



Homogeneous Photocatalytic Degradation of Reactive Orange M2R Dye in Aqueous Medium

S. Harikengaram^{1*}, M. Robinson², A. Chellamani³

^{1*}Department of Chemistry, Pasumpon Muthuramalinga Thevar College, Melaneelithanallur, Tirunelveli, TN, India.

²Department of Chemistry, St. John's College, Palayamkottai, Tirunelveli, TN, India.

³Department of Chemistry, Manonmanium Sundaranar University, Tirunelveli, TN, India.

Received : 02.04.2014 Accepted : 01.05.2015

Abstract

The chemical degradation of reactive orange M2R dye under irradiation of UV light by Fenton's reagent has been investigated spectrophotometrically in aqueous medium. Hydroxyl free radicals are the most reactive chemical species for the degradation process. The influence of pH and initial concentrations of the dye, Fe²⁺ and H₂O₂ on the degradation rate has been investigated and the optimum operational conditions were determined. The photobleaching process follows first-order kinetics. Acidic pH range favours the degradation rate. The results of the study showed that photo-Fenton process is an effective and an economic treatment process for the complete mineralization of the reactive orange M2R dye. A suitable tentative mechanism for the degradation of the dye by photo-Fenton system has been proposed.

Keywords: Fenton's Reagent; Photocatalytic degradation; Reactive orange M2R dye.

1. INTRODUCTION

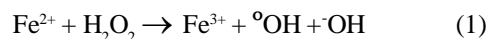
Many different types of synthetic dyes such as azo, vat, indigo are used in textile, paper, leather, ceramics, cosmetics, food processing and ink industries (Buitron *et al.* 2004; Hasnat *et al.* 2005; Beker and Salker, 2006). Among these dyes, the azo dyes constitute the largest and the most important class of commercial dyes (Behnajady *et al.* 2007; Robinson *et al.* 2001). Wastewaters originating from dyes production and application industries pose a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature (Kusic *et al.* 2006; Papic *et al.* 2004; Vander Zee *et al.* 2001). Also the dyes in wastewater affect photosynthetic activity in

environment due to reduced light penetration and may be toxic to aquatic lives (Solmaz *et al.* 2006). It is therefore essential either to remove the dyes from wastewater or to treat them in such a way so as to minimize their effects on the environment and also to decolourize the water. Commonly employed methods for colour removal such as adsorption, coagulation-flocculation, oxidation and electrochemical methods are quite expensive and have operational problems (Lin and Peng, 1996; Karthikeyan *et al.* 2012; Ramakrishnan and Viraraghavan, 1997). The limitations of conventional wastewater treatment methods can be overcome by the application of advanced oxidation processes (AOPs) (Neamtu *et al.* 2004).

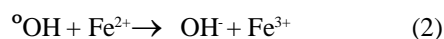
In recent years, advanced oxidation processes (AOPs) have been intensively investigated for the

*S. Harikengaram Tel.No.:+919443282127
E-mail: harikengaram2009@gmail.com

treatment of waters and wastewaters. AOPs defined as processes are generating hydroxyl radicals ($^{\circ}\text{OH}$) are considered to be promising alternatives to conventional processes due to their efficiency in oxidizing a great variety of organic contaminants (Sabhi and Kiwi, 2001; Galindo *et al.* 2001). One of the promising AOPs is Fenton's reagent and this reagent appears to be a very powerful oxidizing agent. The Fenton's reagent is an aqueous solution of H_2O_2 and ferrous ion mixture to produce highly reactive hydroxyl radicals in acidic medium (eq.1) (Chemarro *et al.* 2001; Zhao *et al.* 2004).



Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} (eq.2).



In photo-Fenton process in addition to the above reactions the formation of hydroxyl radical also occurs by the following reaction (eq.3) (Rathi *et al.* 2003; Lucas and Peres, 2006).



The rate of organic pollutant degradation could be increased by irradiation of Fenton's reagent with UV or visible light (Photo-Fenton process). The illumination leads not only to the formation of additional hydroxyl radicals but also recycling of ferrous catalyst by reduction of Fe^{3+} . In this way, the concentration of Fe^{2+} is increased and the overall reaction is accelerated.

The aim of the present work is to investigate the influence of various parameters on the photocatalytic degradation of Reactive Orange M2R dye (ROM2R) by UV light irradiation in the presence of Fenton's reagent. In this paper we examine the effects of concentrations of H_2O_2 , Fe^{2+} , initial concentrations of dye and pH on the degradation of dye and the results are analysed.

2. RESULTS & DISCUSSION

The chemical structure and UV-visible spectrum of ROM2R dye are shown in Fig. 1 and Fig. 2 respectively. The photochemical degradation of ROM2R dye was observed at 488 nm.

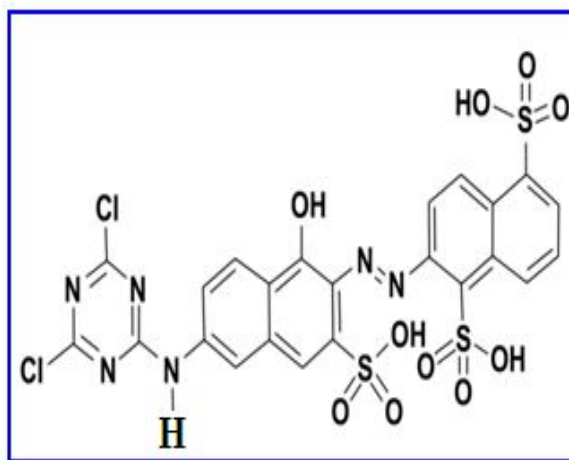


Fig. 1: Structure of ROM2R ($\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{N}_6\text{O}_{10}\text{S}_3$, 715.52)

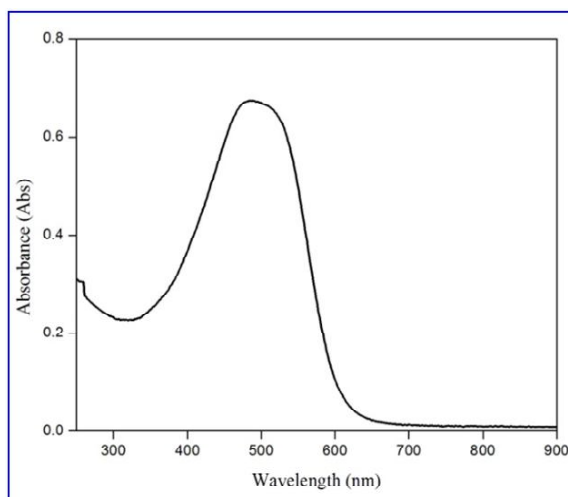


Fig. 2: UV-visible absorption spectrum of Reactive Orange M2R Dye

The optimum conditions for the photodegradation of dye were [Dye] = 0.1 mM, [FeSO₄] = 1 mM, [H₂O₂] = 10 mM and pH = 3. The result of photocatalytic bleaching of dye is graphically represented in Fig. 3. It was observed that the absorbance of dye solution decreases with increasing time of irradiation indicating that the dye was degraded on irradiation. A plot of log (Absorbance) versus time was linear indicating that the reaction follows pseudo-first order kinetics. The rate constant, k was calculated from the expression $k = 2.303 \times \text{slope}$. The optimum rate constant for the reaction was determined as $k_1 = 10.95 \times 10^{-4} \text{sec}^{-1}$.

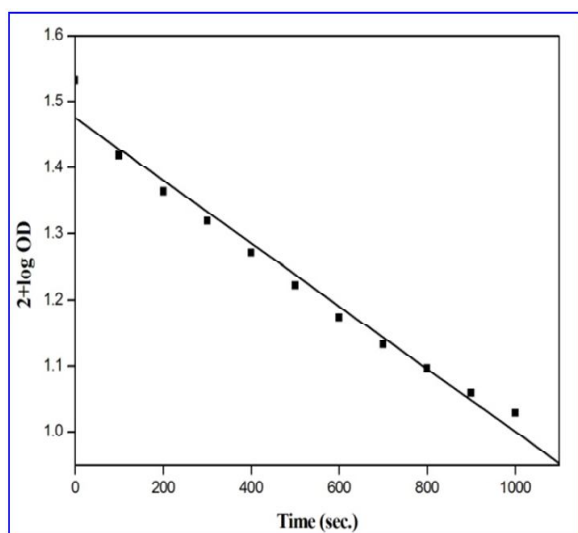


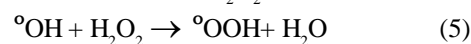
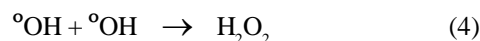
Fig. 3: A plot showing a typical run of photobleaching of ROM2R dye by photo-Fenton reagent under the optimized conditions.

2.1 Effect of concentration of H₂O₂

In a photo-Fenton based system the oxidant concentration is a key factor that can significantly influence the degradation of organics. The effects of H₂O₂ concentration on the degradation of ROM2R dye were studied and the results are shown in Fig. 4. The results indicate that the degradation of ROM2R dye is increased by increasing the concentration of H₂O₂.

The decolourization rate constant increases from 2.022×10^{-4} to $18.718 \times 10^{-4} \text{sec}^{-1}$. At high concentration of H₂O₂, the rate again decreases.

This can be explained on the basis that at higher concentration of H₂O₂, more hydroxyl radical is produced which degrade more dye molecules. The optimum dosage of H₂O₂ was found to be 0.01 M, with further increasing of H₂O₂ concentration, degradation efficiency is decreasing due to the scavenging nature of H₂O₂ towards OH radicals (eq.5) when it is present in higher concentration (Tamimi *et al.* 2008; Muthuvel *et al.* 2012).



The result is the formation of perhydroxy radicals which are significantly less reactive species than hydroxyl radicals and thus directly influence in the degradation.

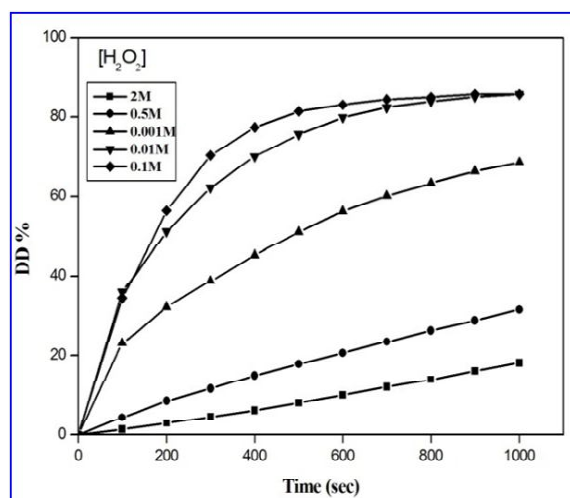


Fig. 4: The degradation degree of [ROM2R] = 0.1 mM with different initial concentrations of H₂O₂ in the presence of [Fe²⁺] = 1 mM in photo-Fenton processes at pH 3.0.

The best photodegradation of the dye was possible with $[\text{H}_2\text{O}_2] = 10 \text{ mM}$. But due to very fast degradation of dye it was difficult to determine the rate constant for low concentration of dye. Hence 1 mM of H_2O_2 was used for further experiment.

2.2 Effect of concentration of ferrous ion

Amount of ferrous ion is one of the main parameter to influence the photo-Fenton process. In this study, to obtain the optimum initial Fe^{2+} ion concentration, the investigation was carried out in the range of 0.05 mM to 0.5 mM at $\text{pH}=3$. The Fig. 5 displays the effect of ferrous ion concentration on the degradation of dye. The decolourization rate constant increases from 1.148×10^{-4} to $10.948 \times 10^{-4} \text{ sec}^{-1}$. The increase in ferrous ion concentration in the reaction mixture is accompanied by enhanced generation of OH radicals, consequently increasing the rate of photodegradation. The optimum concentration of ferrous ion for the degradation reaction was found to be 1 mM .

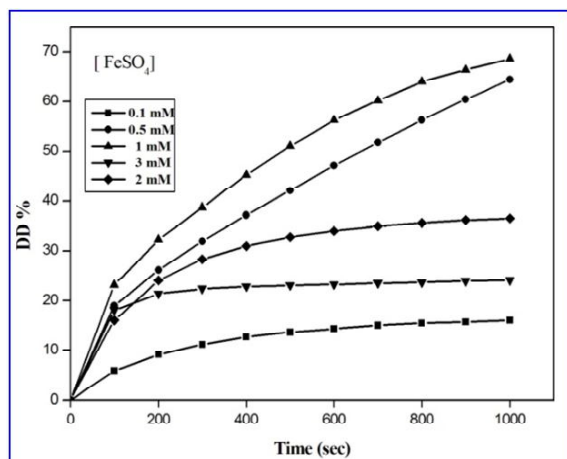


Fig. 5: The degradation degree of different initial concentrations of Fe^{2+} in the presence of $[\text{Dye}] = 0.1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 1 \text{ mM}$ in photo-Fenton processes at $\text{pH} 3.0$.

On the other hand, when the ferrous ion concentration is too high, the reaction mixture became

more turbid and this suppressed the penetration of UV light and hence photo-activity of reaction decreases. This in turn decreased the formation of OH radicals, lowering the photodecomposition ability (Gamal, 2010; Kitsiou *et al.* 2009).

2.3 Effect of initial concentration of dye

In order to study effectiveness of photocatalysis with increasing pollutant concentration, experiments were conducted by varying the amount of ROM2R (0.1 mM to 0.5 mM) at $\text{pH} 3$ with 1 mM of Fe^{2+} and 1 mM of H_2O_2 . These results are shown in Fig. 6. The results reveal that the degradation degree of dye decreases with the increase in the concentration of dye. Also the rate constant decreases from 6.469×10^{-4} to $2.88 \times 10^{-4} \text{ sec}^{-1}$.

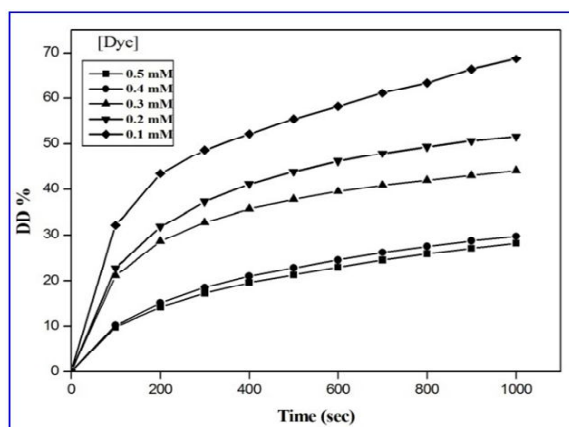


Fig. 6: The degradation degree of different initial concentrations of ROM2R in the presence of $[\text{Fe}^{2+}] = 1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 1 \text{ mM}$ in photo-Fenton processes at $\text{pH} 3.0$.

In this photo-Fenton process at higher dye concentration the penetration of photons entering into solution also decreases thereby lowering the hydroxyl radical production (Vaishnav *et al.* 2011; Surana *et al.* 2011; Muthuvel *et al.* 2012). Hence, the percentage of degradation of the dye decreases with the increase in dye concentration.

2.4 Effect of pH

The pH value effects the oxidation of organic substances both directly and indirectly. The effect of pH on the degradation of ROM2R dye was investigated in the pH range 2.0 to 4.0. Fig.7 shows the effect of initial solution pH on the degradation of dye. It shows that the percentage of degradation of dye strongly depends on pH of the reaction medium. The rate of degradation of dye increases with increasing pH upto 3 and then decreases (Li *et al.* 2009; Ameta *et al.* 2012). The optimum pH value was found to be about 3.

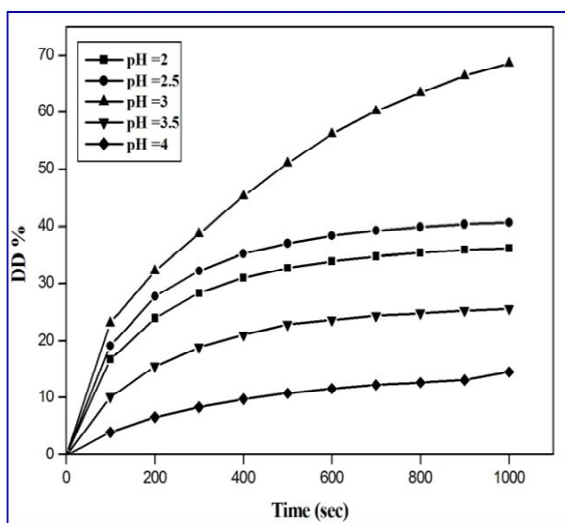
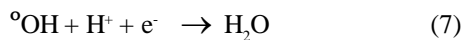


Fig. 7: The degradation degree of ROM2R at different pH in the presence of [Dye] = 0.1mM, [Fe²⁺] = 1 mM, [H₂O₂] = 1mM in photo-Fenton processes

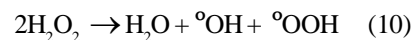
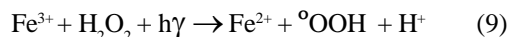
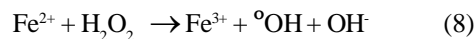
The degradation of the dye is decreased at pH>3, because iron is precipitated as hydroxide which resulted in a reduction in the transmission of radiation (Faust and Hoigne, 1990). Another reason for the inefficient degradation at pH >3 is due to the dissociation and auto-decomposition of H₂O₂ (Badway *et al.* 2006). The low degradation at pH 2 (pH<3) is also due to the hydroxyl radical scavenging of H⁺ ions (eq. 7) (Lucas and Peres, 2006; Tamimi *et al.* 2008).



Mechanism

On the basis of experimental observation and the existing literature, a tentative mechanism has been proposed for degradation of ROM2R dye with photo-Fenton system.

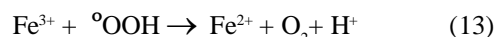
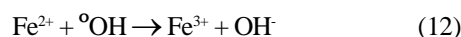
In the presence of Fe²⁺, the peroxide breaks down to ^oOH and OH⁻, according to the following reaction (eqs. 8,9,10)



The incorporation of ^oOH with H₂O₂ also produces OOH radicals (eq.10)

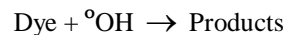


Ferrous ion may undergo oxidation to ferric ions with ^oOH (eq. 12) while ferric ions are reduced to ferrous ions by the incorporation of OOH radicals, giving H⁺ ions (eq. 13)



The perhydroxy radicals (^oOOH) 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 oxidising species was confirmed using the hydroxyl radical scavenger 2-propanol, which drastically reduced the rate of photodegradation.

The hydroxyl radicals 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 CO_2 , H_2O , NO_2^- , NO_3^- and SO_4^{2-} . These products are harmless to the environment. Further, these products of simple molecule or ions were detected and their presence in the reaction mixture was ascertained by usual chemical methods.

3. MATERIAL & METHODS

3.1 Reagents

Photocatalyst $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, 99% purity) and H_2O_2 (Merck, 30% purity) were used for photocatalytic degradation. Commercial grade Reactive Orange M2R dye obtained from Color Chem (India) Ltd was used without purification. All other chemicals were used AR grade. All the solutions were prepared with deionized water.

3.2 Experimental procedure and analysis

All experiments were carried out in a 1 litre thermostated bath glass photoreactor equipped with magnetic stirrer. A known volume of the dye solution was taken in the reactor. Predetermined amount of Fe^{2+} ion solution and H_2O_2 solution were added into the dye solution. The pH of the dye solution was adjusted by adding dil. H_2SO_4 or NaOH . The solution was then illuminated by UV light with magnetic stirring. The photodegradation was carried under 125W UV mercury lamp with the main emission at 365 nm. At a given time of intervals, the analytical samples withdrawn from the reaction mixture and then stored in the dark for needed analysis. The absorbance spectrum was determined with ELICO SL-218 Double Beam UV-visible spectrophotometer and the degradation of ROM2R dye was monitored by recording the absorbance at $\lambda_{\text{max}} \sim 488 \text{ nm}$ as a function of illumination time. The decolourization degree percentage (DD%) and rate constant values were calculated as follows (Abo-Farha, 2010; Kazi Nazrul Islam et al. 2013).

$$\text{DD\%} = \{(A_0 - A_t) / A_0\} \times 100$$

Where, A_0 is the initial intensity of colour

A_t is the intensity of colour at 't'.

The rate constant k was calculated from the expression $k = 2.303 \times \text{slope}$.

4. CONCLUSIONS

In the present work, the degradation of reactive orange M2R dye by photo-Fenton system has been investigated. The percentage of dye degradation and rate were influenced by the concentration of H_2O_2 , the concentration of Fe^{2+} , the initial concentration of dye and pH of the solution. The kinetic studies reveal that photocatalytic bleaching of the dye follows first-order kinetics. The optimum conditions for the degradation of photo-Fenton process is observed at pH 3, with the $[\text{Fe}^{2+}] = 1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 10 \text{ mM}$, $[\text{dye}] = 0.1 \text{ mM}$.

ACKNOWLEDGEMENT

The authors are grateful to the management of P.M.T.College and St.John's College and M.S.University for providing facilities to carry out this research work.

REFERENCES

- Abo-Farha, S. A., Comparative study of Oxidation of some azo dyes by different advanced oxidation processes: fenton, fenton-like, photo-fenton and photo-fenton-like., 6(10), 128-142 (2010).
- Ameta, N., Sharma, J., Sharma, S., Kumar, S and Punjabi, P. B., Copper modified iron oxide as heterogeneous photo-fenton reagent for the degradation of coomasie brilliant blue R-250, *Indian J. Chem.*, 51A, 943-948 (2012).
- Badawy, M. I., Ghaly, M. Y. and Gad-Allah, T. A., Advanced oxidation processes for the removal of organophosphorous pesticides from waste water, *Desalination.*, 194, 166-175 (2006).
doi:10.1016/j.desal.2005.09.027

- Buitron, C. L., Quezada, M. and Moreno, G., Aerobic degradation of the azo dye acid red 151 in a sequencing batch biofilter, *Bioresour. Technol.*, 92, 143-149(2004).
doi:10.1016/j.biortech.2003.09.001
- Berker, P. and Salker, A. V., Photocatalytic degradation of textile azo dye over $Ce_{1-x}S_{nx}O_2$ series, *Mater. Sci. Engg. B.*, 133, 55-60(2006).
doi:10.1016/j.mseb.2006.05.007
- Behnajady, M. A., Modirshahla, N., Daneshvar, N. and Rabbani, M., Photocatalytic degradation of an azo dye in a tubular continuous-flow photoreactor with immobilized TiO_2 on glass plates, *Chem. Eng.*, 127, 167-176(2007).
doi:10.1016/j.ccej.2006.09.013
- Chamarro, E., Marco, A. and Esplugas, S., Use of fenton's reagent to improve organic chemical biodegradability, *Water Res.*, 35, 1047-1051(2001).
doi:10.1016/S0043-1354(00)00342-0
- Faust, B. C. and Hoigne, J., Photolysis of Fe(III) hydroxyl complexes as sources of OH radicals in clouds, fog and rain, *Atmos. Environ.*, 24, 79-89(1990).
doi:10.1016/0960-1686(90)90443-Q
- Gamal, A. M., Comparative efficiencies of the degradation of C.I. mordant orange 1 using UV/ H_2O_2 , fenton and photo-fenton processes, *Nat. Sci.*, 8(10), 8-15(2010).
- Galindo, C., Jacques, P. and Kalt, A., Photochemical and photocatalytic degradation of an indigo dye: A case study of acid blue 74(AB74), *J. Photochem. Photobiol A: Chem.*, 141, 47-56 (2001).
doi:10.1016/S1010-6030(01)00435-X
- Hasnat, M. A., Siddiquy, I. A. and Nuruddin, A., Comparative photocatalytic studies of degradation of a cationic and an anionic dye, *Dyes Pigments.*, 66, 185-188(2005).
doi:10.1016/j.dyepig.2004.09.020
- Karthikeyan, S. and Sivakumar, P., The effect of activating agents on the activated carbon prepared from *feronia limonia* (L.) swingle (Wood Apple) shell, *J. Environ. Nanotechnol.*, 1(1), 5-12 (2012).
doi:10.13074/jent.2012.10.121009.
- Kazi Nazrul Islam, S., Md, Kurny, A. S. W. and Gulshan, F., Photocatalytic efficiency of mill scale for the degradation of textile dye by photo-fenton and photo-ferrioxalate system under UV and sunlight, *Environ. Ecol. Res.*, 1(3), 129-134(2013).
- Kitsiou, V., Filippidis, N., Mantzavinos, D. and Poullos, I., Heterogeneous and homogeneous photocatalytic degradation of the insecticide imidacloprid in aqueous solution, *Appl. Catal. B: Environ.*, 86, 27-35 (2009).
dx.doi.org/10.1016/j.apcatb.2008.07.018
- Kusic, H., Bozic, A. L., and Koprivanac, N., Fenton type processes for minimization of organic content in coloured wastewaters: Part I: Processes optimization, *Dyes Pigments.*, 1-8(2006).
- Li, Ronyxi, Yang, C., Chen, H., Zeng, G., Yu, G. and Guo, J., Removal of triazophos pesticide from wastewater with fenton's Reagent, *J. Hazard. Mat.*, 167(1-3), 1028-1032(2009).
- Lin, S. H. and Peng, F. C., Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge, *Water Res.*, 30, 587-593(1996).
doi:10.1016/0043-1354(95)00210-3
- Lucas, M. S. and Peres, J. A., Decolourization of the azo dye reactive black 5 by fenton and photo-fenton oxidation, *Dyes Pigments.*, 71, 236-244(2006).
doi:10.1016/j.dyepig.2005.07.007
- Muthuvel, I., Krishnakumar, B. and Sawaminathan, M., Solar active fire clay based hetero-fenton catalyst over a wide pH range for degradation of acid violet 7, *J. Environ. Sci.*, 24 (3), 529-535(2012).
doi:10.1016/S1001-0742(11)60754-7
- Neamtu, M., Yediler, A., Siminiceanu, I., Macoveanu, M. and Kettrup, A., Decolourisation of disperse red 354 azo dye in water by several oxidation processes-a comparative study, *Dyes Pigments.*, 60, 61-68(2004).
doi:10.1016/S0143-7208(03)00129-3
- Papic, S., Koprivanac, N., LoncaricBozic, A. and Metes, A., Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/ carbon adsorption process, *Dyes Pigments.*, 62, 291-298(2004).
doi:10.1016/S0143-7208(03)00148-7

- Ramakrishna, K. and Viraraghavan, T., Dye removal using low cost adsorbents, *Water Sci. Technol.*, 36(2-3), 189-196 (1997).
[doi:10.1016/S0273-1223\(97\)00387-9](https://doi.org/10.1016/S0273-1223(97)00387-9)
- Rathi, A., Rajor, H. K. and Sharma, R. K., Photodegradation of direct yellow-12 using UV/H₂O₂/Fe²⁺, *J. Hazard. Mater.*, 102, 231-241(2003).
[doi:10.1016/S0304-3894\(03\)00213-9](https://doi.org/10.1016/S0304-3894(03)00213-9)
- Robinson, T., McMullan, G., Marchant, R. and Nigam, P., Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative, *Bioresour. Technol.*, 77, 247-255(2001).
[doi:10.1016/S0960-8524\(00\)00080-8](https://doi.org/10.1016/S0960-8524(00)00080-8)
- Sabhi, S. and Kiwi, J., Degradation of 2,4-dichlorophenol by immobilized iron catalysts, *Water Res.*, 35, 1994-2002(2001).
[doi:10.1016/S0043-1354\(00\)00460-7](https://doi.org/10.1016/S0043-1354(00)00460-7)
- Solmaz, S. K. A., Birgul, A., Vstun, G. E. and Yonar, T., Colour and COD removal from textile effluent by coagulation and advanced oxidation processes, society of dyers and colourists, *Color. Technol.*, 122, 102-109 (2006).
[doi:10.1111/j.1478-4408.2006.00016.x](https://doi.org/10.1111/j.1478-4408.2006.00016.x)
- Surana, M., Mehta, P., Pamecha, K. and Kabra, B. V., The decolourization and mineralization of azo dye reactive yellow 86 in aqueous solution by photo-fenton reagent, *D. Pharma.Chemica.*, 3(2), 39-47(2011).
- Tamimi, M., Qourzal, S., Barka, N., Assabbane, A. and Ait-Ichou, Y., Methomyl degradation in aqueous solutions by fenton's reagent and the photo-fenton system, *Sep. Purif. Technol.*, 61, 103-108 (2008).
- Vaishnave, P., Ameta, G., Kumar, A., Sharma, S. and Ameta, S. C., Sono-photo-fenton and photo-fenton degradation of methylene blue, *J. Indian. Chem. Soc.*, 88, 397-403(2011).
- Van der Zee, F. P., Lettinga, G. and Field, J., Azo dye decolorization by anaerobic granular sludge, *Chemosphere.*, 44, 1169-1176(2001).
[doi:10.1016/S0045-6535\(00\)00270-8](https://doi.org/10.1016/S0045-6535(00)00270-8)
- Zhao, X-K., Yang, G-P., Wang, Y-J. and Gao, X-C., Photochemical degradation of dimethyl thalate by fenton's reagent, *J. Photochem. Photobiol. A: Chem.*, 161, 215-220(2004).
[doi:10.1016/S1010-6030\(03\)00344-7](https://doi.org/10.1016/S1010-6030(03)00344-7)