Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

J. Chem. Pharm. Res., 2010, 2(4):655-662

ISSN No: 0975-7384
CODEN(USA): JCPRC5

Photocatalytic Degradation of diazinic ring- containing azo dye (Direct Yellow 12) by Photo-Fenton Reagent

Menka Surana[#], Preeti Mehta*, Kavita Pamecha[**] and B.V. Kabra[**]

Department of Chemistry, Mewar University, Chittorgarh (Raj.)
**Department of Chemistry, Institute of Technology and Management, Bhilwara (Raj.)*
[**] Department of Chemistry, M.L.V.Govt. College, Bhilwara (Raj.)

ABSTRACT

Photocatalytic decolourization of dyes using AOP is a new concern among researchers since it offers an attractive method for decolorization of dyes and breaks them into simple mineral form. The oxidation using Fenton Reagent has been found to be a promising treatment method for the effective decolorization and degradation of dyes. A detailed investigation of photodegradation of Direct Yellow-12 (DY12) using H_2O_2/Fe^{+2} *has been carried out. Results indicate that dye degradation is dependent on concentration of Dye (DY12), photocatalyst (Fenton reagent),* H_2O_2 *and pH of the experimental solutions. The optimum conditions for the photobleaching of dye had been established. The kinetics of degradation of the dye in the dilute aqueous solutions follows first order kinetics. The results indicated that the treatment of the dye by Photo-Fenton reagent was efficient at optimum conditions.*

Keywords- Direct Yellow-12, Photo- Fenton, Photocatalytic, Decolourization, Photobleaching

INTRODUCTION

The world is facing the challenge of purification of water and other resources. A lot of industries especially textile, dyeing and printing industries have generated environmental problems like aesthetic pollution, eutrophication and perturbation of aquatic ecosystem. Waste waters originating from dyes production and application industries pose a major threat to the surrounding ecosystems because of their toxicity and potentially carcinogenic nature [1]. Apart from the aesthetic problems relating to colored effluent, dyes strongly absorb sunlight. It affects the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem [2]. Therefore, this problem of textile waste waters caused by residual dyes during the dyeing process needs more effort to be studied and investigated. The limitations of conventional waste water treatment methods can be overcome by the application of the so called advanced oxidation processes (AOPs) [3].

AOPs are based on the generation of very reactive species such as hydroxyl radicals ($^{\bullet}OH$), which have a strong oxidation potential [$E^0 = + 2.80$ V], second only to fluorine. Hydroxyl radicals rapidly and non-selectively oxidize a broad range of organic pollutants [4]. Common AOPs involve Fenton, Fenton-like processes, ozonation, high voltage electrical discharge (corona) process, TiO_2, photo catalysis, radiolysis, wet-oxidation and various combination of these methods [5-8]. Fenton's oxidation, one of the oldest AOPs, is relatively cheap, easily operated and maintained [9-12]. It has the advantages of coagulation and catalytic oxidation, as well as being able to generate oxygen in water. Fenton and Fenton type processes have proven to yield very good results either for complete mineralization of azo dyes or for their transformation into less complex structures that are more easily biodegradable [13-15].

Direct Yellow-12 (DY12) is widely used in textile industries. As, it causes great potential of pollution of water environment, a proper treatment is necessary before discharge into the environment. Therefore, it is planned to undertake the title investigation. The objective of the present study is to evaluate the dependence factors for the color removal rate such as concentration of Dye (DY12), photocatalyst (Fenton reagent), H_2O_2 and pH of the experimental solutions.

EXPERIMENTAL SECTION

Materials

For the present studies the commercial disazo dye Direct Yellow-12 (C.I No. 24895, Aldrich) (Fig: 1) having 95% dye content was used. Photocatalyst $FeSO_4$ (Merck, 99% purity) and H_2O_2 (Merck, 6% purity) were used for photocatalytic degradation. For the photobleaching process, $1x10^{-3}$M (0.722g/l) stock solution of dye Direct Yellow-12 was prepared in double distilled water and diluted as required. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. All laboratory reagents were of analytical grade.

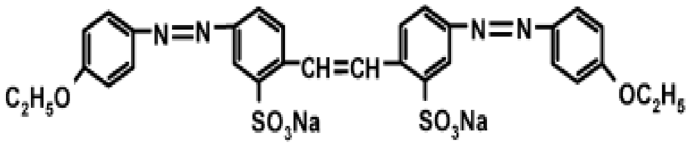


Fig - 1 : Structure of Direct Yellow-12

Molecular formula – $C_{30}H_{26}N_4Na_2S_2O_8$ *Molecular weight = 686.60*

Procedure and Analysis

The reaction mixture was prepared by taking 3 ml of Direct Yellow-12 dye solution ($1x10^{-3}$ M), 2.5 ml of $FeSO_4$ ($1x10^{-3}$ M), 2.5 ml of H_2O_2 (6%) in a round bottom flask. The total volume of the reaction mixture was made 100 ml by adding double distilled water. The concentration of different ingredients in the reaction mixture was [Dye] =$3x10^{-5}$ M, [$FeSO_4$] =$2.5x10^{-5}$ M, [H_2O_2] = 4.87 $x10^{-2}$ M.

To carry out the photobleaching, the reaction mixture was irradiated under light source (2 x 200 W Tungsten lamps). Water filters were used to cut off thermal radiation. The pH of the solution was measured by pH meter (Systronics, 106). The progress of the reaction was observed at definite time intervals by measuring absorbance using spectrophotometer (Schimadzu, UV-1700, Pharmaspec) at 390 nm. The rate of decrease of colour with time was continuously monitored. After complete mineralization, the presence of NO_2^-, NO_3^-, SO_4^{2-} ions and evolution of CO_2 were tested by standard procedure.

RESULTS AND DISCUSSION

Control experiments (in absence of photocatalyst, light) confirm the necessity of photocatalyst, light to follow the photocatalytic path for the photobleaching of dye.

The photocatalytic degradation of Direct Yellow-12 was observed at 390 nm. The optimum conditions for the photobleaching of dye were [Dye] =$3x10^{-5}$ M, [$FeSO_4$] =$2.5x10^{-5}$ M, [H_2O_2] = 4.87 $x10^{-2}$ M and pH=3. The result of photocatalytic bleaching of Direct Yellow-12 is graphically presented in Fig.2.

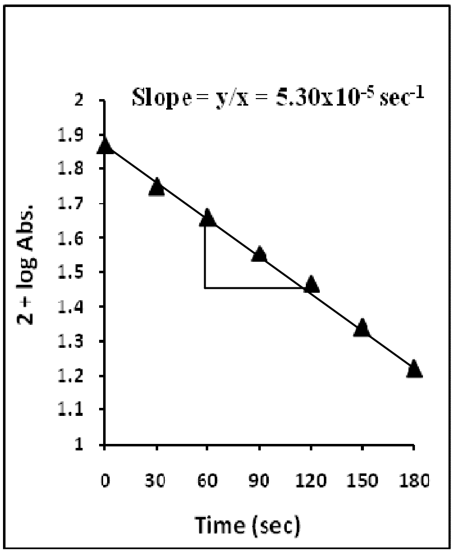


Fig-2: A plot showing a typical run of photobleaching of Direct Yellow-12 by Photo-Fenton reagent under the optimized conditions

It was observed that absorbance (Abs.) decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation. A graph between 2 + log Abs. and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Direct Yellow-12 follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression.

$$\textbf{Rate (k)} = 2.303 \times \textbf{Slope}$$
$$= 12.20 \times 10^{-5}\ \text{sec}^{-1}$$

The effect of variation in various reaction parameters has been studied, e.g. pH, concentration of the dye, concentration of $FeSO_4$ and concentration of H_2O_2.

Effect of variation in hydrogen ion concentration on the rate of decolorization of the dye

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of $^{\bullet}OH$ production in the Fenton's reaction. At high pH (pH > 3), the generation of $^{\bullet}OH$ gets slower because of the formation of the ferric hydroxo complexes.

On the other hand, at very low pH (< 2.0), hydrogen ions acts as $^{\bullet}OH$ radical scavengers. The reaction is slowed down due to the formation of complex species $[Fe(H_2O)_6]^{+2}$, which reacts more slowly with peroxide compared to that of $[Fe(OH)(H_2O)_5]^{+2}$.

In this study, photodegradation was performed at different pH from 1 to 4.5. Fig - 3 also prove that pH 3 is the optimal pH for DY12 decolorization. Hence all subsequent experiments were carried out at pH 3.

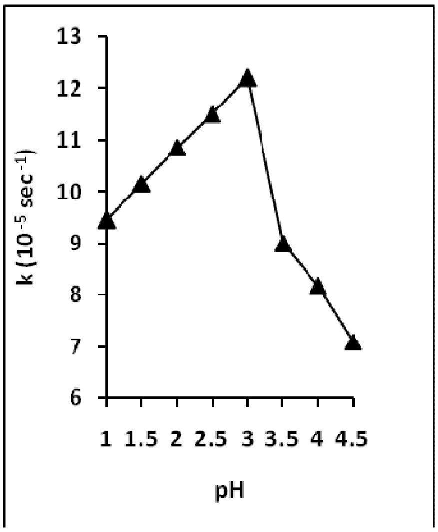


Fig- 3: A plot showing effect of variation in hydrogen ion concentration on the rate of decolorization of the dye by Photo-Fenton reagent

Effect of variation in dye concentration on the rate of decolorization of the dye

The effect of dye concentration on the degradation of Direct Yellow-12 was studied at different concentrations varying from 1.0×10^{-5} M to 8.0×10^{-5} M keeping all other factors identical. The result (Fig-4) reveals that the rate of photobleaching of dye decreases with the increase in the concentration of the dye. The reason behind it is that the increase in the initial concentration of the dye lies in consistency of the hydroxyl radicals concentrations for all the dye molecules and therefore the rate of decolorization decreases.

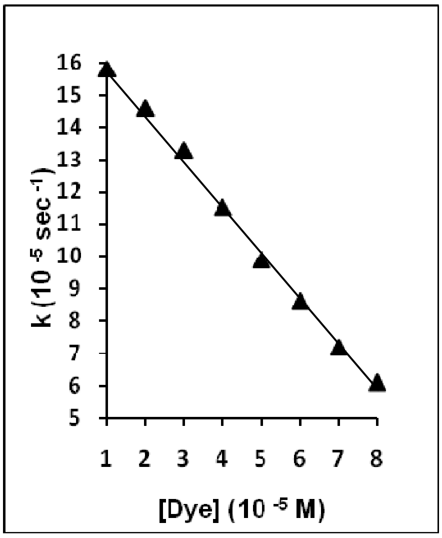


Fig- 4: A plot showing effect of variation in dye concentration on the rate of decolorization of the dye by Photo-Fenton reagent

Effect of variation in catalyst concentration on the rate of decolorization of the dye

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 Fig-5 reveals that the rate of photobleaching of dye increases with the increase in the concentration of catalyst $FeSO_4$ up to 2.5 x 10^{-5} M. The increase in ferrous ions in the reaction mixture is accompanied by enhanced generation of $^{\bullet}OH$ radicals, consequently increasing the rate of photodegradation. After the optimal Fe^{2+} addition, the higher dose of Fe^{2+} resulted in a brown turbidity that causes the recombination of $^{\bullet}OH$ radicals and Fe^{2+} reacts with $^{\bullet}OH$ as a scavenger. Therefore, on further increase, the rate becomes almost constant.

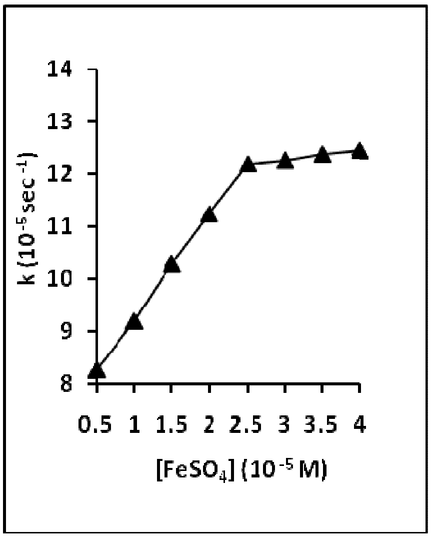


Fig- 5: A plot showing effect of variation in catalyst concentration on the rate of decolorization of the dye by Photo-Fenton reagent

Effect of variation in hydrogen peroxide concentration on the rate of decolorization of the dye

The effect of H_2O_2 concentration on the degradation of DY12 is shown in Fig - 6. The result reveals that the rate of photobleaching of dye increases with the increase in the concentration of H_2O_2 upto 4.87 x10^{-2} M. This can be explained on the basis that at higher concentration of H_2O_2, more hydroxyl radicals are produced which degrade more dye molecules.

Further increase in [H_2O_2] has negligible effect due to the recombination of $^{\bullet}OH$ radicals and also hydroxyl radicals reaction with H_2O_2 contributing to the $^{\bullet}OH$ scavenging capacity.

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2$$
$$^{\bullet}OH + H_2O_2 \longrightarrow {}^{\bullet}O_2H + H_2O$$
$$^{\bullet}O_2H + {}^{\bullet}OH \longrightarrow H_2O + O_2$$

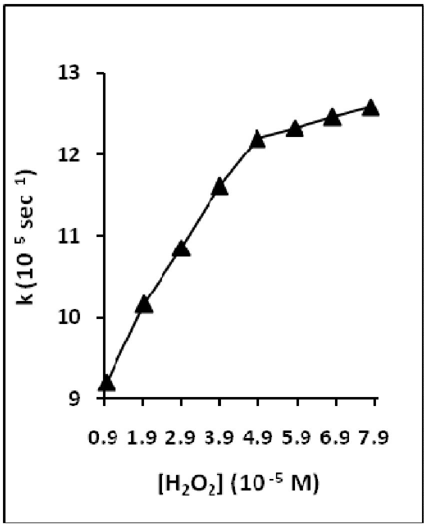


Fig- 6: A plot showing effect of variation in hydrogen peroxide concentration on the rate of decolorization of the dye by Photo-Fenton reagent

Mechanism

The mechanism of Fenton oxidation is based on the generation of $^{\bullet}OH$ radicals by the catalytic decomposition of H_2O_2 in acidic media. In presence of Fe^{2+}, the peroxide breaks down to $^{\bullet}OH$ and OH^{-}, according to the following reactions (Eqn.1, 2, 3).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad \textbf{(1)}$$

$$Fe^{3+} + H_2O_2 + hv \longrightarrow Fe^{2+} + {}^{\bullet}OOH + H^{+} \quad \textbf{(2)}$$

$$2\,H_2O_2 \longrightarrow H_2O + {}^{\bullet}OH + {}^{\bullet}O_2H \quad \textbf{(3)}$$

Ferrous ions will undergo oxidation to ferric ions by the addition of $^{\bullet}OH$ radicals, while ferric ions are reduced to ferrous ions by the incorporation of $^{\bullet}OOH$ radicals producing H^{+} ions (Eq: 3, 4).

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^{-} \quad \textbf{(3)}$$
$$Fe^{3+} + {}^{\bullet}O_2H \longrightarrow Fe^{2+} + O_2 + H^{+} \quad \textbf{(4)}$$

$^{\bullet}$OOH radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules. The participation of the $^{\bullet}$OH radical as an active oxidizing species was confirmed using the hydroxyl radical scavenger 2-Propanol, which drastically reduced rate of degradation.

The hydroxyl radical attacks on dye molecule and abstracts a hydrogen atom or adds itself to double bonds.

After continuous irradiation, the complete mineralization of dye occurred via converting into end products.

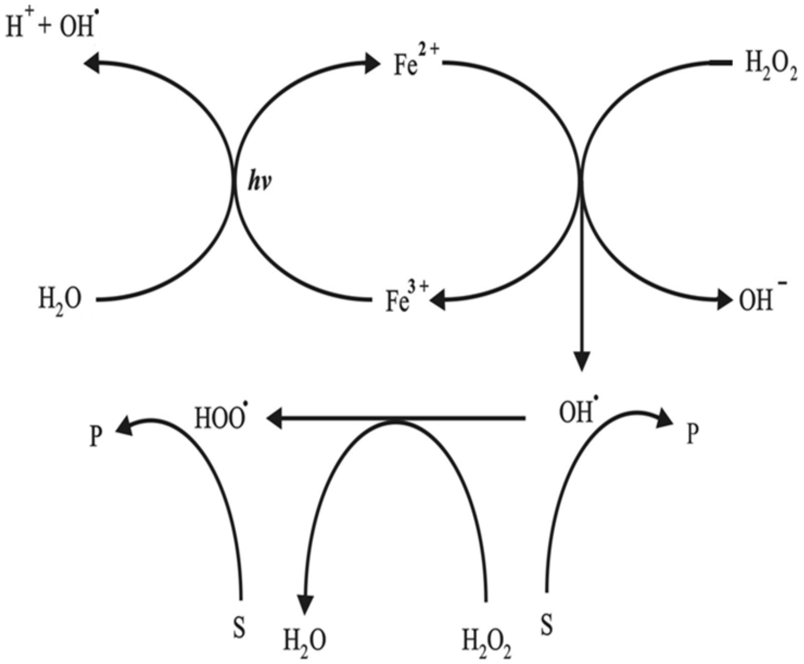
The end products are simple molecules or ions and less harmful to the environment (Eq: 5).

$$\mathbf{C_{30}H_{26}N_4Na_2S_2O_8 \xrightarrow{OH^-} Intermediates \longrightarrow End\ Products}$$

Direct Yellow-12 (S) **(P)** **(5)**

End products $\equiv$ $\mathbf{CO_2 + H^+ + H_2O + NO_2^- + NO_3^- + SO_4^{2-}}$

The end products were detected and their presence in the reaction mixture was ascertained either by chemical test or by ion selective electrode method.



Where S = Dye and P = End Products

Fig.7: A Schematic representation of Photo-Fenton Chemistry

Nitrate ions were detected and confirmed using nitrate ion selective electrode which is having a solid-state PVC polymer membrane. Nitrite ions were detected and confirmed by a chemical test

---

using H_2SO_4 and $FeSO_4$. A positive test for presence of nitrite ions is indicated by a dark brown solution, arising from the iron nitric oxide complex. Sulphate ions were detected and confirmed by gravimetric analysis in which excess of barium chloride solution was used and sulphate ions are precipitated as $BaSO_4$. CO_2 was confirmed by introducing the gas to freshly prepared limewater. The test solution (limewater) turns milky which indicates its presence.

The whole process is picturised (Fig.7)

Acknowledgments

The authors are thankful to Prof. Ramesh Chandra (Vice Chancellor, Mewar University, Gangrar), Dr.V.K.Vaidya (Retired Principal, M.L.V. Govt. College, Bhilwara), Dr.R.L. Pitliya (Principal, S.D. College, Bhilwara) and Dr.P.K.Jain (Head, Department of Chemistry, M.L.V. Govt. College, Bhilwara) for continuous encouragement in accomplishing this work.

REFERENCES

[1] H Kusic; AL Bozic; N Koprivanace. *Dyes and Pigments*, **2006,** 1.
[2] SKA Solmaz; A Birgul; GE Vstun; T Yonor. *Society of dyers and colourists, color. Technol.*, **2006**, 122, 102.
[3] M Neamtu; A Yedilar; I Siminiceanu; M Macoveanu; A Kettrup. *Dyes and Pigments*, **2004**, 60, 61.
[4] N Daneshwar; D Salari; AR Khatee. *J. Photochem. Photobiol. A: Chem.* **2003**, 157, 111.
[5] PR Gogate; AB Pandit. *Advances in Environ. Res*., **2004**, 8, 553.
[6] HS El-Desoky; MM Ghoneim; R El-Sheikh; NM Zidan. *J. Hazard. Mater.,* **2010**, 175 858.
[7] YH Huang; HT Su; LW Lin. *J. Environ. Sci.,* **2009**, 21, 35.
[8] A Serra; X Domenech; C Arias; E Brillas. *J. Peral, Appl. Catal. B: Environ*., **2009**, 89 ,12.
[9] F Fu; Q Wang; B Tang. *J. Hazard. Mater*., **2010**, 174, 17.
[10] B K Mert; T Yonar; MY Kilic; K Kestioglu. *J. Hazard. Meter.*, **2010**, 174, 122.
[11] K Swaminathan; S Sandhya; A Gamarlin Sophia; K Pachhade; YV Subrahmanyam. *Chemosphere*, **2003**, 50, 619.
[12] TM Elmorsi; YM Riyad; ZH Mohamed; HMH Abd; El Bary. *J. Hazard. Mater*., **2010**, 174, 352.
[13] I Arslan; IA Baleioglu; DW Bahnemann. *Water Res*., **2002**, 36, 1143.
[14] M Perez; F Torrades; X Domenech; J Peral. *Water Res*., **2002**, 36, 2703.
[15] M Neamtu; I Siminiceanu; A Yediler; A Kettrup. *Dyes and Pigments*, **2002**, 53, 93.