Acta Chimica
&
Pharmaceutica Indica

Acta Chim. Pharm. Indica: 1(1), 2011, 57-64

EFFECTIVE DEGRADATION OF AN AZO DYE ACID RED -183 BY FENTON AND PHOTOFENTON TREATMENT

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(*Received : 11.10.2011, Revised : 19.10.2011, Accepted : 23.10.2011*)

ABSTRACT

Among the available advanced oxidation processes, Fenton and photo-Fenton processes are of special interest because they make possible achievement of high reaction yields with a low treatment cost. Fenton and photo-Fenton reactions as stand-alone processes and as pretreatment of an aerobic biological treatment for acid red-183 reactive dye degradation have been carried out at pilot plant scale. Photo-Fenton oxidation was conducted using a compound parabolic collector (CPC) solar photo-reactor. When applying photo-Fenton reaction as a single process, 10 mg/L^{-1} Fe (II) and 250 mg/L^{-1}H_2O_2 for 250 mg/L^{-1}, acid red-131 treatment, and 20 mg/L^{-1}Fe (II) and 500 mg/L^{-1}H_2O_2 for 250 mg/L^{-1} acid red-131 treatments closely reproduced the laboratory mineralization results, with 85 and 90 % dissolved organic carbon (DOC) removal respectively.

Key words: Environmental pollution, Textile pollution, acid-red-183, Fenton treatment, Photo-Fenton treatment, Dye degradation, Aerobic biological treatment, Solar photo reactor, Parabolic collector.

INTRODUCTION

The growth in industry and the changes in manufacturing processes have resulted in an increase in the volume and complexity of wastewater discharges to the environment. Many traditional and novel treatment processes are being modified and developed to try to eliminate the release to surface waters of the diverse chemical substances found in wastewater discharges[1]. Many industries use dyes and pigments to color their products. Among which, Azo dyes, constituting the largest class among the synthetic colorants, are considered as the widespread environmental pollutants associated with many important industries such as textile, food colorants, printing and cosmetic manufacturing. The textile industry is one of those industries that consume plenty of water in their manufacturing process. The water is primarily employed in the dyeing and finishing operations in which cloths are dyed and processed to finished products. About 100 L of water are consumed on the average for every tone of clothes processed[2]. The water used in dyeing and finishing processes finally ends up as waste water which needs to be treated before discharge. The release of such colored wastewaters into the environment is a dramatic source of aesthetic pollution, eutrophication and perturbations in aquatic life. It has been reported that some of them are toxic[3], mutagenic[4] and carcinogenic[3] compounds. For the majority of them, their half-lives under sunlight are greater than 2000 h[4] and their resistance to biological and even chemical degradation[3], makes them hazardous for the environment even at low concentration. Tiruppur and Coimbatore are the two important industrial cum residential areas located in

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Tamil Nadu, the southern part of India. In these areas, people of both sexes irrespective of their age are afflicted with many water borne diseases which is mainly attributed to their drinking water contaminated with effluents discharged from the nearby textile industries. Recently, the Madras High court has warned these industries and ordered them to treat their effluents before letting them out into the atmosphere and also cautioned them that if it is not done properly, those industries would be closed in the near future. Therefore, the problem associated with the dyes has become the burning issue in southern part of India. This has become not only the perennial problem to the industries (main source of income for the local people) but also to the society at large. Though, several attempts have been made all over the world for the removal of dyes, a complete and feasible solution has not been found yet[3]. Hence, the treatment of these waste waters is becoming a matter of great concern and it is urgent to develop sound and cost-effective treatment technologies to reach related standards before being discharged to the environment. Fenton process employs iron ions (Fe^{2+}) and hydrogen peroxide (H_2O_2), which produce hydroxyl radicals ($^{\cdot}OH$). If hydrogen peroxide is added to an aqueous system containing organic compounds with excess ferrous ions in a strong acidic medium, the following redox reactions will occur

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{-}OH + {}^{-}OH \qquad \ldots(1)$$

$$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \qquad \ldots(2)$$

Hydroxyl ions are formed at pH 7.5-8. So, residual decolorized dye molecules can be coagulated and precipitates. Fenton process was used for COD and color removal from textile wastewater by many authors. The formation of small flocks at a greater amount was observed in the wastewater during Fenton treatment. These flocks are Fe hydroxyl flocks formed as a result of successive reactions of their little sizes. It was stated that chemical coagulation with polyaluminium chloride would be more effective by rapid removal of these flocks. Besides, the coagulation with polyaluminium chloride is a useful process after Fenton process, which is used in the removal of dissolved solids, suspended solids, organic and inorganic compounds in wastewater[6]. In dark Fenton reaction (Eq.1), hydroxyl radicals are generated by the interaction between H_2O_2 and ferrous salts. The generated Fe^{3+} can be reduced by reaction with the exceeding H_2O_2 to form again ferrous ion in a catalytic mechanism (Eqs.3 and 4).

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\bullet} + Fe^{2+} + H^{+} \qquad \ldots(3)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \qquad \ldots(4)$$

Radicals can play different roles that lead to an improvement of the reaction yields.

Homogeneous photo-Fenton or photo-Fenton like process, which could generate hydroxyl radical ($^{\bullet}OH$) and destroy organic pollutants significantly, have been reported for treatment of dye effluents[6]. In these systems, the catalysts of iron ions are dissolved in water so they are called homogeneous photo-Fenton systems[6].

EXPERIMENTAL

Acid red-183 was chosen as a refractory model pollutant and purchased from Aldrich. The other reagents used in the present study H_2O_2 (35%w/w) and $FeSO_4.7H_2O$ were also obtained from Aldrich. This particular azo dye was selected for this study since its molecular structure is exactly known and is frequently used as a dye for dyeing cotton, woolen and nylon and other polyamine clothes worldwide and as well as in Tiruppur and Coimbatore. Some important physiochemical properties of the selected dye are given in Table 1. For both the Fenton and photo-Fenton treatments, 150 mg/L aqueous dye solution corresponding to 265.5 μM AR 183) was prepared in distilled water[6]. The reason, why particularly 150 selected in the present study is that the earlier published research articles[7] as well as private communications with technical staff from local dye house indicate that the dye concentration typically encountered in effluents originating from the cotton and polyamide dyeing factories is in the range of 10 – 200 mg/L. Environmental characterization of 150 mg/L aqueous solution of the selected dye in terms of COD, DOC and absorbance parameters is presented in Table 2.

Fenton process

Fenton process experiments were carried out at room temperature (32 ± 2°C) using varying $FeSO_4.7H_2O$ and H_2O_2 (35%, w/w) dosages at varying pH values in order to determine optimum dosages to yield better results in COD and color removal. Fenton process was performed according to the well known Kuo's procedure with slight modification. During the determination of optimum pH value, $FeSO_4.7H_2O$ and H_2O_2 dosages were fixed at constant value. Sedimentation over 2 h was applied following the pH adjustment (7.5-8) after 2 min of rapid mixing (100 min^{-1}) were applied at Jar test set up. Analyses were carried out on wastewater supernatant, which was taken after 2 h precipitation.

Photo-Fenton process

Photo reactor and light source

Irradiation was performed in a thermostatic (T = 32 ± 2°C) well stirred cylindrical Pyrex cell of 300 ml capacity. The solution volume was 200 mL. in photo-Fenton process, analytical grade H_2O_2 (35%, w/w, Merck) and $FeSO_4.7H_2O$ (99.9%, Merck) were used as received to generate hydroxyl radical ($^{\bullet}OH$) in aqueous solution. Irradiation was done with a 6W Philips black light fluorescent lamp placed over the cell was used as artificial light source. The intensity of the incident UVA light measured employing a luminometer was 0.6 $mWcm^{-2}$. The pH of the solution was adjusted 2.8 – 3.0. A Pyrex cylindrical jacket located around the plugging tube contained circulating water to absorb IR radiation and avoid heating of the solution. The photon flux of the UV radiation reaching the exposed inner part of the reactor was measured to be 6×10^{-6} mil of photon/s.

Degradation of acid red

The experiments were carried out in a photocatalytic oxidation reactor, which was shown in Feng's experiments. In the centre of the cylindrical reactor, one UV light tube was used as a light source. The temperature was controlled to 32°C during the experiments and solution pH was adjusted to 3.0 unless otherwise specified. The initial concentration of acid red-183 was 100 mg/L, the concentration of the concentration of catalyst was 1.0 g/L and the concentration of H_2O_2 was 10 mmol/L except otherwise specified. All experiments were carried out under constantly stirring to make the catalyst good dispersion. Deionized water was used throughout the work. The reaction was initiated when the UV light was turned on and H_2O_2 was added to the acid red-183 solutions. pH was measured by a Mettler Toledo pH meter in solution.

At given intervals of degradation, a sample was analyzed by UV-Vis spectroscopy using Shimadzu UV spectrophotometer at an appropriate wavelength, which is the maximum wavelength of Acid Red-183. The concentration of Acid Red-183 converted through the standard curve method of dyes. Total organic carbon (TOC) was analyzed by TOC analyzer (Shimadzu TOC-Vcph) to evaluate the mineralization of dye. Before analysis, all the samples were immediately treated with scavenging reagent to obtain accurate TOC data. To evaluate the leaching of the catalyst, the iron concentration in the solution after reaction was determined by ICP-AES (IRIS IntrepidIIXSP). The discoloration degree and mineralization degree were defined by the Eqs. (3) and (4), respectively.

$$X_{DIS}\,(\%) = \frac{(1 - C_t)\ x\,100}{C_o} \qquad \ldots(3)$$

$$X_{TOC}\ (\%) = \frac{(1 - TOC_t)\ x\ 100}{TOC_o} \qquad \ldots(4)$$

Table 1: Physiochemical properties of the textile dye acid red – 183

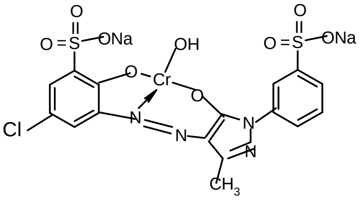
Trade Name	AR-183
Molecular formula $C_{16}H_{11}ClN_4Na_2O_8S_2.xCr$	
Molecular weight (g/mol)	584.84
C.I. number	18,800
λ_{max} (nm)	497
Molecular structure 	

Table 2: Environmental characterization of 150 mg/L textile dye acid red-183 (265.5 µM)

COD (mg O_2/L)	77.50
DOC (mg C/L)	21.69
Absorbance at λ_{max} (cm^{-1})	1.56 at 497 nm

RESULTS AND DISCUSSION

Fenton process

Fenton process experiments were conducted at room temperature (30 ± 2°C) using varying $FeSO_4.7H_2O$ (Merck) and H_2O_2 (Merck, 35%,w/w) dosages at varying pH values in order to determine optimum dosages give better results in COD and color removal. Fenton process was performed considering Kuo's method[5]. During the determination of optimum pH value, $FeSO_4$ and H_2O_2 dosages were fixed at constant value. Sedimentation over 2 h was applied following the pH adjustment (7.5-8) after 2 min of rapid mixing (100 min^{-1}) and 20 min of slow mixing (30 min^{-1}) were applied at jar test set up. Analyses were performed on wastewater supernatant, which was taken after 2 h precipitation.

The main process variables affecting the rate of Fenton's reaction are the molar concentrations of the oxidant (H_2O_2) and catalyst (Fe^{2+}), particularly the Fe^{2+}: H_2O_2 molar ratio. Increasing the H_2O_2 concentration is important to obtain high oxidation efficiencies, while elevating the Fe^{2+} concentration directly enhances the oxidation rate[8,9]. However, it should be kept in mind that if the concentration of one reactant is increased to observe its positive effect, thereby keeping the other one constant, the Fe^{2+}: H_2O_2 molar ratio and hence, the oxidation condition will change significantly. When one of the reagents is provided in excess, a dramatic reduction in the oxidation efficiency is expected. This can be explained by the scavenging reactions of OH.

$$Fe^{2+} + {}^{\cdot}OH \rightarrow HO^{-} + Fe^{3+}\ (k_{30}{}^{o}C = 8.5 \times 10^{8}\ M^{-1}s^{-1}) \qquad \ldots(3)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet}\ (k_{30}{}^{o}C = 5.5 \times 10^{7} M^{-1}s^{-1}) \qquad \ldots(4)$$

Theoretically speaking, advanced oxidation of organic compounds is fast when ferrous ion is present at a concentration varying between 2 and 5 mM, e.g. a concentration range were sufficient $^{\bullet}OH$ are produced and Fe^{2+} is still highly soluble in water at pH 7.5-8. In the present study, a set of preliminary (baseline) experiments was conducted with 150 mg/L aqueous AR 183 solution at an initial pH of 7.5 at different Fe^{2+}: H_2O_2 molar ratios selected as 2:10, 2:20, 2:40, 4:10, 4:20 and 4:40 (in mM). These selected Fe^{2+} and H_2O_2 concentrations are corresponding to optimum Fenton molar ratios (1:5 and 1:10). The most suitable molar ratio for each dye was individually determined upon inspection of the obtained color and COD-DOC removal rates. In order to examine the extent of degradation, possible nitrite, nitrate, sulphate and carboxylic acid formation was also followed. Table 3 presents percent COD and DOC removal efficiencies obtained after 10 min and 30 min Fenton treatment for the dye selected. Since color removal was very fast and practically complete (>95%) within the first 2 min of the reaction, color abatement was not further considered as a critical process parameter in these baseline experiments. From the Table 3, it is understood that the treatment efficiencies generally speaking increased with increasing Fe^{2+} and H_2O_2 concentrations, as expected. However, the improvement in treatment efficiencies was more dramatic when either the catalyst or the oxidant concentration was doubled at lower concentration of the other reagent (2 mM in the case of Fe^{2+} and 20 mM for H_2O_2). From these findings, it can be inferred that the most suitable Fe^{2+}: H_2O_2 molar ratio was found to be 1:5 at Fe^{2+} and H_2O_2 concentrations of 4 and 20 mM, respectively, coinciding with the highest COD and DOC removal efficiencies for both 10 and 30 min Fenton treatment. In a related investigation conducted with the Fenton's reagent, an optimum ratio of 1:4 was established for the treatment of simulated acid dyebath effluent bearing azo and anthraquinone dyes[7].

Table 3: Results obtained for the baseline Fenton experiments conducted with 150 mg/L aqueous AR183 (256.5 µM) at different Fe^{2+}: H_2O_2 molar ratio and an initial pH of 6.5

Fe^{2+}: H_2O_2 (mM : mM)	COD removal (%)		DOC removal (%)	
	t_{10}	t_{30}	t_{10}	t_{30}
2 : 10	57	62	51	54
2 : 20	36	40	34	42
2 : 40	54	58	48	50
4 : 10	48	44	43	42
4 : 20	58	62	52	54
4 : 40	59	64	49	52

Color

Considering the results obtained in the preliminary Fenton experiments, it was decided to continue the study under the following reaction conditions; initial pH (pH_o) = 6.5; Fe^{2+} = 4mM and H_2O_2 = 20 mM. Fig. 1 presents color abatement rates for the dye AR 183 under the above mentioned working conditions. From the figure, it is vivid that color removal was practically complete within the first 2 min of Fenton reaction. For AR 183, 99% was achieved after 30 min. the rapid decolorization rates can be explained by the fast reaction between Fe^{2+} and H_2O_2 to produce a sufficient amount of $^{\bullet}OH$ that promptly cleaved the dye chromophore. In other words, the *in situ* formed oxidants (free radicals such as $^{\bullet}OH$ and $HO_2^{\bullet}$) had enough oxidation capability to degrade the chromophore of the studied dye at a high degree (>90%). Fast color removal was accompanied with a parallel, rapid decrease in H_2O_2 concentration (only 40% of the initial H_2O_2 remained in the reaction solution after 5 min Fenton treatment and was almost completely consumed at the end of the treatment process) indicating rapid consumption of H_2O_2 during the early stage of textile dye degradation via Fenton treatment has been before by many scientists[11].

COD

Fig. 2 presents changes in COD during Fenton treatment of the dye AR 183. From the figure, it is evident that COD abatement started right after initiation of the reaction and slowed down after only 5 min treatment most probably due to the accumulation of advanced oxidation intermediates that are more resistant to further oxidation than the textile dye, as well as completion of the decolorization process. In this case only, partial COD removal was achieved at the end of the reaction due to the fact that after cleavage of the dye chromophore of the reaction slows down such that the highly complex structured dye molecule is only partially degraded to relatively small fragments such as carboxylic acids, aldehydes, ketones, and alcohols[12,13]. For this reason, complete oxidation of the dyes was not expected. This behaviour was attributed to the relatively short retention time selected for the treatment process and low reagent does leading to incomplete degradation and accumulation of stable oxidation intermediates in the reaction medium.

DOC

DOC abatement of the dye AR 183 was followed under the Fenton treatment conditions and shown in Fig. 2. From this figure, it is apparent that results obtained for DOC and COD removals were almost parallel to each other; DOC abatement proceeded very fast and showed an asymptotic behaviour during the first 5 min of the reaction, speculatively due to the accumulation of oxidation intermediates and consumption of the of the Fenton's reagents.

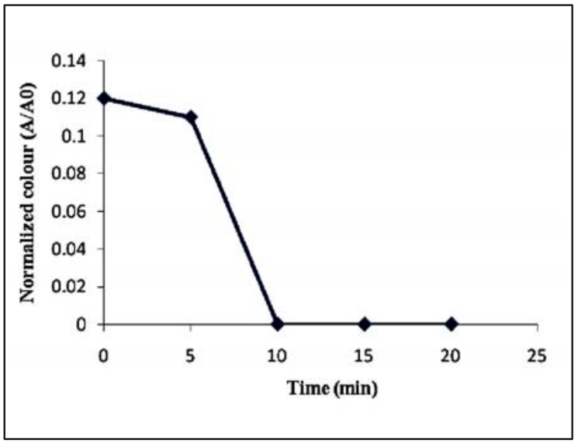


Fig. 1: Normalized colour abatement durng Fenton treatment of 150 mg/L AR 183 (Fe^{2+} = 4 mM; H_2O_2 = 20 mM; pH$_o$ = 6.5)

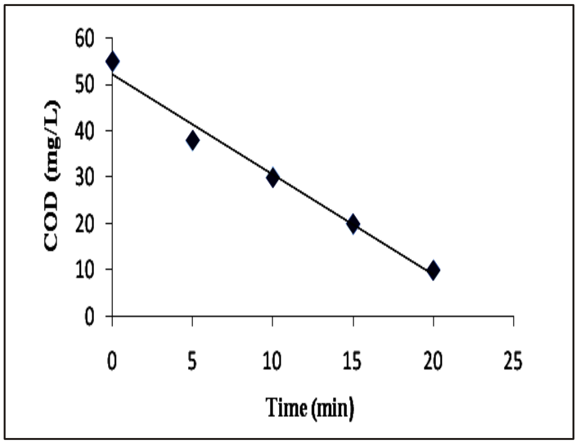


Fig. 2: COD abatement during Fenton treatment of 150 mg/L AR 183 (Fe^{2+} = 4 mM; H_2O_2 = 20 mM; pHo = 6.5

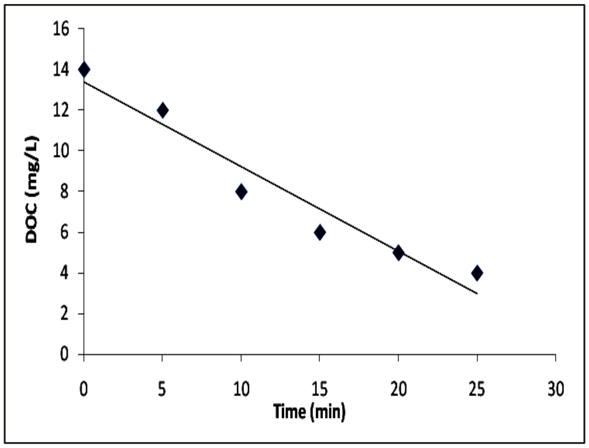


Fig. 3: DOC abatement during Fenton treatment of 150 mg/L AR 183 (Fe^{2+} = 4 mM; H_2O_2 20 mM; pHo 6.5)

Photo-Fenton process

It was found that the optimal concentrations of $FeSO_4.7H_2O$ and H_2O_2 for the AR-183 degradation were 0.4 mmol dm^{-3} of Fe^{3+} and 0.44 mol dm^{-3} of H_2O_2 when the AR-183 concentration was 0.2 mmol dm^{-3}. These concentrations of Fe^{3+} and H_2O_2 were subsequently used in all the later degradation reactions except mentioned elsewhere. AR-183 was scarcely decomposed over several hours of irradiation in the H_2O_2 homogeneous solution after 180 min of photolysis. About 80% of AR - 183 was disappeared when both Fe^{2+} and H_2O_2 were present after reaction for 140 min in the dark. However, AR - 183 was degraded completely illuminated by visible light for 60 min. In the dark, ca. 68% TOC removal occurred in the first 90 min and 100% TOC was removed after 160 min of visible light irradiation. We can see directly from these results that visible light irradiation accelerates greatly the degradation of AR 183. A probable photo-Fenton degradation mechanism under visible light irradiation is given as follows:

$$(\text{AR } 183) + h\upsilon \rightarrow (\text{AR } 183)^* \text{ (Visible light)} \quad \ldots(9)$$

$$(\text{AR } 183)^* + Fe^{3+} \rightarrow (\text{AR } 183)^+ + Fe^{2+} \quad \ldots(10)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad \ldots(11)$$

$$(\text{AR } 183)^+ + {}^{\bullet}OH \rightarrow \text{Degraded or mineralized products} \quad \ldots(12)$$

The degradation of dyes under visible light irradiation involves excitation (Eq.9) and electron transfer from excited dye molecules into Fe^{3+} ions (Eq. 9). Then the generated Fe^{2+} ion reacts with H_2O_2 as Eq. 1 to form .OH radicals which can mineralize the organic compounds. Here, the first two steps (Eqs. 9 and 10) are the initial process induced by visible light.

There must be a substance that can absorb the visible light then the overall process can proceed. This result indicates that visible light irradiation cannot accelerate the Fenton degradation of the substrates that do not absorb the visible light.

CONCLUSION

Many industries use dyes and pigments to color their products. Among azo dyes, constituting the largest class among the synthetic colorants, are considered as the widespread environmental pollutants associated with many important industries such as textile, food colorants, printing and cosmetic manufacturing. The textile industry is one of those industries that consume plenty of water in their manufacturing process. The effluent containing such colored water causes lot of health problems and hence the removal of such pollutants plays a pivotal role in the sustainability of environment. Even though, many methods have been used to remove such colorants, they have one or other shortcomings. Among the available advanced oxidation processes, Fenton and Photo-Fenton processes are of special interest because they make possible achievement of high reaction yields with a low treatment cost. Therefore in the present investigation, Fenton and Photo-Fenton reactions as stand-alone processes and as pretreatment of an aerobic biological treatment for acid red-183 reactive dye degradation have been carried out at pilot plant scale. When applying photo-Fenton reaction as a single process, 10 mgL^{-1} Fe (II) and 250 mgL^{-1} H_2O_2 for 250 mgL^{-1}, acid red-131 treatment and 20 mgL^{-1} Fe (II) and 500 $mgL^{-1}H_2O_2$ for 250 mgL^{-1} acid red-131 treatments closely reproduced the laboratory mineralization results, with 85 and 90 % dissolved organic carbon (DOC) removal respectively.

ACKNOWLEDGEMENTS

A.R. gratefully acknowledges the funding support rendered by the University Grants Commission, New Delhi for his major research project [F.No 35-147/2009(SR)]. He thanks the Principal and the Management of Sir Theagaraya College, Chennai-21 for the constant encouragement given. His thanks are due to Mr. P. Sakthivel, Sastra University, Tanjore for the spectral recording.

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