

## Chemical oxidation of methylene blue using a Fenton-like reaction

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### Abstract

Oxidation by Fenton-like reactions is proven and economically feasible process for destruction of a variety of hazardous pollutants in wastewater. We report herein the oxidation of methylene blue, a basic dye of thiazine series using a Fenton-like reaction at normal laboratory temperature and at atmospheric pressure. The effects of different parameters like the initial concentrations of dye,  $\text{Fe}^{2+}$ , and  $\text{H}_2\text{O}_2$ , pH of the solution, reaction temperature, and added electrolytes on the oxidation of the dye present in dilute aqueous solution in the concentration range  $(3.13\text{--}9.39) \times 10^{-5} \text{ mol dm}^{-3}$  ( $10\text{--}30 \text{ mg l}^{-1}$ ) have been assessed. The results indicate that the dye can be most effectively oxidized in aqueous solution at dye: $\text{Fe}^{2+}$ : $\text{H}_2\text{O}_2$  molar ratio of 1:1.15:14.1. More than 98% removal of the dye could be achieved in 1 h in the pH range 2.2–2.6 at 299 K which corresponds to about 81% reduction of the initial COD. The results will be useful for designing the treatment systems of various dye-containing wastewaters. © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

With the increase of industrialization and urbanization, the requirement of removal of small amounts of toxic pollutants in the ppm or ppb level from industrial wastewater and contaminated groundwater is increasingly becoming significant. Chemical process industries, such as oil refineries, petrochemical units, dye and dye intermediate manufacturing industries, textile units, industries making paper, pharmaceuticals, cosmetics and synthetic detergents, and tanneries are the typical industries that discharge toxic organic compounds

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at low concentrations to the nearer water bodies, thus making the water polluted. It is necessary to develop novel and cost-effective technologies to treat this wastewater.

A variety of physical, chemical, and biological methods are presently available for treatment of wastewater discharged from various industries. Biological treatment is a proven technology and cost-effective, but it suffers from a number of disadvantages. Physical methods such as liquid–liquid extraction, ion-exchange, adsorption, air or steam stripping, etc. are also ineffective on pollutants which are not readily adsorbable or volatile, and have further disadvantage that they simply transfer the pollutants to another phase rather than destroying them. In contrast, chemical oxidation methods can result in almost complete mineralization of organic pollutants and are effective for wider range of organics. The oxidation with Fenton's reagent based on ferrous ion and hydrogen peroxide is a proven and effective technology for destruction of a large number of hazardous and organic pollutants.

Fenton-like reactions exploit the reactivity of the hydroxyl radical produced in acidic solution by the catalytic decomposition of  $\text{H}_2\text{O}_2$ .



The  $\text{HO}^\bullet$  radical is the main reactant in the process capable of detoxifying a number of organic substrates via oxidation. It is twice as reactive as chlorine and its position is second in the oxidation potential series next to fluorine. The kinetic activity of this radical is also tremendous. It reacts almost in a diffusion-controlled manner with second-order rate constant in the range  $10^9$ – $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [1–3] with a variety of reductants including addition to double bonds [4].

The method of Fenton's oxidation may not be applicable to alkaline solutions or sludges with strong buffering capacities. Another disadvantage of Fenton's treatment is the production of iron sludge, which must be disposed [5]. Costs of application of Fenton's reagent are expected to be quite low as compared to other oxidation processes, such as UV radiation/hydrogen peroxide process. The main chemical cost of Fenton's reagent is the cost of  $\text{H}_2\text{O}_2$ . So, it is important to optimize the amount of  $\text{H}_2\text{O}_2$  in the Fenton's oxidation technology.

H.J.H. Fenton [6] in as early as 1894 reported that ferrous ions strongly promote the oxidation of malic acid by hydrogen peroxide. Subsequent work has shown that the combination of  $\text{H}_2\text{O}_2$  and a ferrous salt "Fenton's reagent" is an effective oxidant of a wide variety of organic substrates. About 40 years later, Haber and Weiss [7] proposed that the hydroxyl radical is the actual oxidant in such systems. In the 1940s, Merz and Waters [8,9] proposed the mechanistic scheme to determine the relative susceptibilities of various substrates to hydroxyl radical attack. Since then, the importance and ubiquity of hydroxyl radicals have become increasingly apparent, and oxidations with hydroxyl radicals have been studied with increasing vigor.

Destruction of a range of toxic organic compounds was studied mainly in homogeneous aqueous phases [10–23], though reports are available using iron minerals in heterogeneous way [24,25]. Complete degradation of phenols [10], various chlorophenols [11,12], cresol, and 2,4-dinitrophenol [13,14], perchloroethylene [15], 2,4-dinitrotoluene [16], aromatics like benzene, toluene, and xylene [17], chlorobenzene [18], 2-chlorobiphenyl [19],

2,4-dichlorophenoxy acetic acid, and 2,4,5-trichlorophenoxy acetic acid [20], and formaldehyde [21] could be achieved using  $\text{H}_2\text{O}_2$  and iron salts within a reasonable time. Although, in most of these reactions, a cent percent degradation is accompanied with a cent percent mineralization, there are reports of partial mineralization also [18,19]. A partial removal of various polyaromatic hydrocarbons from contaminated soils [22] and color of the dye wastewater at pH around 3–5 with partial removal of COD were also reported [23].

A few instances of pretreatment of phenolic compounds using Fenton's reagent to reduce the toxicity [26] and to improve the biodegradability [27] of phenolic wastewater prior to biological treatment have also been reported.

Although, most degradations in Fenton-like reactions have been interpreted as oxidation by HO; however, a combined oxidation–reduction mechanism may account for some of the transformations observed at relatively higher  $\text{H}_2\text{O}_2$  concentrations, for example the degradations of pentachlorophenol [12], organometallic insecticides [24], trichloroethylene [28], nitrophenols and nitrobenzene [29], and 2,4,6-trinitrotoluene [30,31]. In the enhanced desorption and transformation of chloroaliphatic compounds from soil samples proved beyond doubt that Fenton-like reactions in which potential reductants like superoxide radical anions ( $\text{O}_2^{\bullet-}$ ) and hydroperoxide anions ( $\text{HO}_2^-$ ) along with hydroxyl radicals are generated may provide a universal treatment matrix in which contaminants are desorbed and then oxidized and reduced in a single system [32].

Besides these chemical treatments, photo-assisted Fenton-like reactions as a source of hydroxyl radicals has shown to be effective in the environmental detoxification and photo-degradation of non-biodegradable contaminants, including textile dyes [33–36].

Methylene blue is a basic dye extensively used for dyeing and printing cotton, silk, etc. It is also used as a medicinal dye because of its antiseptic properties [37]. To the best of our knowledge, no systematic investigation appears to have been done on the degradation of methylene blue using Fenton-like oxidations. In the present work, the effectiveness of the  $\text{Fe}^{2+}$ – $\text{H}_2\text{O}_2$  towards oxidative degradation of the dye has been demonstrated. The initial rate of the degradation of the dye as a function of concentrations of dye,  $\text{Fe}^{2+}$ , and  $\text{H}_2\text{O}_2$  has also been reported.

## 2. Experiments

### 2.1. Chemicals

Methylene blue (Qualigens, India),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (B.D.H.),  $\text{H}_2\text{O}_2$  (30% w/v),  $\text{H}_2\text{SO}_4$ , NaOH,  $\text{K}_2\text{Cr}_2\text{O}_7$ , Mohr Salt, NaCl,  $\text{Na}_2\text{SO}_4$ , KCl,  $\text{K}_2\text{SO}_4$ , and KBr are all of E. Merck, A.R. or G.R. grades and used as received. Commercial grade lime and alum were procured from a local supplier. All solutions were made in distilled water.

### 2.2. Experimental

Glass beakers (250 and 500 ml) containing aqueous dye solutions were placed on a magnetic stirrer for continuous stirring. A digital pH-meter (model 335, Systronics, India) was used for pH measurements. A thermometer was placed in the solution to measure the

temperature of the aqueous phase. Most of the experiments were carried out at 299 K with some at lower or higher temperatures for a comparison. The required amount of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  were added simultaneously into the dye solution, and subsequently the concentrations of the dye were determined spectrophotometrically using a Shimadzu UV-160A spectrophotometer at 665 nm, the absorption maxima of the dye, at different time in order to study the course of the degradation reactions. Most of the experiments were conducted twice in identical conditions. The difference in results in two consecutive experiments did not exceed more than 3%.

In the range  $3.13 \times 10^{-6}$  to  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$  ( $1\text{--}10 \text{ mg l}^{-1}$ ), the absorbance at 665 nm of the dye versus concentration plot showed excellent linearity ( $r > 0.99$ ) with zero intercept.

### 3. Results and discussion

The kinetics of oxidative degradation of methylene blue with  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  were studied in detail. The effects of initial concentration of dye,  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ , pH, temperature, etc. were investigated. The effects of electrolytes such as sodium chloride, sodium sulfate, potassium chloride, potassium sulfate, potassium bromide, etc. on the kinetics of degradation were also determined.

#### 3.1. Action of acids and alkalis on aqueous dye solution

The aqueous solution of the dye neither gives any precipitate nor shows any intense coloration by the action of concentrated sulfuric acid. When the dye solution was treated with sodium hydroxide solution, no remarkable change was observed. In order to test whether the addition of lime, a common coagulant, into the dye solution caused precipitation of the dye, 1 g of lime was added into 50 ml of  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$  of dye solution and the slurry was stirred for 2 h. The solution upon filtration of the slurry was checked for its absorbance and it was found that practically no precipitation of the dye occurred. It is to be noted that the addition of lime into aqueous solution of auramine, a basic dye of diphenylamine series, produced remarkable removal of the dye from aqueous solutions [38]. Similarly, the addition of 1 g of alum to 50 ml of  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$  aqueous dye solution did not result in precipitation of the dye. Conventional primary treatment, therefore, did not cause any removal of methylene blue from dilute aqueous solutions.

#### 3.2. AOP experiments

Of all the advanced oxidation processes, the Fenton-like oxidation process was selected as it is advantageous over other technologies to degrade a wide variety of hazardous organics and also this treatment is quite cost-effective. The  $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$  oxidation has been studied for aqueous dye solutions having dye concentration in the range  $(3.13\text{--}9.39) \times 10^{-5} \text{ mol dm}^{-3}$  ( $10\text{--}30 \text{ mg l}^{-1}$ ). The concentrations of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  were varied in the range from  $7.16 \times 10^{-6}$  to  $1.79 \times 10^{-4} \text{ mol dm}^{-3}$  ( $0.4\text{--}10 \text{ mg l}^{-1}$ ) and  $5.88 \times 10^{-5}$  to  $5.88 \times 10^{-2} \text{ mol dm}^{-3}$  ( $2\text{--}2000 \text{ mg l}^{-1}$ ), respectively.

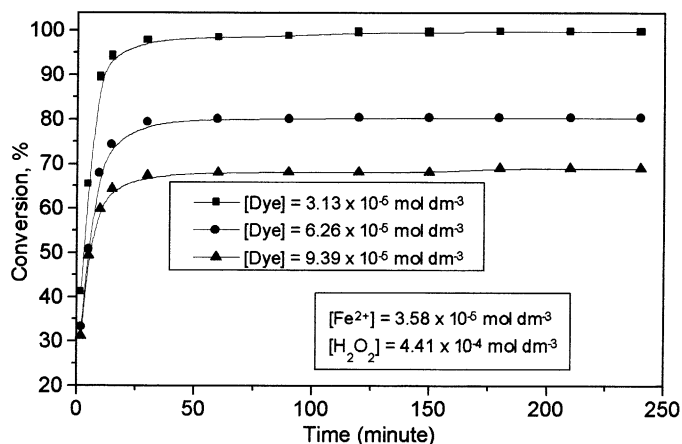


Fig. 1. Conversion of the dye vs. time profile for different initial dye concentrations.

### 3.3. Effect of initial dye concentration on dye degradation

In a typical experiment, a dye solution of  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$  was stirred with  $3.58 \times 10^{-5} \text{ mol dm}^{-3} \text{ Fe}^{2+}$  and  $4.41 \times 10^{-4} \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$  solutions when a rapid reaction occurred, and within 10 min almost 90% of dye was decayed; rest of the reaction took about 2 h for practically complete degradation of the dye when the solution became colorless. The degradation reaction can be roughly divided into two phases: first  $\sim 10$  min of reaction occurs rapidly, and then sluggishly.

In order to investigate the effect of initial dye concentration on the rate of degradation, dye solutions having  $6.26 \times 10^{-5}$  and  $9.39 \times 10^{-5} \text{ mol dm}^{-3}$  were separately treated with  $3.58 \times 10^{-5} \text{ mol dm}^{-3} \text{ Fe}^{2+}$  and  $4.41 \times 10^{-4} \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$  solutions. In both the cases, the reaction took place at a fast rate initially and subsequently the rate of oxidation dropped. The fractional conversion was 80% for  $6.26 \times 10^{-5} \text{ mol dm}^{-3}$  dye and 68% for  $9.39 \times 10^{-5} \text{ mol dm}^{-3}$  dye after a period of 2 h. Results are shown in Fig. 1.

### 3.4. Effect of $[\text{Fe}^{2+}]$ on dye degradation

Baseline experiments were performed to determine the effect of  $\text{Fe}^{2+}$  only in the absence of  $\text{H}_2\text{O}_2$  on the degradation of the dye when practically no degradation was achieved. With  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$  of dye solution, the rate of degradation showed remarkable dependence on the initial  $\text{Fe}^{2+}$  concentration used. Subsequently, experiments were performed at different  $\text{Fe}^{2+}$  concentrations ( $7.16 \times 10^{-6}$  to  $7.16 \times 10^{-5} \text{ mol dm}^{-3}$ ) for fixed initial concentration of  $\text{H}_2\text{O}_2$  and dye of  $4.41 \times 10^{-4}$  and  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$ , respectively. By comparing the results of the dye after 1 h, it was found that the conversion increased as the  $\text{Fe}^{2+}$  concentration was increased from  $7.16 \times 10^{-6}$  to  $3.58 \times 10^{-5} \text{ mol dm}^{-3}$ , and becomes practically constant ( $\sim 98.5\%$ ) when it exceeds  $3.58 \times 10^{-5} \text{ mol dm}^{-3}$ . Below  $7.16 \times 10^{-6} \text{ mol dm}^{-3}$  of  $\text{Fe}^{2+}$ , the degradation reaction is too sluggish to account for any

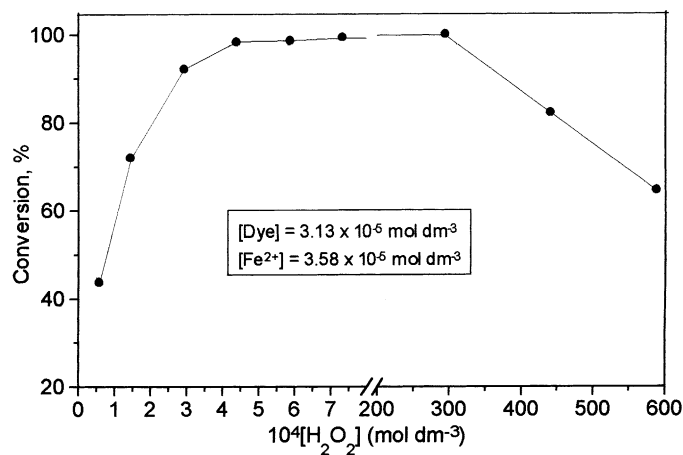


Fig. 2. Effect of  $[\text{H}_2\text{O}_2]$  on the conversion of the dye in 1 h.

practical significance. Thus, from the extent of degradation of the dye after 1 h, we find that there is an optimum  $\text{Fe}^{2+}$  concentration for the most effective degradation of  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$  dye solution. Keeping the dye and  $\text{H}_2\text{O}_2$  fixed at above concentrations, we studied the effect of variation of  $\text{Fe}^{2+}$  concentration for complete destruction of the dye.

### 3.5. Effect of $[\text{H}_2\text{O}_2]$ on dye degradation

In order to investigate the effect of  $\text{H}_2\text{O}_2$  concentration on the degradation kinetics, experiments were conducted at different  $\text{H}_2\text{O}_2$  concentrations with  $3.13 \times 10^{-5}$  and  $3.58 \times 10^{-5} \text{ mol dm}^{-3}$   $\text{Fe}^{2+}$  solutions. In all experiments, we observed that the concentration of the dye dropped instantaneously as  $\text{H}_2\text{O}_2$  was added. The  $\text{H}_2\text{O}_2$  concentration was varied from  $5.88 \times 10^{-5}$  to  $5.88 \times 10^{-2} \text{ mol dm}^{-3}$ . At a fixed  $\text{Fe}^{2+}$  concentration of  $3.58 \times 10^{-5} \text{ mol dm}^{-3}$ , the  $\text{H}_2\text{O}_2$  concentration of  $4.41 \times 10^{-4} \text{ mol dm}^{-3}$  was effecting in degrading about 98% of dye in 30 min at a temperature of 299 K. The fractional conversion after 1 h remains almost same for  $\text{H}_2\text{O}_2$  concentration of  $4.41 \times 10^{-4}$  to  $2.94 \times 10^{-2} \text{ mol dm}^{-3}$ . Beyond  $2.94 \times 10^{-2} \text{ mol dm}^{-3}$ , a decrease in fractional conversion of the dye was observed and this is shown in Fig. 2. Therefore, there is an optimum  $\text{H}_2\text{O}_2$  concentration that is effective for the degradation of the dye. The selection of this optimum concentration is important from the commercial point of view (due to the cost of  $\text{H}_2\text{O}_2$ ). De et al. [39] have reported the existence of an optimum  $\text{H}_2\text{O}_2$  concentration for the degradation of phenol by Fenton's reagent.

The occurrence of an optimum  $\text{H}_2\text{O}_2$  concentration for the degradation of methylene blue by Fenton's reagent could be explained as follows. At low  $\text{H}_2\text{O}_2$  concentration, the  $\text{HO}^\bullet$  radicals preferentially attack the benzene ring of the organic contaminant present in wastewater. At high  $\text{H}_2\text{O}_2$  concentration, however, there is a competition between the substrate and  $\text{H}_2\text{O}_2$ ; in other words,  $\text{H}_2\text{O}_2$  in high concentration acts as a scavenger of the highly potent  $\text{HO}^\bullet$  radicals to produce perhydroxyl radical,  $\text{HO}_2^\bullet$  (Eq. (4)), which is rather innocent towards redox act. It has much lower oxidation capabilities than  $\text{HO}^\bullet$  [16,17], and

as the  $pK_a$  for its distribution with superoxide anion (Eq. (5)) is as high as 4.8 [1,32], so under the pH range 2.2–2.6 studied here, generation of  $O_2^{\bullet-}$ , a significant reductant, may be neglected. Overall efficacy of  $Fe^{2+}$ - $H_2O_2$  is thus found to be low at relatively higher  $H_2O_2$  concentrations.



### 3.6. Determination of optimum ratio of [dye]:[ $Fe^{2+}$ ]:[ $H_2O_2$ ]

To determine the optimum ratio of [dye]:[ $Fe^{2+}$ ]:[ $H_2O_2$ ] on dye degradation, experiments were conducted by varying the  $Fe^{2+}$  and  $H_2O_2$  concentrations, keeping the dye concentration fixed at  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$ .

To determine the effect of [dye]:[ $Fe^{2+}$ ] ratio on the degradation efficiency, experiments were performed by varying the dye: $Fe^{2+}$  molar concentration ratio at a fixed  $H_2O_2$  concentration of  $4.41 \times 10^{-4} \text{ mol dm}^{-3}$ . The percent conversion of the dye as a function of the dye: $Fe^{2+}$  concentration is presented in Fig. 3a, which shows that the fractional conversion of the dye was maximum at a dye: $Fe^{2+}$  molar ratio around 0.87 (10:2 in  $\text{mg l}^{-1}$ ) in 2 h. Further increase in [ $Fe^{2+}$ ] has negligible effects. Fig. 3b shows the percent conversion of the dye as a function of  $Fe^{2+}$ : $H_2O_2$  molar ratio at a fixed [ $Fe^{2+}$ ] of  $3.58 \times 10^{-5} \text{ mol dm}^{-3}$  for a reaction time of 2 h. The results indicate that the conversion of the dye increases with the increase in the  $Fe^{2+}$ : $H_2O_2$  ratio and becomes independent of [ $H_2O_2$ ] when this ratio exceeds  $\sim 0.08$ , which corresponds to  $H_2O_2$  amounting  $4.41 \times 10^{-4} \text{ mol dm}^{-3}$ . This is the minimum [ $H_2O_2$ ] required for the maximum conversion (more than 99%) of the dye under the experimental conditions. The optimum molar ratio of  $Fe^{2+}$ : $H_2O_2$  is thus found to be around 0.08 (2:15 in  $\text{mg l}^{-1}$ ) at a solution pH between 2 and 3. It is reported that the decomposition of  $H_2O_2$  catalyzed by iron leading to the formation of  $HO^{\bullet}$  radicals occurs best when the molar ratio of  $Fe^{2+}$ : $H_2O_2$  is kept at a value of 1:15 at a solution pH of 3 [40]. This is in agreement with the present finding. To determine the effect of  $H_2O_2$ :dye ratio on the degradation efficiency, experiments were performed by varying the  $H_2O_2$  concentration keeping the concentrations of dye and  $Fe^{2+}$  fixed at  $3.13 \times 10^{-5}$  and  $3.58 \times 10^{-5} \text{ mol dm}^{-3}$ , respectively. A plot of percent conversion of the dye at 2 h as a function of  $H_2O_2$ :dye concentration ratio is shown in Fig. 3c. It appears that the extent of degradation of the dye increases, and reaches a maximum (more than 99%) when this ratio reaches around 14.1 which corresponds to  $4.41 \times 10^{-4} \text{ mol dm}^{-3} H_2O_2$ . It can therefore be concluded that the optimum ratio of  $H_2O_2$ :dye is 14.1:1. After combining the above results, we can conclude that a  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$  aqueous dye solution can be effectively degraded at a [dye]:[ $Fe^{2+}$ ]:[ $H_2O_2$ ] concentration ratio of 1:1.15:14.1.

### 3.7. Effect of temperature on the fractional conversion of the dye

Experiments were conducted at four different temperatures between 281 and 328 K under otherwise uniform conditions to investigate the effect of temperature on the degradation kinetics of aqueous dye solutions. The results are shown in Fig. 4. A substantial increase in

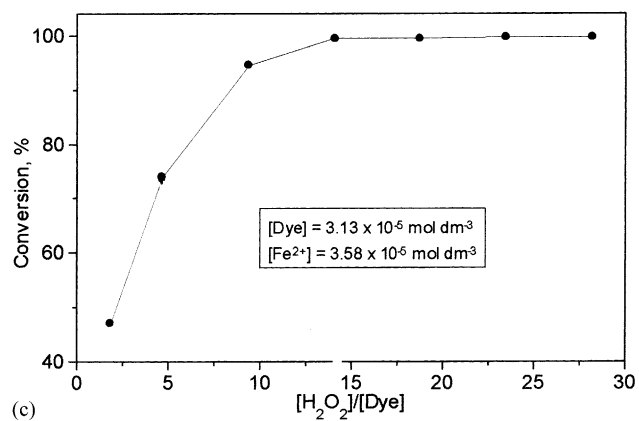
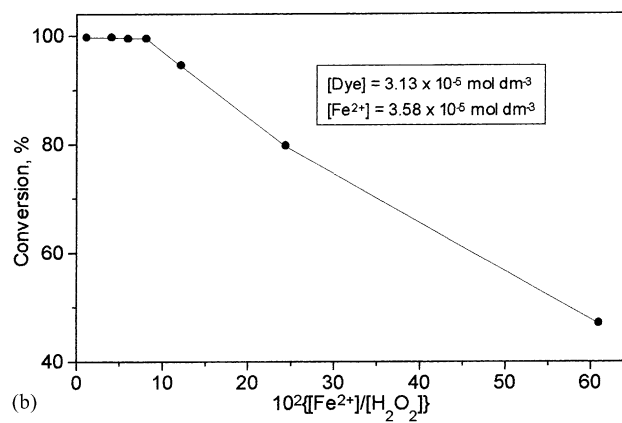
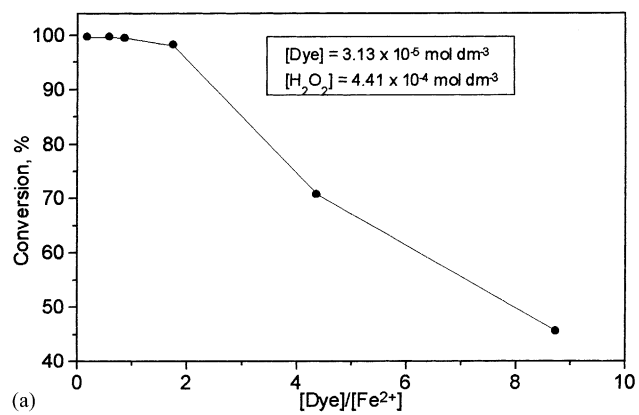


Fig. 3. (a) Effect of [dye]:[Fe<sup>2+</sup>] ratio on the conversion of the dye in 2 h; (b) effect of [Fe<sup>2+</sup>]:[H<sub>2</sub>O<sub>2</sub>] ratio on the conversion of the dye in 2 h; (c) effect of [H<sub>2</sub>O<sub>2</sub>]:[dye] ratio on the conversion of the dye in 2 h.



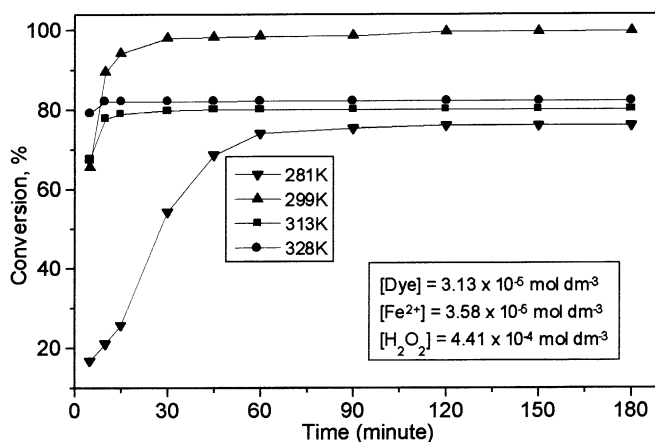


Fig. 4. Effect of temperature on the conversion of the dye.

the extent of degradation of the dye was observed when the reaction temperature was raised from 281 to 299 K. A further increase in the reaction temperature from 299 to 313 K resulted in the decrease in the extent of degradation of the dye. Moreover, there was practically no difference in the rate and extent of degradation of the reaction in the temperature between 313 and 328 K. At higher reaction temperatures, perhaps, the thermal decomposition of the hydrogen peroxide resulted in the reduction of its effective concentration towards making hydroxyl radicals, and this was possibly the reason behind lower conversion of the dye at higher reaction temperatures.

### 3.8. Effect of electrolytes on conversion

Industrial wastewater might contain a number of salts, more generally electrolytes, dissolved in them. It was therefore thought worthwhile to investigate the effect of dissolved electrolytes such as sodium chloride, potassium chloride, sodium sulfate, potassium sulfate, etc. on the rate and the extent of the oxidative degradation of the dye. The effect of dissolved electrolytes was studied only at the optimum concentrations of the dye,  $\text{H}_2\text{O}_2$ , and  $\text{Fe}^{2+}$ . It was observed that the presence of halide salts at the same concentration level substantially decreased the rate and the extent of degradation, whereas for sulfate salt, the lowering in the extent of degradation is much less pronounced. It is not clear why halides reduced the rate of conversion of the dye; it might be due to the interaction of the electronegative chloride anion with the hydroxyl radical that inhibited the rate of the degradation reaction. The effects are shown in Fig. 5.

### 3.9. Effect of pH on the conversion of the dye

In all the experiments reported herein, a sharp drop in solution pH from around 5.5 to around 2.5 within minutes was observed. Subsequently, the change in pH was negligible

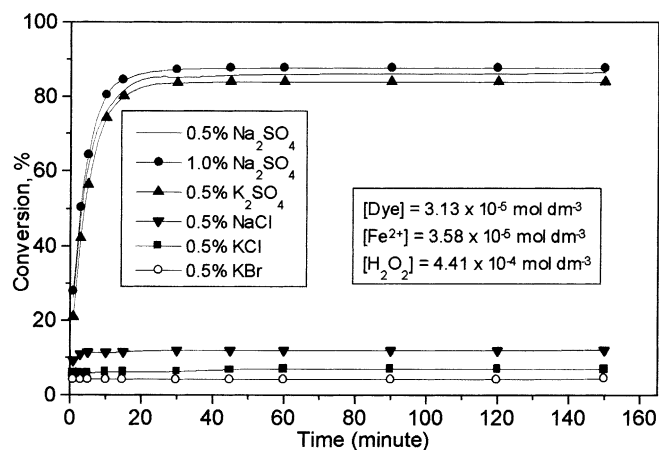


Fig. 5. Effect of added electrolytes on the conversion of the dye.

and is shown in Fig. 6. The drastic drop in pH in the early part of the reaction is probably due to the formation of some acidic reaction intermediates which could not be characterized. De et al. [39] reported similar observations for the degradation of phenol and chlorophenols by UV/H<sub>2</sub>O<sub>2</sub> photo-oxidation.

To find the optimum pH for maximum conversion of the aqueous dye solutions, reactions were carried out at different pH in the range, 1.7–12 by adding H<sub>2</sub>SO<sub>4</sub> or NaOH, and the effect of pH on the conversion of the dye is shown in Fig. 7 from which it is evident that maximum conversion of about 99% was achieved within 2 h when the solution pH was around 2.5 after a few minutes from the start of the reaction. When the initial pH was set at

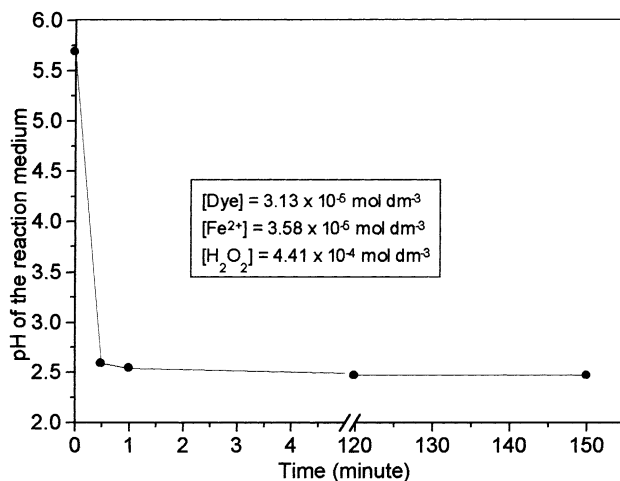


Fig. 6. Change of pH of the reaction during the conversion of the dye.

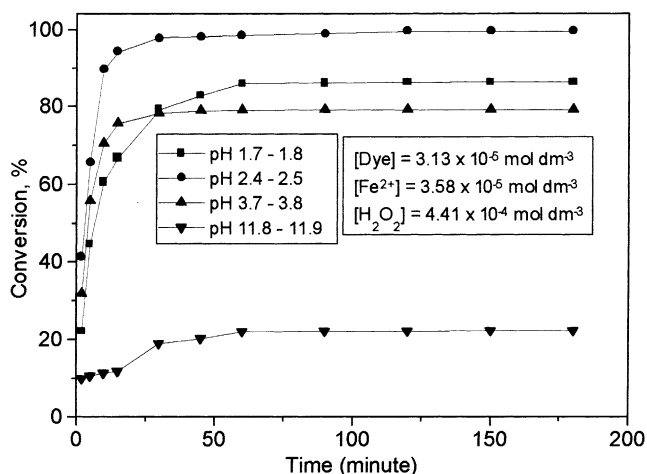


Fig. 7. Effect of pH on the conversion of the dye.

10, there was a sharp drop in pH to 3.8 in the early stage of the degradation and 79% of the dye was converted in 3 h. The initial pH when adjusted at 1.8 dropped marginally to 1.7 and under this condition 86% conversion was observed. In the another extreme, when the initial pH was maintained in the higher alkaline range, e.g. 12, the pH of the solution on addition of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  did not fall sharply as above and about 22% conversion was observed in 3 h. Possibly iron precipitated out of the aqueous phase as hydroxide in the higher pH and the efficiency of the degradation became poor. From the foregoing, it appears that a pH between 2 and 3 is the most effective in the degradation reactions reported here. This is in agreement with the observation that complete mineralization of pentachlorophenol by Fenton's reagent may be done [12] at pH between 2 and 3, and also a pH of around 3.5 was most effective for degradation of a simulated dye wastewater [23].

### 3.10. Conversion of the dye based on COD measurements

All the results reported here so far are based on analysis of the dye solutions spectrophotometrically. It was thought important to measure the COD of the dye solutions after the degradation in order to verify whether the dye actually degraded by Fenton-like reactions employed here or the disappearance of color was due to some other effect such as complex formation. To determine the reduction in the COD of the reaction medium, initial COD (before oxidation) and final COD (after oxidation) of the aqueous dye solutions were measured [41]. All the experiments showed that more than 80% reduction of COD has occurred in the final solution, which proves that the color of the dye solutions was discharged through oxidative degradation. When a  $3.13 \times 10^{-5} \text{ mol dm}^{-3}$  dye solution was treated with  $3.58 \times 10^{-5} \text{ mol dm}^{-3}$  of  $\text{Fe}^{2+}$  and  $4.41 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{H}_2\text{O}_2$ , more than 99% decoloration, measured on spectrophotometer, was observed in 2 h; however, the reduction in COD was found to be ~89%. There is a little discrepancy observed between the

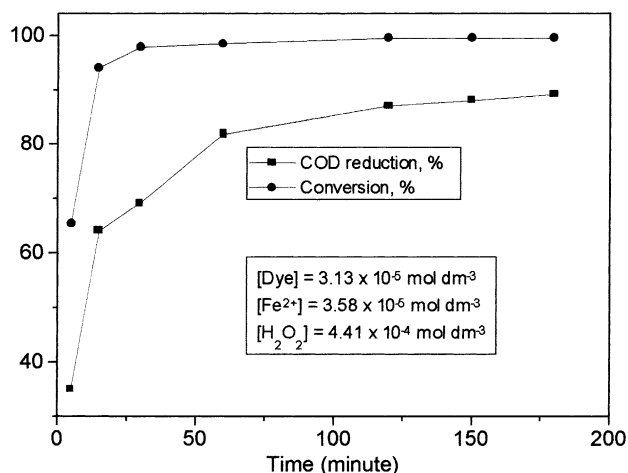


Fig. 8. Plot of COD reduction and the conversion of the dye with time.

reduction of color and percent removal of the dye as calculated from the COD test (Fig. 8). Such discrepancies have also been reported earlier for the oxidative degradation of phenol by UV/H<sub>2</sub>O<sub>2</sub> [42].

### 3.11. Determination of initial rates

As found from the concentration versus time plots, the concentration of the dye changes very rapidly in the first few minutes of the degradation and subsequently this rate slows remarkably. In the present work, the reactions have been monitored by noting the change of the dye degradation only; no attempt has been made to determine the hydrogen peroxide or ferrous concentrations in the reaction medium at different time intervals.

An attempt has been made to represent the rate of the degradation reaction in the form of a power-law equation for the initial period of reaction. The initial rates were calculated by drawing a tangent at time  $t = 0$  on the concentration versus time profile. The kinetic analysis was done for those experiments in which the dye concentration was varied in the range  $(3.13\text{--}9.39) \times 10^{-5} \text{ mol dm}^{-3}$ , the H<sub>2</sub>O<sub>2</sub> concentration was varied from  $2.94 \times 10^{-4}$  to  $8.82 \times 10^{-4} \text{ mol dm}^{-3}$ , and the concentration of Fe<sup>2+</sup> was varied from  $1.79 \times 10^{-5}$  to  $7.16 \times 10^{-5} \text{ mol dm}^{-3}$ .

The initial rate of degradation of the dye is given by

$$-r_{A_0} = kC_{A_0}^m C_{B_0}^n C_{C_0}^p$$

where  $C_{A_0}$ ,  $C_{B_0}$ , and  $C_{C_0}$  are, respectively, the initial concentrations of dye, Fe<sup>2+</sup>, and H<sub>2</sub>O<sub>2</sub>,  $m$ ,  $n$ , and  $p$  the respective orders, and  $k$  the rate constant. Keeping  $C_{B_0}$  and  $C_{C_0}$  constant, the initial dye concentration  $C_{A_0}$  was varied and the initial rates were determined from the concentration versus time profile. The initial rates and concentrations are given in Table 1. A plot of  $\ln(-r_{A_0})$  against  $\ln C_{A_0}$  was found to be linear ( $r > 0.98$ ), whence

Table 1  
Initial rates of degradation of methylene blue at different initial concentrations of dye, Fe<sup>2+</sup>, and H<sub>2</sub>O<sub>2</sub>

Reactants	Initial concentration × 10 <sup>5</sup> (mol dm <sup>-3</sup> )	Initial rate × 10 <sup>5</sup> (mol dm <sup>-3</sup> min <sup>-1</sup> )
Dye	3.13	0.81
	6.26	1.91
	9.39	3.23
Fe <sup>2+</sup>	1.79	0.45
	3.58	0.81
	5.37	1.15
	7.19	1.51
H <sub>2</sub> O <sub>2</sub>	29.4	0.57
	44.1	0.81
	58.8	0.92
	73.5	1.20
	88.2	1.27

Table 2  
Orders with respect to the reactants and rate constants for the degradation of methylene blue

Reactants	Order	Rate constant × 10 <sup>-6</sup> (dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1.836</sup> min <sup>-1</sup>
Dye	1.25	6.27 ± 1.15
Fe <sup>2+</sup>	0.84	5.84 ± 1.38
H <sub>2</sub> O <sub>2</sub>	0.74	6.03 ± 2.43

the slope of the line yielded the order ( $m$ ) with respect to the dye. Similarly, the effects of varying Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations on the initial rates of degradation were assessed whence  $n$  and  $p$  were evaluated. The values are given in Table 2. From the values of the orders, we find that the degradation of the dye is practically first order with respect to the dye in the initial period of the reactions. From the intercepts of such linear plots, we get the values of rate constants for the initial period of degradation reaction. The rate constants are reported in Table 2. The rate constant values obtained by varying independently the dye, Fe<sup>2+</sup>, and H<sub>2</sub>O<sub>2</sub> are close to each other within experimental uncertainties suggest that the experiments reported here are consistent.

#### 4. Conclusions

The kinetics of oxidative degradation of methylene blue by Fenton-like reactions in the temperature between 281 and 328 K was studied in a batch reactor. The optimum concentrations of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> were, respectively,  $3.58 \times 10^{-5}$  and  $4.41 \times 10^{-4}$  mol dm<sup>-3</sup> for the degradation of a  $3.13 \times 10^{-5}$  mol dm<sup>-3</sup> dye solution at 299 K. The rate of degradation of the dye was found to be very rapid in the initial period of reaction, leading to almost 90% conversion of the dye in 10 min along with a sharp drop in the solution pH. Dissolved

electrolytes such as NaCl, NaBr, etc. suppressed the rate of degradation, possibly due to the interaction of the anions with the hydroxyl radical. The rate of degradation was found to be practically independent of temperature in the range studied in this work.

The initial rate of degradation could be expressed in terms of a power-law equation as follows:

$$\text{Rate} = kC_{A_0}^{1.25}C_{B_0}^{0.84}C_{C_0}^{-0.74}$$

where rate is in  $\text{mol dm}^{-3} \text{ min}^{-1}$ , concentrations in  $\text{mol dm}^{-3}$ , and the unit of rate constant in  $(\text{dm}^3 \text{ mol}^{-1})^{1.836} \text{ min}^{-1}$ .

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