

Advanced Oxidation Processes for the Degradation of Water Pollutants

George Jogi¹, Rani Varghese²

¹Student, Department of Chemistry, Christ College, Irinjalakuda, Thrissur, India

²Assistant Professor, Department of Chemistry, Christ College, Irinjalakuda, Thrissur, India

Abstract: Degradations of a textile dye effluent have been investigated using Fenton and photo-Fenton reactions. The concentration of Fe (II) selected was 10^{-5} M, 5×10^{-6} M and 10^{-6} M. and the concentrations of H_2O_2 selected were 10^{-2} M and 10^{-3} M. In order to perform photo-Fenton reaction, the reaction mixture after dark-Fenton reaction is irradiated for different time intervals in bright sunlight. Best degradations was obtained for a photo-Fenton reaction in which the concentration of Fe(II) was 10^{-6} M and the concentration of H_2O_2 was 10^{-2} M for an irradiation time of 2 hours.

Keywords: Enter key words or phrases in alphabetical order, separated by commas.

1. Introduction

Environmental pollution is a constant threat to the biosphere. Industrial effluents, combustion of fuels, ionizing radiation, etc., cause air pollution. The increased applications of fertilizers, pesticides and herbicides in modern agriculture and related fields and the ever-expanding chemical industry result large amounts of chemical waste materials disposed in rivers, seas and ocean. The major consequence of such increased use of pollutant chemicals is that water resources become heavily charged with pollutants. New technologies are being developed in the past few years for the destruction of hazardous organic chemicals that pollute drinking water. Major contaminants which persist in water and cause many ecological problems include pesticides, herbicides, dyes, detergents and a wide variety of industrial effluents. The conventional methods used for the purification of drinking water such as flocculation, filtration, sterilization, reverse osmosis and adsorption on activated carbon have proved to be inadequate to degrade the stable aromatic ring of these pollutants. Direct photo-degradation under sunlight and biodegradation have little effect on most of these pollutants and those with sufficient solubility in water are capable of penetrating deep into soil and even reach ground water.

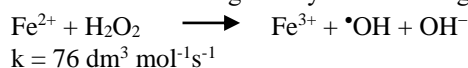
The concept of advanced oxidation process was introduced first in 1987 by Glaze *et. al.* AOPs have been developed to detoxify non-biodegradable wastewater.¹ In general, processes that generate the highly reactive radical, the hydroxyl radical ($\bullet OH$) which is capable of oxidizing organic contaminants in water are named as AOPs.² $\bullet OH$ is one of the most powerful oxidizing agents, which can attack organic molecules rather

nonselectively, with rate constants ranging from 10^6 to 10^{10} $dm^3 mol^{-1} s^{-1}$. Such reactions result in their complete mineralization into inorganic products or their conversion into non-toxic compounds. Due to its high reactivity, $\bullet OH$ is very unstable and must be continuously generated *in situ*.

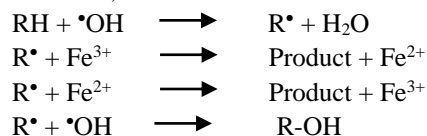
The most widely studied homogeneous AOPs include H_2O_2/UV , ultrasound, O_3/UV , radiolysis of water and aqueous solutions under oxidizing conditions, Fenton reaction (Fe^{II}/H_2O_2) and photo-Fenton reaction ($Fe^{II}/H_2O_2/UV$). The most commonly used heterogeneous photocatalytic oxidation systems are TiO_2/UV and $TiO_2/H_2O_2/UV$.

The important measure of the success of an AOP is the extent of mineralization of target pollutants to CO_2 and inorganic ions as this denotes the overall destruction of possibly toxic organic intermediates in addition to the parent contaminant itself.³ One common problem with AOP is the high demand of electrical energy and UV-lamps, which increase the total cost of these processes. A very promising possibility of cost reduction is the application of sunlight for irradiation purposes.⁴

Fenton's reaction is given by the following reaction.



The $\bullet OH$ generated in the Fenton reaction can react with aqueous organic pollutants whereby intermediate radicals are produced which can be oxidized by Fe(III) or reduced by Fe(II) forming stable products. The reaction scheme can be represented as,⁷

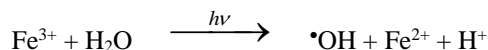


The rate constants for the above reactions are substrate-specific.

The use of Fenton's reagent to oxidize toxic organics began in late sixties. Now, there are several reports that show Fenton reaction can effectively be used for the destruction of several aqueous organic pollutants. The major advantages of Fenton's reagent as a hazardous waste treatment technology are, (i) both iron and H_2O_2 are cheap and non-toxic, (ii) there is no mass transfer limitation due to its homogeneous catalytic nature, (iii) there is no involvement of light so that the reactor design is

much easier than UV- light systems.

In Fenton reaction, Fe(III) ions get accumulated in the reaction medium and after all the Fe(II) ions are exhausted, the reaction practically stops. By irradiating the system with UV or UV-Visible light, the accumulated Fe(III) can be reduced to Fe(II)⁸ whereby the Fenton reaction can be made catalytic in iron.



Thus the efficiency of dark-Fenton reaction can be increased in both ways, one by generating an additional $\bullet\text{OH}$ in the above step and the other by recycling Fe(II). The major advantage of this process is its light sensitivity upto wavelengths of 600 nm, *i. e.*, illuminations by visible light can be utilized which overcomes the common drawback of relatively high cost for UV-lamps and electrical energy compared to other AOPs.

Dyes are a large group of compounds almost exclusively organic in nature used for coloring of textiles, inks, food products etc. The basic raw materials of synthetic dyes are compounds, such as benzene, that are derived from the destructive distillation of coal. For this reason synthetic dyestuffs are often popularly known as coal-tar dyes. Of all the groups of dyes the azo dyes are the most generally useful and widely employed.

Dye house effluents contain large amounts of dyes. The strong color of discharged dyes even at very small concentrations has a huge impact on aquatic environment. Traditional water purification methods like adsorption on activated carbon, filtration, flocculation, ultrafiltration, reverse osmosis etc. can only transfer these pollutants from water thereby causing secondary pollution. In recent years AOPs have been found to be highly effective in the complete mineralization of dyes.

In the present work, a textile effluent has been selected as the target compound. Dyes are toxic and are relatively stable for long periods in the environment. Their persistence in natural water and even in ground water is detected which is indicated by the color imparted to water by them. So reliable technologies are to be developed for the successful destruction or detoxification of these pollutants. Advanced Oxidation Processes (AOPs) are becoming increasingly popular for the effective degradation of organic pollutants to nontoxic compounds. AOPs generate hydroxyl radical ($\bullet\text{OH}$) which can react nonselectively with almost all organic compounds at diffusion controlled rates. We have made use of two major AOPs –dark Fenton reaction and photo-Fenton reaction. The progress of the reactions was monitored using UV-Visible Spectrophotometry.

2. Materials and methods

Commercially available high purity chemicals were used without further purification for the entire study. Ferrous sulfate and hydrogen peroxide (30% w/v) were obtained from E.

Merck India Ltd., Mumbai. A textile dye has been selected as a target compound. Photochemical methods and dark-Fenton reaction were used in the entire study. All experiments were performed in distilled water. The samples were kept in dark before and after irradiations.

The dark-Fenton reaction was performed by adding required amounts of ferrous sulfate solution to a mixture of substrate and the required amount of H_2O_2 with continuous stirring on a magnetic stirrer. All the solutions were kept in dark before and after irradiations. After 20 minutes the stirring is stopped, the mixture is neutralized with NaOH solution and the precipitated Fe(III) was removed by filtration. The filtrate was analyzed by UV-Visible spectrophotometry. Sunlight has been utilized for photo-irradiations. Irradiations with sunlight were carried out at the middle of bright sunny days (March/April at Irinjalakuda, Kerala). Spectrophotometric measurements were carried out on a Perkin-Elmer UV-Visible spectrophotometer.

3. Results and Discussion

A. Dark-Fenton Reaction

In order to carry out Fenton reactions in the dark, 10 ml of the dye sample was used. The concentrations of H_2O_2 selected were 10^{-2} M and 10^{-3} M. The reaction mixture, covered well with black paper was stirred on a magnetic stirrer. The concentration of Fe (II) selected was 10^{-5} M, 5×10^{-6} M and 10^{-6} M. It was added to the reaction mixture during stirring. The stirring is continued for 30 minutes and then analyzed by UV-Visible spectrophotometry.

The UV-Visible absorption spectrum of dye sample is shown in figure 1 and the spectrum taken after Dark-Fenton reaction is shown in figure 2, 3, 4, 5, 6 and 7.

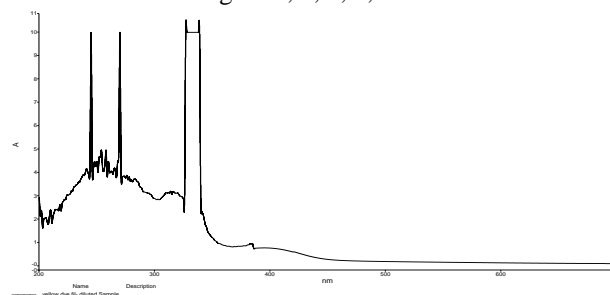


Fig. 1. The UV – Visible absorption spectrum of the dye sample

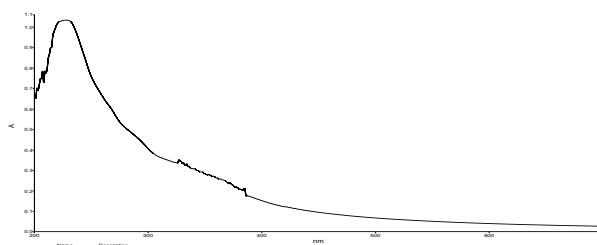


Fig. 2. The UV-Visible absorption spectrum of the dye after dark-Fenton reaction (The concentration of Fe (II) selected was 10^{-5} M the concentration of H_2O_2 selected was 10^{-2} M).

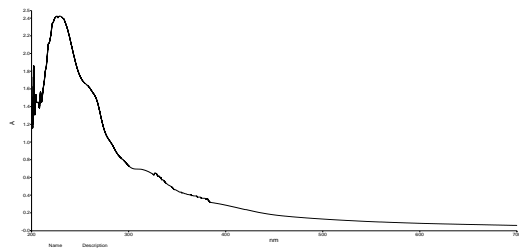


Fig. 3. The UV-Visible absorption spectrum of the dye after dark-Fenton reaction (The concentration of Fe (II) selected was 5×10^{-6} M the concentration of H_2O_2 selected was 10^{-2} M).

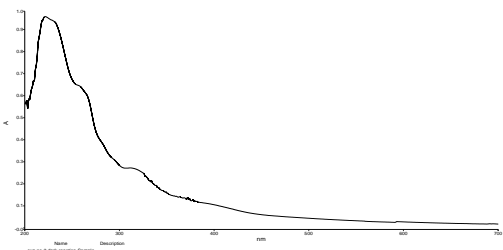


Fig. 4. The UV-Visible absorption spectrum of dye after dark-Fenton reaction (The concentration of Fe (II) selected was 10^{-6} M the concentration of H_2O_2 selected was 10^{-2} M).

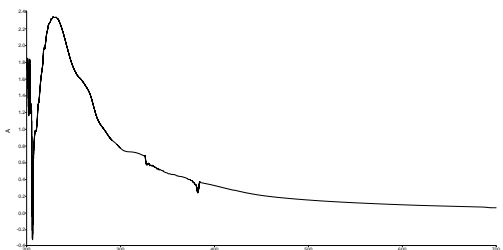


Fig. 5. The UV-Visible absorption spectrum of dye after dark-Fenton reaction (The concentration of Fe (II) selected was 10^{-5} M the concentration of H_2O_2 selected was 10^{-3} M)

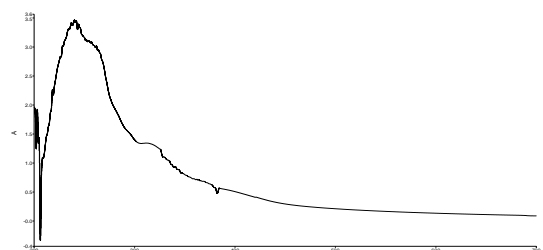


Fig. 6. The UV-Visible absorption spectrum of dye after dark-Fenton reaction (The concentration of Fe (II) selected was 5×10^{-6} M the concentration of H_2O_2 selected was 10^{-3} M)

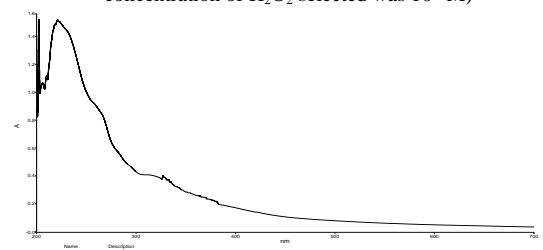


Fig. 7. The UV-Visible absorption spectrum of dye after dark-Fenton reaction (The concentration of Fe (II) selected was 10^{-6} M and the concentration of H_2O_2 selected was 10^{-3} M)

It was observed that after dark-Fenton reaction the color of the reaction mixture has been decreased. From figure 1, it is evident that the color of it is due to the absorption peak at 340-360 nm. Fig. 2 to 7 show that this peak has been disappeared. This shows that the dye has been started degrading.

The mechanism of Fenton reaction⁹ and the pathways through which it leads to the mineralization of the pollutant⁹ are well documented. The most accepted mechanism is that the $\bullet OH$ generated in the Fenton reaction can react with aqueous organic pollutants whereby intermediate radicals are produced which can be oxidized by Fe(III) or oxidized by Fe(II) forming stable products.¹⁰ However an alternative interpretation of the Fenton reaction postulates the formation of a ferryl cation. Some reports assume that the initial Fe(II)- H_2O_2 reaction is a two-electron process to yield $Fe^{IV}OH$ which in turn decomposes to Fe(III) and $\bullet OH$. In certain cases the ferryl radical decomposes rapidly but in the presence of suitable ligands around iron *e.g.* porphyrin rings, the Fe(IV) state might be stabilized sufficiently to become the primary oxidant which can oxidize organic compounds but in a way quite distinguishable from free $\bullet OH$.¹¹ In the present case, the formation of such a Fe^{IV} state is highly improbable because there are no such ligands to stabilize the Fe^{IV} state. Therefore the attack of $\bullet OH$ on the dye molecule is expected to be the major process. The so formed intermediates can be oxidized by Fe(III) or reduced by Fe(II) leading to the formation of various products.

B. Photo-Fenton Reaction

In order to perform photo-Fenton reaction, the reaction mixture after dark-Fenton reaction is used. 7 ml of the solution is taken and irradiated for different time intervals in bright sunlight. Three different concentrations of Fe(II) were selected, 10^{-5} M, 5×10^{-6} M and 10^{-6} M and the concentrations of H_2O_2 selected were 10^{-2} M and 10^{-3} M. The solutions are covered with black paper before and soon after irradiation. The irradiation times chosen are 5, 15, 30, 45, 60, 75 and 120 minutes. The UV-Visible absorption spectra are taken and are shown in figures 8 to 13.

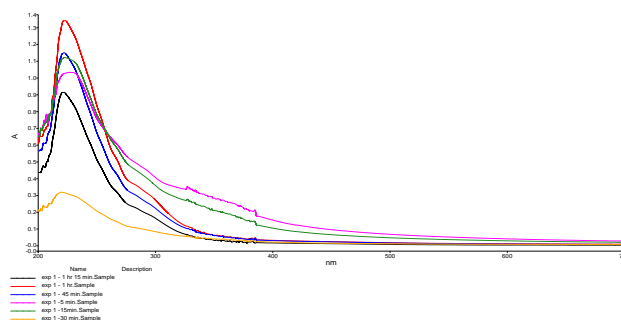


Fig. 8. The UV-Visible absorption spectrum of dye after photo-Fenton reaction for different times of irradiation. (The concentration of Fe(II) selected was 10^{-5} M and the concentration of H_2O_2 selected was 10^{-2} M).

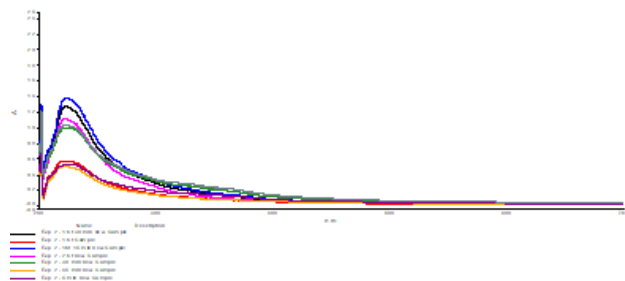


Fig. 9. UV-Visible absorption spectrum of dye after photo-Fenton reaction for different times of irradiation. (The concentration of Fe(II) selected was 5×10^{-6} M and the concentration of H_2O_2 selected was 10^{-2} M)

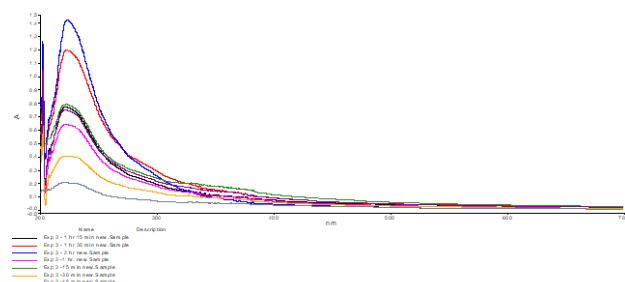


Fig. 10. The UV-Visible absorption spectrum of dye after photo-Fenton reaction for different times of irradiation. (The concentration of Fe(II) selected was 10^{-6} M and the concentration of H_2O_2 selected was 10^{-2} M)

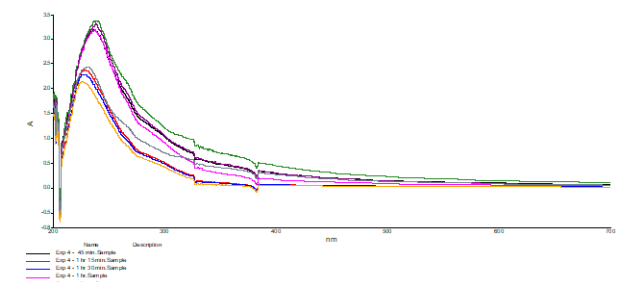


Fig. 11. The UV-Visible absorption spectrum of dye after photo-Fenton reaction for different times of irradiation. (The concentration of Fe(II) selected was 10^{-5} M and the concentration of H_2O_2 selected was 10^{-3} M)

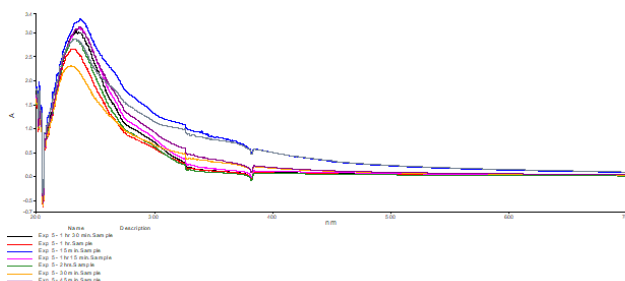


Fig. 12. The UV-Visible absorption spectrum of dye after photo-Fenton reaction for different times of irradiation. (The concentration of Fe(II) selected was 5×10^{-6} M and the concentration of H_2O_2 selected was 10^{-3} M).

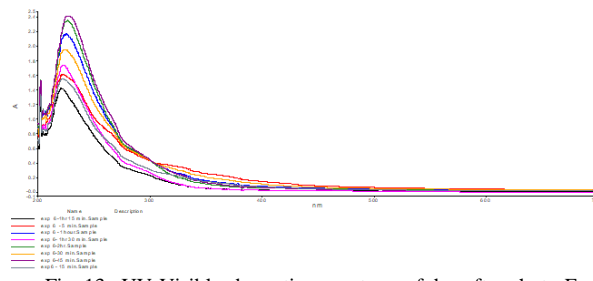


Fig. 13. UV-Visible absorption spectrum of dye after photo-Fenton reaction for different times of irradiation. (The concentration of Fe(II) selected was 10^{-6} M and the concentration of H_2O_2 selected was 10^{-3} M).

Figures 8 to 13 show results of degradations after photo Fenton reactions.

It has been observed that in Fenton reaction, Fe(III) ions get accumulated in the reaction medium and after all the Fe(II) ions are exhausted, the reaction practically stops. By irradiating the system with UV or UV-Visible light, the accumulated Fe(III) can be reduced to Fe(II)⁸ whereby the Fenton reaction can be made catalytic in iron. Thus the efficiency of dark-Fenton reaction can be increased by recycling Fe(II). Photo-Fenton process gives optimum results at pH around 3 where almost 50% of the Fe(III) exists as Fe(OH)²⁺ complex which is the major photoactive species that generates $\bullet OH$ upon illumination.⁷ Below this pH the concentration of Fe(OH)²⁺ declines and at higher pH the Fe(III) precipitates as oxyhydrates. The major advantage of this process is its light sensitivity upto wavelengths of 600 nm, *i. e.*, illuminations by visible light can be utilized which overcomes the common drawback of relatively high cost for UV-lamps and electrical energy compared to other AOPs.

From figures it is evident that the dye has been started degrading. The most effective degradation was observed in the case of Fe(II) $10^{-6} \text{ mol dm}^{-3}$ and H_2O_2 $10^{-2} \text{ mol dm}^{-3}$ for 2 hrs irradiation. The most accepted mechanism for photo-Fenton reaction is that the $\bullet OH$ generated from the Fe(OH)²⁺ complex can react with aqueous organic pollutants whereby intermediate radicals are produced which can be oxidized by Fe(III) or oxidized by Fe(II) forming stable products. Reaction of $\bullet OH$ can proceed by addition to double bonds having sufficient electron density or by hydrogen abstraction from alkyl or hydroxyl groups or by electron transfer. At this stage of illumination, the primary degradation products of the dye have started to degrade forming low molecular weight products.

4. Conclusion

In this work, dye factory effluent was collected and its degradation was studied. Two different AOPs have been selected viz., Fenton reaction and photo-Fenton reaction. Experiments were performed for different times of irradiations with bright sunlight and for different concentrations of H_2O_2 and Fe(II). It was observed that all the AOPs are highly effective in the degradation of the target compound. The most effective degradation was observed in the case of Fe(II) 10^{-6} mol

dm^{-3} and H_2O_2 10^{-2} mol dm^{-3} for 2 hrs of irradiation. The complete mineralizations need further irradiations.

References

- [1] W. H. Glaze, F. Beltran, T. Tuhkanen, J- W. Kang, *Ozone Sci. Technol.* 9, 1987, 335.
- [2] W. H. Glaze, Y. Lay, J- W. Kang, *Ind. Eng. Chem. Res.* 34, 1995, 2314.
- [3] P. L. Huston, J. J. Pignatello, *Wat. Res.* 33, 1999, 1238.
- [4] R. Bauer, H. Fallmann, *Res. Chem. Intermed.* 23, 1997, 341.
- [5] H. J. H. Fenton, *Chem. Soc.* 65, 1894, 899.
- [6] F. Haber, J. J. Weiss, *Proc. R. Soc. London (Biol.)* A147, 1934, 332.
- [7] J. Chen, W. H. Rulkens, H. Bruning, *Wat. Sci. Technol.* 35, 1997, 231.
- [8] Y. Sun, J. J. Pignatello, *Environ. Sci. Technol.* 27, 1993, 304.
- [9] J. L. Weeks, M. S. Matheson, *J. Am. Chem. Soc.* 78, 1956, 1273.
- [10] J. P. H. Hunt, H. Taube, *J. Am. Chem. Soc.* 74, 1952, 5999.
- [11] Y. Oyata, K. Tomizawa, K. Fujii, *Bull. Chem. Soc. Jpn.* 51, 1978, 2628.
- [12] S. Wang, *Dyes and Pigments*, 76(3), 2008, 714.
- [13] T. M. Elmorsi, Y. M. Riyad, Z. H. Mohamed, Hassan M. H. Abd El Berg, *J. Hazard. Mater.* 174(1-3), 2010, 352.
- [14] N. Wang, T. Zheng, G. Zhang, P. Wang, *J. Environ. Chem. Eng.* 4(1), 2016, 762.