. B*, **2002**, *94*, 49–61.
5. N. Daneshvar, H. Ashassi-Sorkhabi and A. Tizpar, *Sep. Purif. Technol.*, **2003**, *31*, 153–162.
6. E. El Qada, S. Allen and G. Walker, *Chem. Eng. J.*, **2008**, *135*, 174–184.
7. V. K. Gupta, R. Jain, A. Nayak, S. Agarwal and M. Shrivastova, *Mat. Sci. Eng. C*, **2011**, *31*, 1062–1067.
8. V. K. Gupta, R. Jain, A. Mittal, T. A. Saleh, A. Nayak, S. Agarwal and S. Sikarwar, *Mat. Sci. Eng. C*, **2012**, *32*, 12–17.
9. V. K. Gupta, D. Pathania, S. Agarwal and P. Singh, *J. Hazard. Mater. B*, **2012**, *243*, 179–186.
10. C. T. Faragoso, R. Battisti, C. Miranda and P. C. De Jesus, *J. Molec. Catal. A: Chem.*, **2009**, *301*, 93–97.
11. M. Kitis, C. D. Adams and G. T. Daigger, *Wat. Res.*, **1999**, *33*, 2561–2568.
12. J. Yoan, Y. Lee and S. Kim, *Wat. Sci. Technol.*, **2001**, *44*, 15–21.
13. M. C. Lu, C. J. Lin, C. H. Liao, W. P. Ting and R. Y. Huang, *Water Sci. Technol.*, **2001**, *44*, 327–32.
14. P. L. Huston, J. J. Pignatello, *Water Res.*, **1999**, *33*, 1238–1246.
15. F. Gosetti, V. Gianotti, S. Angioi, S. Polati, E. Marengo and M. C. Gennaro, *J. of Chromatography A*, **2004**, *1054*, 379–387.
16. T. Parvin, N. Keerthiraj, I. A. Ibrahim, S. Phanichphant and K. Byrappa, *Int. J. Photoenergy*, **2012**, 1–8.
17. Cardoso da Silva, G. L. Bispo, S. P. Pavanelli, R. J. de Cássia, F. Afonso and R. Augusti, *Mass Spectrom.* **2012**, *26*, 1305–1310.
18. S. B. Bukallah, M. A. Rauf and S. S. Ashraf, *Dyes Pigments*, **2007**, *72*, 353–359.
19. M. A. Rauf, S. Ashraf and S. N. Alhadrami, *Dyes Pigments*, **2005**, *66*, 197–203.
20. P. Oancea and V. Meltzer, *Chem. Pap.*, **2014**, *68*, 105–111.

21. A. M. El-Dein, J. A. Libra and U. Wiesmann, *Chemosphere*, **2003**, *52*, 1069–1077.
22. L. G. Devi, K. S. A. Raju, S. G. Kumar and K. E. Rajashekhar, *J. Taiwan Inst. Chem. Eng.*, **2011**, *42*, 341–349.
23. P. Oancea and V. Meltzer, *J. Taiwan Inst. Chem. Eng.*, **2013**, *44*, 990–994.
24. H. Theorell and A. Ehrenberg, *Arch. Biochem. Biophys.*, **1952**, *41*, 462–474.
25. C. G. Hachard and C. H. Parker, “A new sensitive actinometer”, *Proceedings of Royal Society A, London*, 1956, 518–536.