Pelagia Research Library

Der Chemica Sinica, 2011, 2 (2): 177-186

ISSN: 0976-8505
CODEN (USA) CSHIA5

Treatment of water contaminated with Reactive Red 198 (RR198) 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

This study was conducted to assess the removal efficiency of azo dye Reactive Red 198 (RR198) from aqueous medium using the Photo- Fenton process. The Fenton reagent that consists of a mixture of hydrogen peroxide (H_2O_2) and Ferrous ions (Fe^{+2}) was used to generate the hydroxyl radicals ($^{\bullet}OH$) that attacks the target contaminant and degrade it. The influence of the main parameters (concentration of Dye (RR198), concentration of photocatalyst (Fenton reagent, H_2O_2 and pH) that govern the degradation kinetics was evaluated. 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. Complete mineralization of dye RR198 is achieved by Photo- Fenton reagent. The photobleaching process follows first order kinetics in respect to Langmuir-Hinshelwood model.

Keywords- Reactive Red 198, Photo- Fenton, Photobleaching, Mineralization.

INTRODUCTION

Dyeing, desizing and scouring are the major sources of water pollution in textile effluent (1). Discharge of these dyes is undesirable not only for aesthetic reasons but also because they may decrease the absorption of light by water, plants and phytoplankton reducing photosynthesis and the oxygenation of water (2).Many azo dyes and their intermediate products are toxic and mutagenic or carcinogenic to aquatic life and humans (3).

Reactive dyes are extensive used for dyeing process in textile and about 20-40% of these dyes are lost in the effluent. They exhibit a wide variability in chemical structure, primarily based substituted aromatic and hetero cyclic groups. Since reactive dyes are highly soluble in water, their removal from waste water is difficult by conventional coagulation and the activated sludge process (4, 5). The environmental concern of these potentially carcinogenic pollutants in contaminated water has drawn the attention of many research workers.

In recent years, advanced oxidation processes (AOPs) have emerged as contemporary oxidative technique for degradation of detrimental organic compounds. Advanced oxidation processes (AOPs) have provided innovative, cost-effective catalyzed chemical oxidation for treating pollutants in low or high concentration from contaminated soil, sludge and water. Common AOPs involve Fenton (6), Fenton like process (7), ozonation (8), H_2O_2/ UV (9), TiO_2 (10), electron beam irradiation (11), sonolysis (12), wet-air oxidation (13) and various combination of these methods (14).

Fenton Reagent has found to be a promising treatment method for the effective decolourization and degradation of dyes. Fenton reagent exhibits a number of features that make its use advantageous as compared to other methods such as high degree of catalytic efficiency, high degree of specificity and absence of side reactions. Compared with other oxidation processes, the Fenton Reagent is relatively cheap, easily operated and maintained.

The aim of this work to assess the photocatalytic treatment of mono azo dye Reactive Red 198 **(MF: $C_{27}H_{18}ClN_7Na_4S_5O_{15}$, MW: 863.7)** selected due to its toxicity, carcinogenic in nature as well as its presence in wastewater of several industries such as textile dyeing, printing, tannery etc. Thus it is considered worthwhile to see how textile dye RR198 could be degraded in aqueous medium by Fenton reagent. In this study, we report an easy, fast and economical method for the photo degradation of dye RR198 by Fenton reagent.

MATERIALS AND METHODS

Materials

For the present studies the commercial disazo dye Reactive Red 198 (Fig: 1) having 95% dye content was used. Photocatalyst $FeSO_4$ (Merck, 99% purity) and H_2O_2 (Merck, 30% purity) were used for photocatalytic degradation. For the photobleaching process, $1x10^{-3}$M stock solution of dye Reactive Red 198 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.

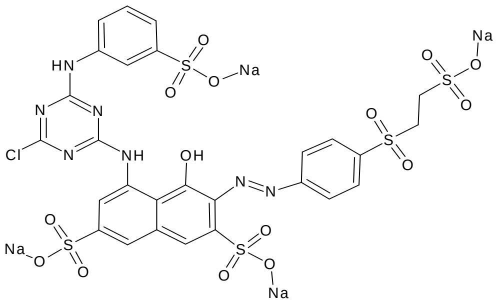


Fig - 1 : Structure of Reactive Red 198
Molecular formula – $C_{27}H_{18}ClN_7Na_4S_5O_{15}$, Molecular weight = 863.70

Procedure and Analysis

The reaction mixture was prepared by taking 3 ml of Reactive Red 198 dye solution (1x10^{-3} M), 3.5 ml of $FeSO_4$ (1x10^{-3} M), 0.6 ml of H_2O_2 (30%) 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, [$FeSO_4$] =3.5 x10^{-5} M, [H_2O_2] = 5.87 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 520 nm. The rate of decrease of color 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 Reactive Red 198 was observed at 520 nm. The optimum conditions for the photobleaching of dye were [Dye] =3x10^{-5} M, [$FeSO_4$] =3.5 x10^{-5} M, [H_2O_2] = 5.87 x10^{-2} M and pH=3. The result of photocatalytic bleaching of Reactive Red 198 is graphically presented in Fig.2.

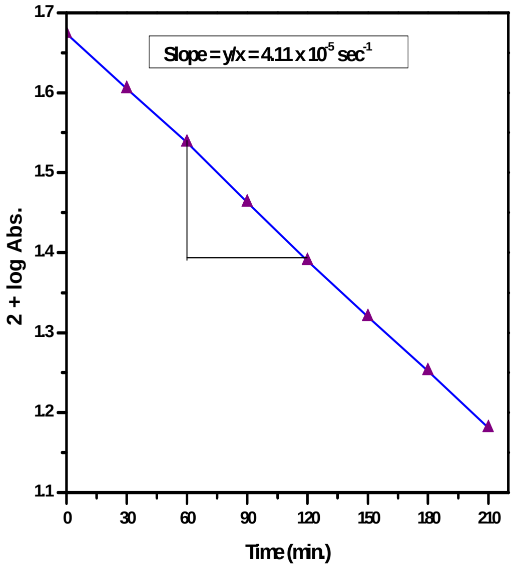


Fig-2: A plot showing a typical run of photobleaching of Reactive Red 198 by Photo-Fenton reagent under the optimized conditions

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 Reactive Red 198 follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression.

$$\textbf{Rate (k)} = 2.303 \times \textbf{Slope} = 9.46 \times 10^{-5}\ \text{sec}^{-1}$$

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 RR198 decolorization. Hence all subsequent experiments were carried out at pH 3.

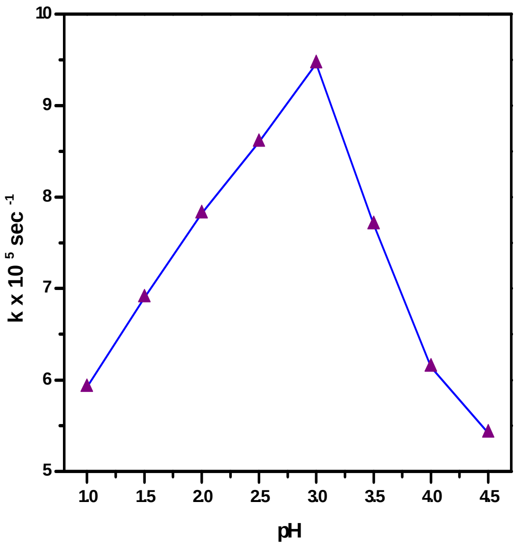


Fig- 3: A plot showing effect of variation in hydrogen ion concentration on the rate of decolorization of the dye by Photo-Fenton reagent

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

The effect of dye concentration on the degradation of Reactive Red 198 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.

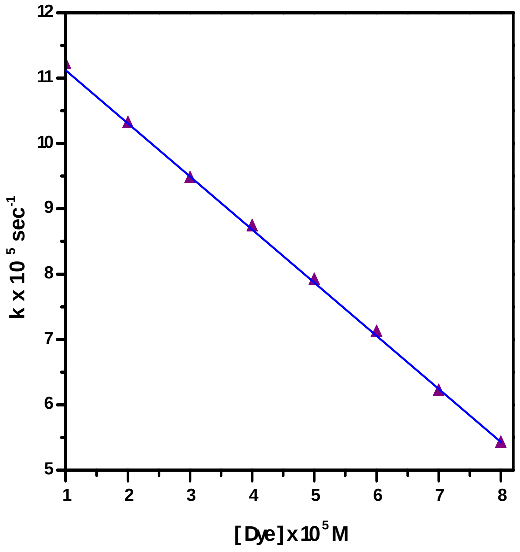


Fig- 4: A plot showing effect of variation in dye concentration on the rate of decolorization of the dye by Photo-Fenton reagent.

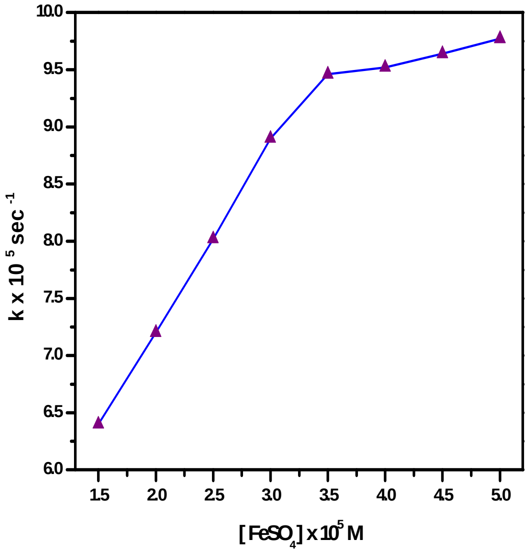


Fig- 5: A plot showing effect of variation in catalyst concentration on the rate of decolorization of the dye by Photo-Fenton reagent.

Effect of variation in 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 3.5 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.

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 RR198 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 5.87 x 10^{-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 (Eqn.1, 2, 3).

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \qquad (1)$$

$$^{\bullet}OH + H_2O_2 \longrightarrow {}^{\bullet}O_2H + H_2O \qquad (2)$$

$$^{\bullet}O_2H + {}^{\bullet}OH \longrightarrow H_2O + O_2 \qquad (3)$$

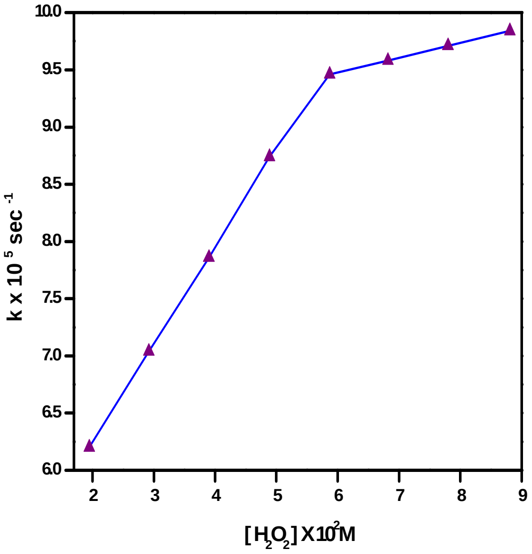


Fig- 6: A plot showing effect of variation in hydrogen peroxide concentration on the rate of decolorization of the dye by Photo-Fenton reagent.

Effect of other homogeneous catalyst Uranyl Acetate

Keeping all the factors identical, the effect of the nature of the photocatalyst on photocatalytic bleaching of Reactive Red 198 was studied by using homogeneous photocatalyst U (VI). It was observed that the rate of photobleaching of Reactive Red 198 markedly increases.

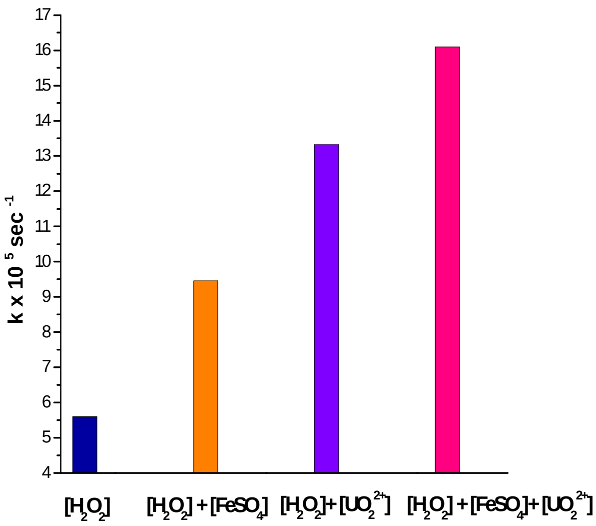


Fig- 7: A plot showing effect of other homogeneous catalyst on the rate of decolorization of the dye by Photo-Fenton reagent.

when $[H_2O_2] = 5.87 \times 10^{-2}$ M, $[FeSO_4] = 3.5 \times 10^{-5}$ M and $[UO_2^{2+}] = 3.5 \times 10^{-5}$ M

A search was made to suggest the combination of ferrous ions by some other active metals, which have special oxygen transfer properties to generate more highly reactive hydroxyl radicals. So the effect of UO_2^{2+} with H_2O_2 was studied which showed appreciable increase in photodegradation of the dye. The reaction rate was found to faster as it generates two hydroxyl radical per uranyl ion (Eqn.4, 5).

$$2UO_2^{2+} + 2H_2O_2 \longrightarrow 2UO^{2+} + 4{}^{\bullet}OH + O_2 \qquad (4)$$

$$2UO^{2+} + O_2 \xrightarrow{hv} 2UO_2^{2+} \qquad (5)$$

On the other hand, when both ferrous ions and uranyl ions were present with hydrogen peroxide, more $^{\bullet}OH$ radicals are formed (one from ferrous ions, two from uranyl ions) from two oxidizing species and hence reaction rate is further enhanced.

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.6, 7, 8).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{6}$$

$$Fe^{3+} + H_2O_2 \xrightarrow{hv} Fe^{2+} + {}^\bullet OOH + H^+ \tag{7}$$

$$2\,H_2O_2 \longrightarrow H_2O + {}^\bullet OH + {}^\bullet O_2H \tag{8}$$

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: 9,10).

$$Fe^{2+} + {}^\bullet OH \longrightarrow Fe^{3+} + OH^- \tag{9}$$

$$Fe^{3+} + {}^\bullet O_2H \longrightarrow Fe^{2+} + O_2 + H^+ \tag{10}$$

$^\bullet$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: 11).

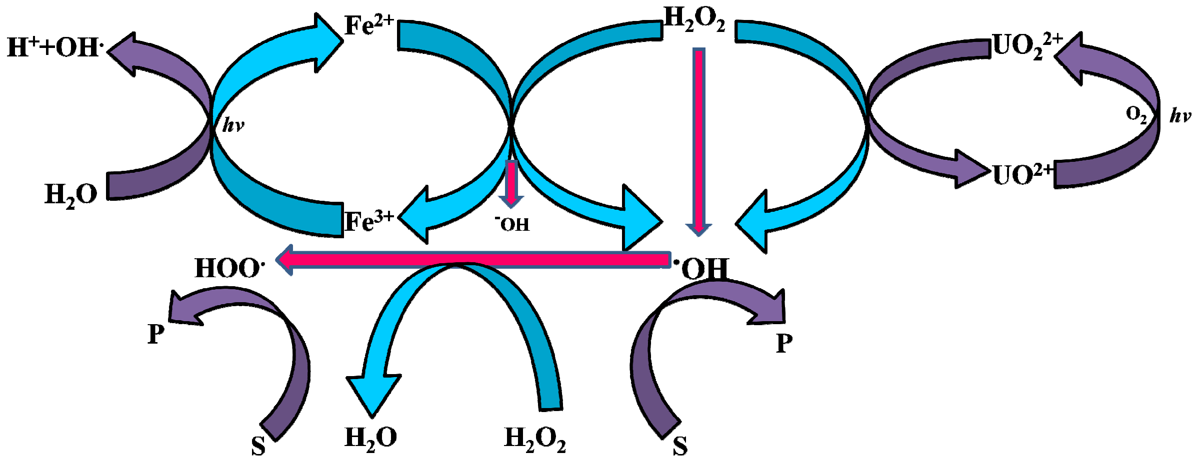
$$\underset{\text{Reactive Red 198 (S)}}{C_{27}H_{18}ClN_7Na_4S_5O_{15}} \xrightarrow{\bullet OH} \text{Intermediates} \longrightarrow \underset{\text{(P)}}{\text{End Products}} \tag{11}$$

End products ≡ $CO_2 + H^+ + H_2O + NO_2^- + NO_3^- + SO_4^{2-}$

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

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.8).



Where S = Dye and P = End Products

Fig.8: A Schematic representation of Photo-Fenton Chemistry

CONCLUSIONS AND FUTURE PERSPECTIVES

Photo- Fenton process was used for the photo-catalytic degradation of dye Reactive Red 198. Based on the results, it can be concluded that the decoloration of dye is strongly dependent on various reaction parameters e.g. pH, concentration of the dye, concentration of $FeSO_4$ and concentration of H_2O_2.

The photocatalytic degradation of Reactive Red 198 was observed at 520 nm. The optimum conditions for the photobleaching of dye were [Dye] $=3x10^{-5}$ M, [$FeSO_4$] $=3.5x10^{-5}$ M, [H_2O_2] = 5.87 $x10^{-2}$ M and pH=3. Kinetic studies reveal that photocatalytic bleaching of Reactive Red 198 follows a first order kinetics.

The great interest of the academic community for the use of AOPs in waste water treatment is reflected by a number of publications that have been produced during the last decade. Major drawbacks of some methods is the use of costly chemicals, high operational cost, increased energy consumption as well as the formation of unknown intermediates which in some cases could be more toxic than the parent compounds. Based on the above, the main future challenges for using AOPs in waste water treatment could be the development of efficient and low cost materials to promote sufficient treatment, the use of renewable energy sources, the targeting of new classes of pollutants and the commercialization of processes which have been so far used in the laboratory.

REFERENCES

[1] I.Bouzdia, C.Ferronato, J. M. Chovelon, M. E. Rammati, J. M. Hermann, *J. Photochem. Photobiol. A*, **2004**, 168, 23.
[2] O. Ozdemir, B. Armagan, M. Turan, M. S. Celik, *Dyes and Pigments*, **2004**, 62, 49.
[3] D. Lawless, N. Serpone, D. Meisel, *J. Phy. Chem.*, **1991**, 95, 5166.

[4] P. Nigam, G. Armour, I. M. Banat, D. Singh, R. Marchant, *Biosource Technology*, **2000**, 72, 219.

[5] F. P. Van der zee, G. Lettinga, J. A. Filed, *Chemosphere*, **2001**, 44, 1169.

[6] S. L. Orozcoa, E. R. Bandala, C. A. Aranclbia, B. Serranoc, C. A. Parraa, I. H. Perezd, *J. Photochem. Photobiol. A: Chemistry*, **2008**, 198, 144.

[7] O. Rozas, D. Contreras, M.A. Modaca, M. Perez- Moya, H.D. Mansilla, *J. Hazardous Materials*, article in press.

[8] B. Ahmet, Y. Ayfer, L. Doris, N. Nese, K. Antonius, *Dyes and Pigments*, **2003**, 58, 93.

[9] M. Ugurlu, I. Kula, *Environ. Sci. Poll. Res*., **2007**, 14, 319.

[10] N. Barka, S.Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, *Arabian J. Chem*., **2010**, 3, 279.

[11] R.Yang, M. Wang, Z. Shen, W. Wang, H. Ma, J. Gu, *Radiation Physics and Chemistry*, **2007**, 76, 1122.

[12] D. Kabita, S. Mukhopadhayay, S. Bhattacharjee, B. Choudhuri, *Appl. Catalysis*, **2006**, 62, 159.

[13] L. Oliviero, J. Barbier, D. Duprez, *Appl. Catal. B*, **2003**, 40, 163.

[14] F.I. Hai, *Critical reviews in Environmental Science and Technology*, **2007**, 37, 315.