

Use of Photo-Fenton Reagent in the Degradation of Basic Yellow 2 in Aqueous Medium

Khandelwal D.H.¹ and Ameta R.^{2*}¹Department of Chemistry, Pacific College of Basic and Applied Sciences, Pacific University, Udaipur-313024, Rajasthan, INDIA²Department of Chemistry, Govt. P.G. College, Nathdwara, Rajasthan, INDIAAvailable online at: www.isca.inReceived 5th October 2012, revised 9th October 2012, accepted 12th November 2012

Abstract

This study was conducted to assess the removal efficiency of Basic Yellow 2 (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 ($\bullet OH$), 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, Basic Yellow 2 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 Basic Yellow 2, the results show that the photo-Fenton method completely oxidizes and degrades Basic Yellow 2 into CO_2 and H_2O . A tentative mechanism for photobleaching of the dye is proposed.

Keywords: Photochemical degradation, solar photo-Fenton, basic yellow 2, AOPs, Photobleaching.

Introduction

Water soluble azo dye Basic Yellow 2 (figure-1) is used for dyeing of leather, jute, tanned cotton, and paints, and as dye components in inking ribbons, ballpoint pastes, oil and waxes, and carbon paper. The most important areas of application are in dyeing paper and in flexographic printing. The direct release of wastewater containing Basic Yellow 2 causes serious environmental problems due to its dark color and toxicity¹. 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 compounds².

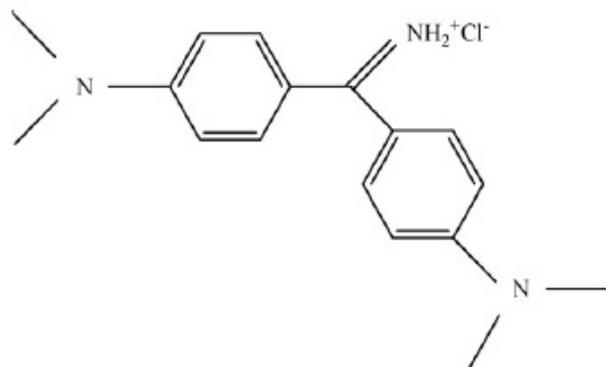
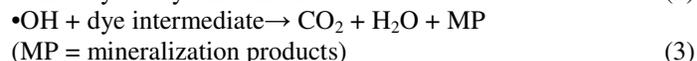


Figure-1

Structure of Basic Yellow 2 ($C_{17}H_{21}N_3 \cdot HCl$, 303.83)

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, which generate $\bullet OH$ radicals³. 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. Xiang¹⁰ reported that dye decolorization is accelerated by the combination of UV irradiation and Fenton's process because it produced $\bullet OH$ radicals directly (equations 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, H_2O_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 radiation¹¹.

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. Walling¹⁴ studied

intermediates in the reaction of Fenton's type reagents. Due to high oxidation rate of the chemical reactions caused by AOPs, the behavior of chemicals changed after the treatment¹⁵. In the photo catalytic reactions, the semi conducting material absorbs light energy more than or equal to energy gap, which generates the holes and electrons, which further give rise to efficient oxidizers of organic dyes¹⁶.

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, H₂O₂, Fe³⁺ and dye concentrations and light intensity) on the degradation of Basic Yellow 2 based on the photo-Fenton process.

Material and Methods

Basic Yellow 2 (Krishna Chemicals, Ankleshwar), anhydrous FeCl₃ (SDFCL) and H₂O₂ (30%, SDFCL), were used in the present investigations. The dye solution of Basic Yellow 2 was prepared in doubly distilled water. The photochemical degradation of BY2 was studied in the presence of Fe³⁺ ion, H₂O₂ and visible light. Stock solutions of Basic Yellow 2 (0.1519 g, 1.0 × 10⁻⁵ M) and FeCl₃ (0.0860 g, 1.06 × 10⁻³ M) were prepared in doubly distilled water (500 and 500 ml, respectively). For the photochemical degradation of BY2, 25 ml of diluted stock dye solution (2.5 × 10⁻⁵ M) and 2.0 ml of diluted stock FeCl₃ solution (2.65 × 10⁻⁴ M) was exposed to light from a 200-watt Tungsten lamp. A water filter was used to cut off thermal radiations. The pH of the solution was measured with a digital pH meter (Toshniwal, Ajmer) and adjusted within a range of 3.0-6.5 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 λ_{max} of the dye was determined using a Shimadzu UV 1700 Pharmspec spectrophotometer. The light intensity was measured using a Solarimeter (CEL, Kodaikanal).

Results and Discussion

The photochemical degradation of basic yellow 2 was observed at λ_{max} = 435 nm. The results for a typical run are given in table -1 and graphically represented in figure-2.

Table-1

Time (min.)	2 + log O.D.
0	1.425
5	1.371
10	1.315
15	1.259
20	1.205
25	1.151
30	1.095

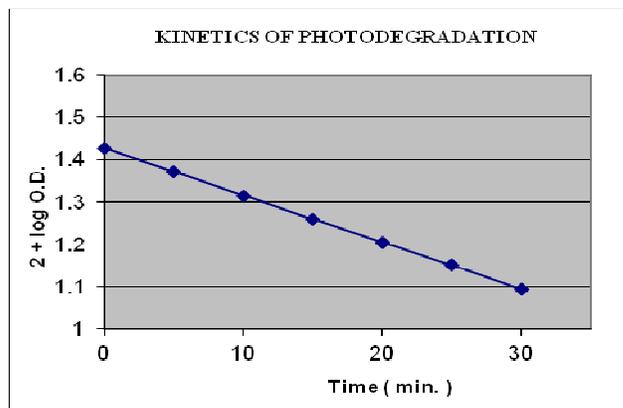


Figure-2

Typical photochemical degradation of Basic Yellow 2 observed at λ_{max} = 435 nm under the optimized conditions of [Basic Yellow 2] = 3.0 × 10⁻⁵ M, H₂O₂ = 1.0 mL, [Fe³⁺] = 2.65 × 10⁻⁴ M, light intensity = 80.0 mW cm⁻² and pH = 4.5

The optical density of basic yellow 2 solution decreases with an increase in the time of irradiation, indicating that basic yellow 2 is consumed on irradiation. The plot of 2 + log OD against time (figure 2) was linear, following pseudo-first order kinetics. The rate constant was determined using the expression k = 2.303 × slope, with an optimum rate constant of k = 4.214 × 10⁻⁴ sec⁻¹.

Effect of variation in pH: The effect of pH on the rate of photocatalytic bleaching of dye was observed. The photodegradation was performed at different pH values from 3.0 to 6.5. The result of figure-3 reveals that the rates of photobleaching of dye basic Yellow 2 increases with an increase in pH up to 5.0, after which it decreases with increasing pH. At pH >4.5, Fe³⁺ decomposes H₂O₂ into water and oxygen, instead of forming hydroxyl radical which is the reactive chemical species for the photobleaching process. Thus, all subsequent experiments were carried out at pH 4.5.

pH VARIATION

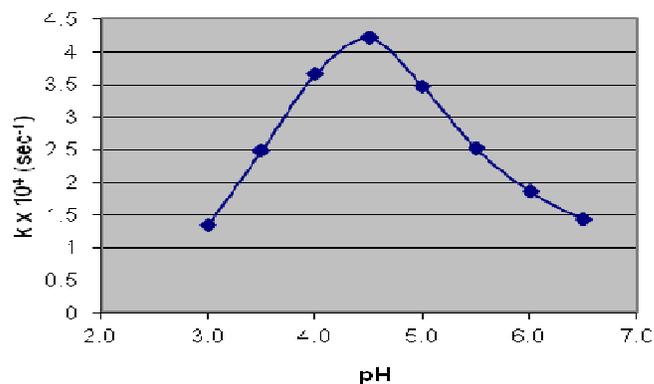


Figure-3

Effect of pH on the photochemical degradation of Basic Yellow 2 observed at λ_{max} = 435 nm under the optimized conditions of [Basic Yellow 2] = 3.0 × 10⁻⁵ M, H₂O₂ = 1.0 mL, [Fe³⁺] = 2.65 × 10⁻⁴ M, light intensity = 80.0 mW cm⁻²

Effect of Dye (Basic Yellow 2) concentration: As shown in figure-4, the rate of photochemical degradation was found to increase with the increase in Basic Yellow 2 concentration up to 4.5×10^{-5} M. A further increase in concentration brought a sudden decrease in the rate of degradation, perhaps because more molecules of Basic Yellow 2 were available for degradation, or because the glut of Basic Yellow 2 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.

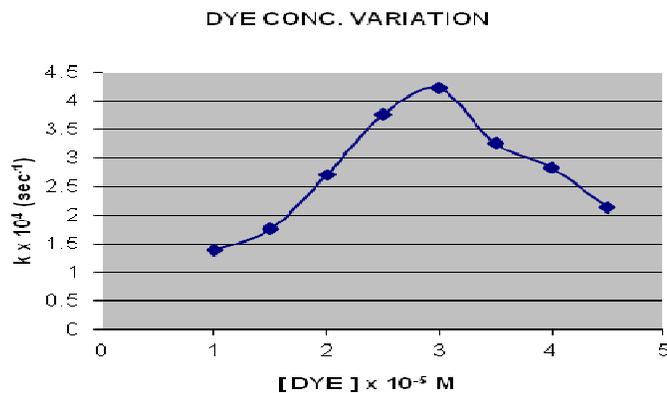


Figure-4

Effect of dye concentration on the photochemical degradation of Basic Yellow 2 observed at $\lambda_{max} = 435$ nm under the optimized conditions of pH = 4.5, $H_2O_2 = 1.0$ mL, $[Fe^{+3}] = 2.65 \times 10^{-4}$ M, light intensity = 80.0 mW cm^{-2}

Effect of Ferric Ion concentration: Keeping all other factors identical, the concentration of catalyst was changed and its effect on the rate of photochemical degradation was observed. The result of figure-5 reveals that the rate of photobleaching of dye increases with the increase in the concentration of Fe^{+3} ion up to 2.65×10^{-4} M. The increase in Fe^{+3} ions in the reaction mixture are accompanied by enhanced generation of $\cdot OH$ radicals, consequently increasing the rate of photodegradation. After the optimal Fe^{+3} additions, the higher dose of Fe^{+3} resulted in a brown turbidity that causes the recombination of $\cdot OH$ radicals and Fe^{+3} reacts with $\cdot OH$ as a scavenger. Therefore, on further increase, the rate becomes almost constant.

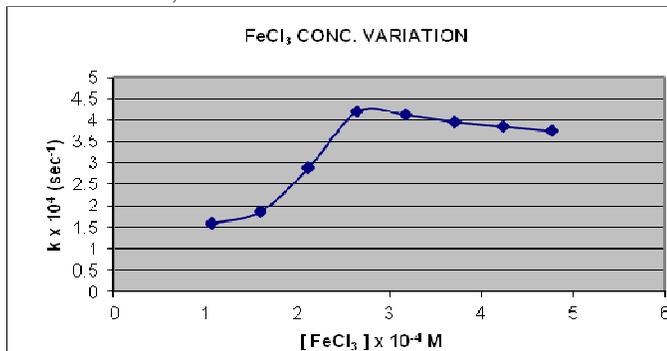


Figure-5

Effect of Fe^{+3} ion concentration on the photochemical degradation of Basic Yellow 2 observed at $\lambda_{max} = 435$ nm under the optimized conditions of pH = 4.5, $H_2O_2 = 1.0$ mL, [Basic Yellow 2] = 3.0×10^{-5} M, light intensity = 80.0 mW cm^{-2}

Effect of H_2O_2 concentration: Keeping all other factors constant, the concentration of H_2O_2 was changed and its effect on the rate of photobleaching was studied. The result reported in figure-6 reveals that the rate of photobleaching of dye increases with the increase the amount of H_2O_2 up to 1.0 mL. Further increase in H_2O_2 has negligible effect as H_2O_2 acts as a scavenger of $\cdot OH$ radicals to produce per hydroxyl radical ($\cdot O_2H$) which has much lower oxidation capacities than $\cdot OH$ radicals.

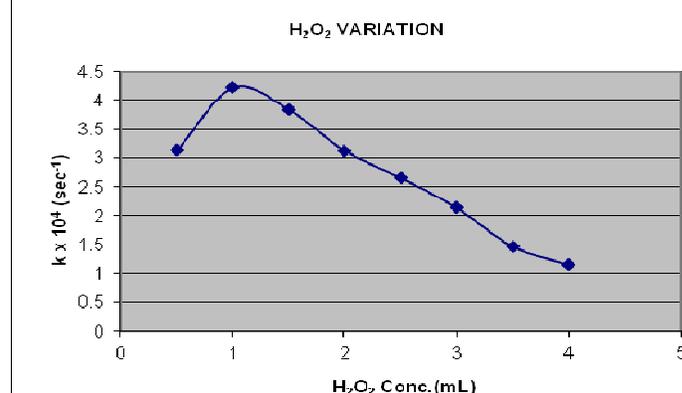


Figure-6

Effect of H_2O_2 concentration on the photochemical degradation of Basic Yellow 2 observed at $\lambda_{max} = 435$ nm under the optimized conditions of pH = 4.5, $[Fe^{+3}] = 2.65 \times 10^{-4}$ M, [Basic Yellow 2] = 3.0×10^{-5} M, light intensity = 80.0 mW cm^{-2}

Effect of Light Intensity: As distance from light source increase, the light intensity decreases. A linear relationship was observed between the rate constant and light intensity (figure-7), which indicates that an decrease in the light intensity decreases the rate of reaction. This may be attributed to the increased number of photons reacting with 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.

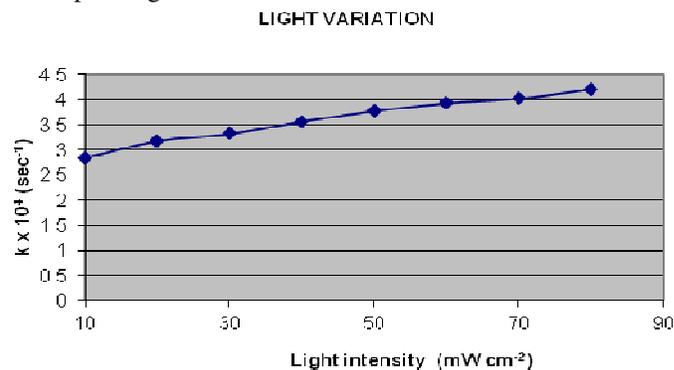
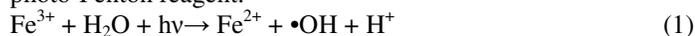


Figure-7

Effect of light intensity on the photochemical degradation of Basic Yellow 2 observed at $\lambda_{max} = 435$ nm under the optimized conditions of [Basic Yellow 2] = 3.0×10^{-5} M, $H_2O_2 = 1.0$ mL, $[Fe^{+3}] = 2.65 \times 10^{-4}$ M, and pH = 4.5

Mechanism: On the basis of experimental observations, which corroborate the existing literature, a tentative mechanism has been proposed for photodegradation of fast green FCF with the photo-Fenton reagent.

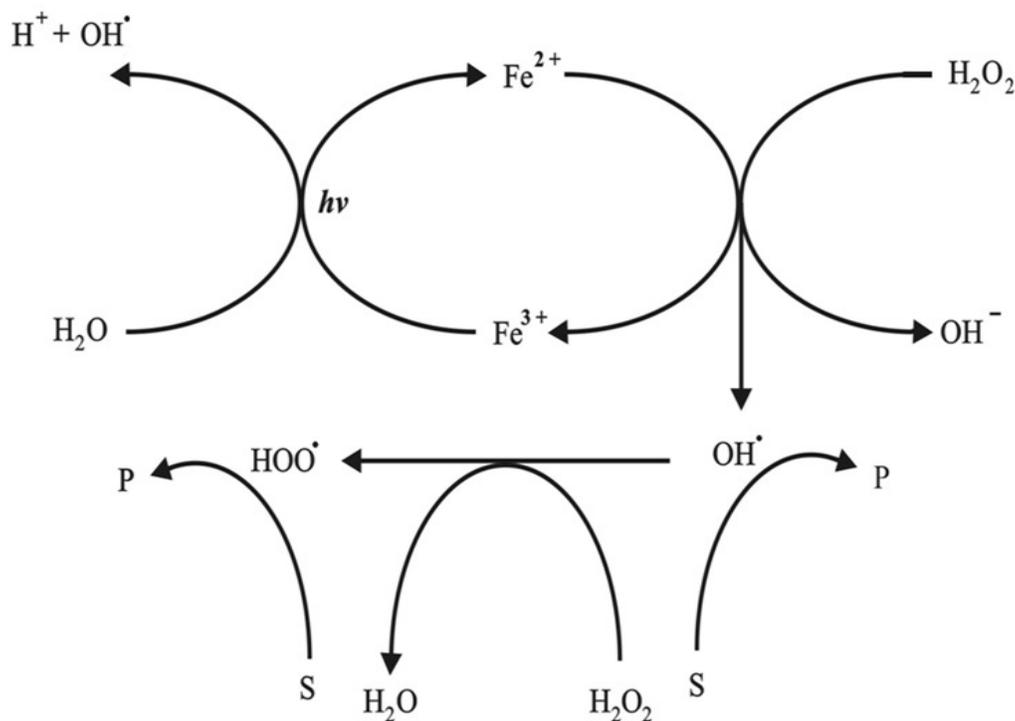


The aqueous solution of ferric ions on exposure to light dissociates water into a proton and $\bullet\text{OH}$ radical and ferric ions are reduced to ferrous ions (equation 1). These ferrous ions will decompose H_2O_2 into a hydroxyl ion and a hydroxyl radical, while ferrous ions undergo oxidation to ferric ions (equation 3). Ferric ions generate $\bullet\text{OOH}$ radicals due to dissociation of H_2O_2 in the presence of light (equation 2). The incorporation of $\bullet\text{OH}$

with H_2O_2 also produces $\bullet\text{OOH}$ radicals (equation 4). Ferrous ions will undergo oxidation to ferric ions by the addition of $\bullet\text{OH}$ radicals, while ferric ions are reduced to ferrous ions by the incorporation of $\bullet\text{OOH}$ radicals, producing H^+ ions (equation 5, 6). $\bullet\text{OOH}$ 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 $\bullet\text{OH}$ radicals include, firstly, the dissociation of H_2O_2 into $\bullet\text{OOH}$ and water or combining to form H_2O_2 molecules (equation 7), and, secondly, a reaction with Basic Orange 2 to give the colorless degradation products (equation 8).

The main advantage of using the photo-Fenton reagent is the cyclic regeneration of the consumed Fe^{2+} 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. The whole process is picturised (figure-8).



Where S = Dye and P = End Products

Figure-8

A Schematic representation of Photo-Fenton Chemistry

Conclusion

Photo-Fenton reaction have attracted the attention of photochemists all over the world because these reactions are capable of converting toxic compounds into non-toxic or less hazardous products. Degradation of dyes by photo-Fenton reagent as an oxidizing agent may open new avenues for the treatment of waste water from dyeing, printing and textile industries.

Acknowledgements

The authors are thankful to Krishna Chemical, Ankleshwar and GNFC Ltd., Bharuch for providing chemicals and laboratory facilities for accomplishing this work and also thankful to Prof. Suresh C. Ameta (Ex President, Indian Chemical Society) for providing excellent guideline regarding the subject.

References

1. Ali M.A. and Bashier S.A., Oxidation of Fast Green FCF by the Solar photo-Fenton Processes, *Food Add. Contam.*, **23**, 452 (2006)
2. Nogueira R.F.P., Silva M.R.A and Trov'ó A.G., Influence of the Iron source on the solar photo-Fenton degradation of different classes of organic compounds, *Solar Energy*, **79**, 384 (2005)
3. Feng J., Hu X., Yue P.L., Zhu H.Y. and Lu G.Q., Oxidation of acidic dye Eosine Y by the Solar photo-Fenton Processes, *Water Res.*, **37**, 3776 (2003)
4. Muruganandham M. and Swaminathan M., Oxidation of Direct dyes with H₂O₂ using ferrous ion as catalyst, *Sep. Purif. Technol.*, **48**, 297 (2006)
5. Malik P.K. and Saha S.K., Enzymatic in-situ generation of hydrogen peroxide for decolorization of Acid Blue 113 by Fenton Process, *Sep. Purif. Technol.*, **31**, 241 (2003)
6. Muruganandham M. and Swaminathan M., Decolorization of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology, *Dyes Pigments*, **72**, 137 (2007)
7. Lucas M.S. and Peres J.A., Declorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigments*, **71**, 235 (2006)
8. Will I.B.S. and Moraes J.E.F., Photo-Fenton degradation of waste water containing organic compounds in solar reactors, *Sep. Purif. Technol.*, **34**, 51 (2004)
9. Zheng H. and Xiang X., Photo-Fenton oxidation process used in the degradation of Rhodamine B, *Spectrosc. Spectr. Anal.*, **24**, 726 (2004)
10. Xiang X. and Zheng H., Photo-Fenton oxidation process used in the degradation of Melachite Green, Chongqing Jianzhu Univ., **26**, 126 (2004)
11. Xu Y., Photocatalytic degradation of textile dye X₃B by heteropolyoxometalate acids, *Chemosphere*, **43**, 1103 (2001)
12. Mogra D., Mehta M., Ameta R. and Ameta S.C., Studies on Photodegradation of Chloropropionic acid by Fenton and other like Reagents., *J. Indian. Chem. Soc.*, **79**, 593 (2002)
13. Mogra D., Ameta R., Chhabra N. and Ameta S.C., Photochemical degradation of Chlorobenzene by photo-Fenton reagent, *Intl. J. Chem. Sci.*, **1**, 211 (2003)
14. Walling C., Intermediates in the reaction of Fenton type reagents, *Acc. Chem. Res.*, **31**, 155 (1998)
15. Munesh Swati and Meena R.C., Photocatalytic Decolorization of Acid Red 186 Using Alternative Developed Photocatalyst MBIR Dowex 11, *Res.J.Chem.Sci.*, **2(9)**, 56-62 (2012)
16. Santhanalakshmi J. and Komalavalli R., Visible Light Induced Photocatalytic Degradation of some Textile Dyes Using Silver Nano Particles, *Res.J.Chem.Sci.*, **2(4)**, 64-67 (2012)