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ORIGINAL ARTICLE

# Kinetics of the oxidative decolorization of some organic dyes utilizing Fenton-like reaction in water

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## KEYWORDS

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**Abstract** The decolorization kinetics of some organic pollutants in water such as commercial dyes, namely, Malachite green (MG), Rhodamine B (RB), Methylene blue (MB) and Crystal violet (CV) were studied using a Fenton-like reagent. The effects of different parameters like the initial dye concentration,  $\text{Fe}^{3+}$ , concentration of  $\text{H}_2\text{O}_2$ , pH of the solution, reaction temperature, and added electrolytes on the kinetics were determined. The results indicate that the optimum pH for the decolorization of all dyes examined is in the range between 3 and 4. The rate of decolorization showed remarkable dependence on the initial  $\text{Fe}^{3+}$  concentration. Using dilute dye solutions in the range of  $(0.30\text{--}1.50 \times 10^{-5} \text{ mol dm}^{-3})$  the rate increased as the  $\text{Fe}^{3+}$  concentration was increased from  $1.5 \times 10^{-4}$  to  $6.0 \times 10^{-4} \text{ mol dm}^{-3}$ , and becomes practically constant when it exceeds  $6.0 \times 10^{-4} \text{ mol dm}^{-3}$ . Below  $1.5 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Fe}^{3+}$ , the decolorization reaction is too sluggish to account for any practical significance. But the decolorization rate of all examined dyes decreased at high  $\text{Fe}^{3+}$  concentrations ( $\geq 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ). There is an optimum  $\text{H}_2\text{O}_2$  concentration in the range of  $0.01\text{--}0.04 \text{ mol dm}^{-3}$  that is effective for decolorization of the dyes. It was observed that the presence of halide salts at the same concentration level substantially decreased the rate and the extent of decolorization, whereas for nitrate salt, there is an increase in the extent of dye decolorization. An increase in the extent of decolorization of the dye was observed when the reaction temperature was raised. The results will be useful for designing the treatment systems of various dye-containing wastewaters. It was also found that the decolorization of the dyes undergoes a fast reaction than the mineralization.

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## 1. Introduction

Synthetic dyes are visible pollutants, which is undesirable even at trace level due to its chemistry and appearance. Many dyes are made water-soluble to meet the color requirements of most fabrics. Textile dyes and other commercial colorants have become a major concern with regard to environmental pollution. A total of 15% of the total world production of dyes is lost during the dyeing process and is released in textile effluents

(Zollinger, 1991). Some frequent users of these chemicals include paper and pulp manufacturing, dyeing of cloth, leather treatment, printing etc. Most of the used solutions containing such dyes are discharged as effluents (Bukallah et al., 2007). The discharge of colored wastes into receiving streams not only affects the aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic activity (Namasivayam et al., 2001). Wastewaters offer considerable resistance for their biodegradation due to the presence of these heat and light stable dyes, thus upsetting aquatic life (Mall et al., 2006). Thus, pollution caused by industrial wastewaters has become a common problem for many countries (Hamadaoui, 2006).

Several methods have been tested for color removal from the industrial effluents to decrease their impact on the environment. These methods include adsorption onto inorganic or organic matrices (Lata et al., 2008; Gong et al., 2008; Rauf et al., 2008; Cheng et al., 2008; Augustine, 2008; Xiaofei and Khalil, 2008; Hameed and El-Khaiary, 2008a,b), chemical precipitation, coagulation, electrocoagulation (Daneshvar et al., 2003).

Recent developments of chemical treatment of wastewater resulted in a considerable improvement in the oxidative decolorization of organic compounds dissolved in aqueous media. Among these methods called advanced oxidation processes (AOPs), homogenous chemical oxidation using ultraviolet radiation in the presence of  $H_2O_2$  (photooxidative decolorization) (Modirshahla and Behnajady, 2006; Jiaqing et al., 2006; Andreozzi et al., 2006), Fenton's reaction (Ntampeglitis et al., 2006) and electro-Fenton processes (Oturán et al., 2008).

In this work, Fenton-like reactions were used for the decolorization of four commercial dyes, namely, Malachite green (MG), Rhodamine B (RB), Methylene blue (MB) and Crystal violet (CV) in dilute solutions. The aim of the study is to examine in detail the effect of the major system parameters on the decolorization kinetics of these dyes. The parameters, which are examined separately, are the solution pH, the concentration of  $H_2O_2$ , the concentration of the  $Fe^{3+}$  ions and the initial

dye concentration. This method seems to decolorize dyes with a variety of molecular structures. The rate of decolorization seems to be affected very little by structure, making it an attractive option for the treatment or pre-treatment of textile effluents containing a wide range of dyes.

## 2. Materials and methods

### 2.1. Reagents

Ferric nitrate [ $Fe(NO_3)_3 \cdot 9H_2O$ ], and 35% hydrogen peroxide ( $H_2O_2$ ) were purchased from Panreac Quimica Comp., Spain. All dyes were purchased from Acros Organics, New Jersey, USA, and were used without further purification. Other chemicals used in the experiment were all of analytical grade. A known dye concentration was prepared in deionized water and used as the stock solution for all studies.

The structures of all dyes used in the study are shown in Fig. 1.

### 3. Experimental procedures

The UV-VIS spectra of the dyes were recorded from 200–800 nm using a UV-VIS-NIR spectrophotometer (JASCO, V-570). The maximum absorbance wavelength ( $\lambda_{max}$ ) of Malachite green (MG), Rhodamine B (RB), Methylene blue (MB) and Crystal violet (CV) are 618, 553, 665 and 590 nm respectively from the spectra.

All experiments were carried out at room temperature,  $25 \pm 1^\circ C$ . Solution pH was adjusted by using nitric acid or sodium hydroxide using a pH meter (OAKTON PC 510). The aqueous dye solutions were placed in measuring flasks (10 ml), the required amount of  $Fe^{3+}$  and  $H_2O_2$  were added into the dye solution, and subsequently the intensity (absorbance) of the dye were measured using a Selecta UV-2005 spectrophotometer at  $\lambda_{max}$ , the absorption maximum for each dye, at different

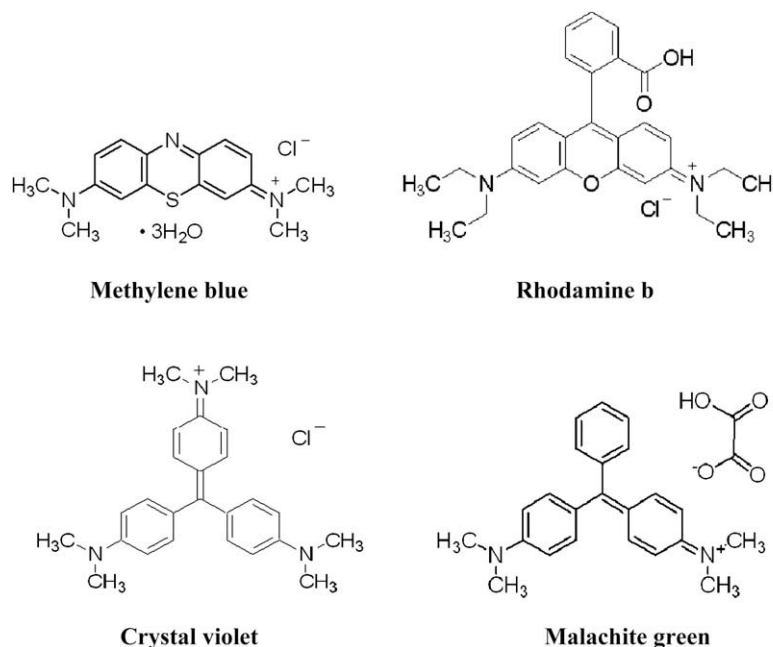


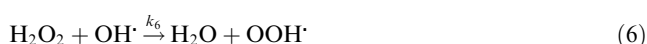
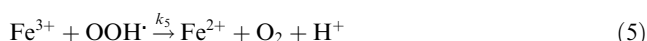
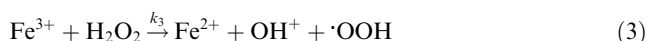
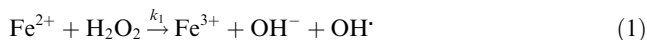
Figure 1 Structures of the used dyes.

time in order to study the course of the decolorization 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%. Total organic carbons (TOC) was analyzed with a Shimadzu 5000 TOC analyzer.

#### 4. Results and discussion

In the literature, Fenton and Fenton-like reactions for the treatment of textile effluents are very efficient in a pH range between 2 and 5 (Lunar et al., 2000a,b). Furthermore, in most papers, it is mentioned that the optimum pH value is around 3 (Lunar et al., 2000b; Kitis et al., 1999; Kang and Hwang, 2000; Schafer and Buettner, 2000).

The general mechanism using Fenton reagents, via which the hydroxyl radicals are produced, is a number of cyclic reactions, which utilize the  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  ions as a catalyst to decompose the  $\text{H}_2\text{O}_2$ . These ions are regenerated in their original state at the end of the cyclic reactions according to the following scheme of reactions (Kitis et al., 1999; Gallard and De Laat, 2000; Ri et al., 2001):



More than 25 reactions occur, several involving the dye molecule, but the above seven are the most significant involving ions and radicals. When a Fenton-like reagent is used, the sequence of reactions begins with reaction (3). There are many bibliographic sources which report that Fenton reagent is more effective than Fenton-like reagent (Gallard and De Laat, 2000; Solozhenko et al., 1995; Li, 1999; Kwon et al., 1999). However, in most cases it seems that it does not matter whether  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  is used. The above sequence of reactions begins very quickly if there is an abundant supply of  $\text{H}_2\text{O}_2$  and of dye.

##### 4.1. 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 decolorization and subsequently this rate slows remarkably. In the present work, the reactions have been monitored by noting the change of the dye only; no attempts have been made to determine the hydrogen peroxide or ferric concentrations in the reaction medium at different time intervals.

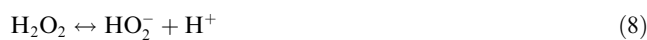
An attempt has been made to represent the rate of the decolorization reaction in the form of a power-law equation for the initial period of reaction. The initial rates were calculated by drawing a tangent at time  $t = 0$  on the concentration versus time profile. The kinetic analysis was done for those experiments in which the dye concentration, ferric ion concentration and hydrogen peroxide concentration were varied in the studied ranges.

##### 4.2. Effect of pH

Fig. 2 illustrates the effect of pH on the rate of decolorization of the examined dyes (MG, RB, MB and CV) in water. The following can be observed from Fig. 2: (1) the dependence of the decolorization rate on the pH is similar for all dyes examined; (2) the decolorization rate reaches a maximum as the pH increases from 3.0–4.0; (3) in highly acidic solutions (= or below 2), the decolorization rates become significantly slower with decreasing pH while a similar behavior is also found in highly alkaline solutions, where above pH 10 the decolorization rate becomes very small (not measurable in the present study, and so, not shown in Fig. 2). Therefore, it seems that the optimum pH for the decolorization of all dyes examined is in the range between 3 and 4. The findings of this study are consistent with other results reported in the literature (Lunar et al., 2000a,b; Kitis et al., 1999; Kang and Hwang, 2000; Schafer and Buettner, 2000; Solozhenko et al., 1995; Li, 1999; Andreozzi et al., 1999).

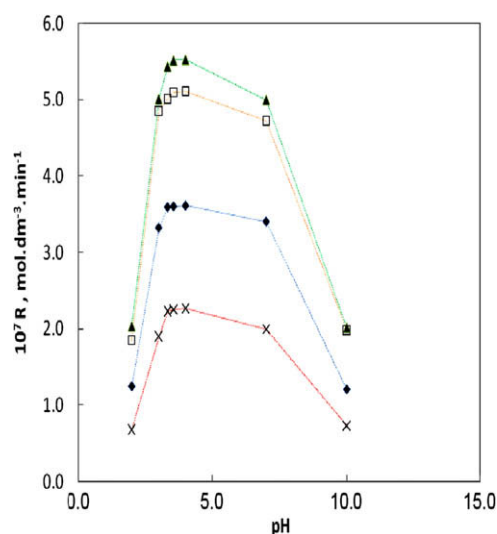
The drastic decrease of the decolorization rate in highly acidic solutions is due to the drastic reduction of hydroxyl radicals produced in the sequence of reactions (1)–(7). High concentrations of hydrogen ions result in the reversal of Eq. (3).

Eq. (3) occurs via the following mechanism:



In highly acidic conditions,  $\text{H}_2\text{O}_2$  is stabilized and this inhibits the production of the intermediate ion  $\text{HO}_2^-$ , which reacts with  $\text{Fe}^{3+}$  to produce  $\text{Fe-OOH}^{2+}$ . The  $\text{Fe-OOH}^{2+}$  ion decomposes to produce  $\text{Fe}^{2+}$ , which is necessary in reaction (1) in order to generate hydroxyl radicals (Lunar et al., 2000b; Ahn et al., 1999). Electron transfer through the solution to  $\text{Fe}^{3+}$ , which occurs by means of  $\text{HO}_2^-$ , is therefore hindered.

At highly alkaline pH, decolorization efficiency is reduced because of the reduction in solubility of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (Schafer and Buettner, 2000) and the formation of  $\text{Fe}(\text{OH})_3$  and



**Figure 2** Effect of pH on the rates of decolorization of different dyes.  $[\text{dye}] = 1.5 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{Fe}^{3+}] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{O}_2] = 0.04 \text{ mol dm}^{-3}$ , at 25 °C, (x) CV, (◆) MG, (□) MB and (▲) RB.

$\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , resulting in the decrease in  $\text{Fe}^{3+}$  ions in the solution and subsequently in a reduction in the concentration of  $\text{Fe}^{2+}$  ions, which are more efficient than  $\text{Fe}^{3+}$  ions because they directly produce  $\text{OH}^\cdot$  (Lunar et al., 2000b).

Also, if the pH is too high, the iron precipitates as  $\text{Fe}(\text{OH})_3$  and catalytically decomposes the  $\text{H}_2\text{O}_2$  to oxygen, which reduces its concentration in the solution, potentially creating a hazardous situation (Lunar et al., 2000a).

#### 4.3. Effect of initial dye concentration

In order to investigate the effect of initial dye concentration on the rate of decolorization, dye solutions having  $0.30 \times 10^{-5}$ ,  $0.75 \times 10^{-5}$ ,  $1.20 \times 10^{-5}$  and  $1.50 \times 10^{-5}$  mol  $\text{dm}^{-3}$  were separately treated with  $3.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$  and  $0.02$  mol  $\text{dm}^{-3}$  solutions. All runs were conducted at the optimum pH. In all cases, the reaction took place at a fast rate initially and subsequently the rate of oxidation dropped.

Generally, the methods of waste treatment are strongly dependent on the initial concentration of the organic substrate (Li, 1999; Centi et al., 2000). This is also consistent with the modeling of the reaction as a first-order kinetic model ( $-d(C_{\text{dye}}/dt) = k_{\text{obs}} C_{\text{dye}}$ ), for the very early stages of the reaction. This also explains the initial rapid drop in the absorbance versus time and subsequently the near leveling off of the absorbance. This implies that Fenton-like reagent is more efficient for a pre-treatment of textile dye effluents. It is observed that, the fractional conversion after 30 min for (MG) was 95% for  $0.3 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , 92% for  $0.75 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , 84% for  $1.2 \times 10^{-5}$  mol  $\text{dm}^{-3}$  and 68.5% for  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ; for (RB) was 90% for  $0.3 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , 84.4% for  $0.75 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , 60.8% for  $1.2 \times 10^{-5}$  mol  $\text{dm}^{-3}$  and 55.3% for  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ; for (CV) was 67% for  $0.75 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , 63% for  $1.2 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , 53% for  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  and 38% for  $3 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ; for (MB) was 100% for  $0.3 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , 100% for  $0.75 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , 83% for  $1.2 \times 10^{-5}$  mol  $\text{dm}^{-3}$  and 77% for  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ .

#### 4.4. Effect of $[\text{Fe}^{3+}]$ on dye decolorization

Baseline experiments were performed to determine the effect of  $\text{Fe}^{3+}$  only in the absence of  $\text{H}_2\text{O}_2$  on the decolorization of the dye when practically no decolorization was achieved. With  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  of dye solutions, the rate of decolorization showed remarkable dependence on the initial  $\text{Fe}^{3+}$  concentration used. Subsequently, experiments were performed at different  $\text{Fe}^{3+}$  concentrations ( $1.5 \times 10^{-4}$  to  $10.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) for fixed initial concentration of  $\text{H}_2\text{O}_2$  and dye of 0.02 and  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , respectively. By comparing the results of the dye after 30 min, it was found that the rate increased as the  $\text{Fe}^{3+}$  concentration was increased from  $1.5 \times 10^{-4}$  to  $6.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , and becomes practically constant when it exceeds  $6.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ . Below  $1.5 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of  $\text{Fe}^{3+}$ , the decolorization reaction is too sluggish to account for any practical significance. But the decolorization rate of all examined dyes decreased at high  $\text{Fe}^{3+}$  concentrations ( $\geq 1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ). Thus from the extent of decolorization of the dye after 1 h, we find that there is an optimum  $\text{Fe}^{3+}$  concentration for the most effective decolorization of  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  dye solution. Keeping the

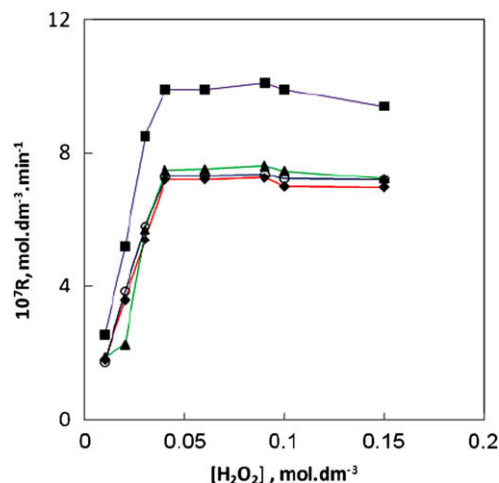
dye and  $\text{H}_2\text{O}_2$  fixed at above concentrations, we studied the effect of variation of  $\text{Fe}^{3+}$  concentration for complete destruction of the dye.

The observed decrease in decolorization reaction rate at high  $\text{Fe}^{3+}$  concentrations is due to the fact that  $\text{Fe}^{2+}$  concentrations increase rapidly through the reactions (3) and (5) and scavenge hydroxyl radicals (Lunar et al., 2000a; Tang and Chen, 1996) through reaction (2). At low  $\text{Fe}^{3+}$  concentrations (below  $1.5 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ), the decolorization rate decreases even more rapidly. This is due to the lack of  $\text{Fe}^{3+}$  and subsequently of  $\text{Fe}^{2+}$ , which is necessary for the formation of hydroxyl radicals (Tang and Chen, 1996). Therefore, at low  $\text{Fe}^{3+}$  concentrations the reaction is starved in  $\text{OH}^\cdot$ , while at high  $\text{Fe}^{3+}$  concentrations the  $\text{OH}^\cdot$  concentration is reduced because of the scavenging effect by  $\text{Fe}^{2+}$ , therefore giving an optimum range between  $1.5 \times 10^{-4}$  and  $6.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ .

#### 4.5. Effect of the $\text{H}_2\text{O}_2$ concentration

Fig. 3 shows the dependence of the decolorization rate of the examined dyes on the  $\text{H}_2\text{O}_2$  at constant dye initial concentration, pH and  $\text{Fe}^{3+}$  concentration was examined. Experiments were conducted at different  $\text{H}_2\text{O}_2$  concentrations with  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  dyes solutions and  $3 \times 10^{-4}$  mol  $\text{dm}^{-3}$   $\text{Fe}^{3+}$  solution. In all experiments, the decolorization of the dye increased as  $\text{H}_2\text{O}_2$  was added. The  $\text{H}_2\text{O}_2$  concentration was varied from 0.01 to 0.15 mol  $\text{dm}^{-3}$ . The  $\text{H}_2\text{O}_2$  concentration of 0.04 mol  $\text{dm}^{-3}$  was affecting the decolorization by about 81% of (CV) dye in 40 min; 94% of (MG) dye in 40 min; 98% of (RB) dye in 40 min and 100% of (MB) dye in 20 min at a temperature of 298 K. The fractional conversion after 1 h remains almost same for  $\text{H}_2\text{O}_2$  concentration of 0.04 to 0.09 mol  $\text{dm}^{-3}$ . But the decolorization rate of all examined dyes decreased at high  $\text{H}_2\text{O}_2$  concentrations ( $\geq 0.1$  mol  $\text{dm}^{-3}$ ). Therefore, there is an optimum  $\text{H}_2\text{O}_2$  concentration that is effective for decolorization of the dye.

The occurrence of an optimum  $\text{H}_2\text{O}_2$  concentration for the decolorization of the examined dyes could be explained as follows. At low  $\text{H}_2\text{O}_2$  concentrations and as the  $\text{H}_2\text{O}_2$  concentra-

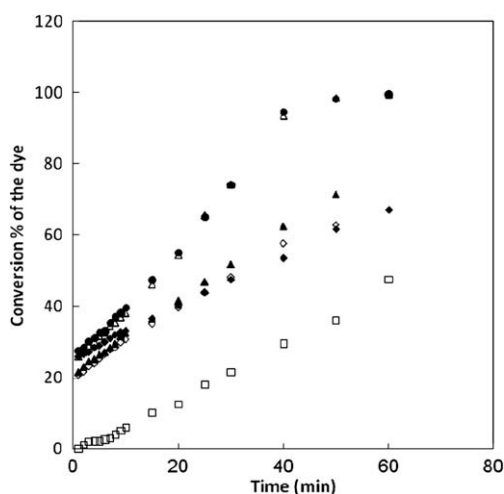


**Figure 3** Effect of the initial  $\text{H}_2\text{O}_2$  concentration on the rate of dye decolorization at pH = 3.5 and 25 °C; [dye] =  $1.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ,  $[\text{Fe}^{3+}] = 6.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ; (■) MB, (○) RB, (◆) MG and (▲) CV.

tion is decreased, the rate rapidly decreases. This occurs because the concentration of  $\text{Fe}^{3+}$  ions produced through reaction (3) and (4) decrease rapidly with decreasing  $\text{H}_2\text{O}_2$  concentration. As a result, the production of hydroxyl radicals through Eq. (3) is drastically reduced. At high  $\text{H}_2\text{O}_2$  concentrations ( $\geq 0.1 \text{ mol dm}^{-3}$ ), the rate tends to decreasing with increasing  $\text{H}_2\text{O}_2$  concentration. This is most probably due to the scavenging of the hydroxyl radicals by the  $\text{H}_2\text{O}_2$  through Eq. (7) (Kitis et al., 1999; Solozhenko et al., 1995). It was also observed from the experiments that at high  $\text{H}_2\text{O}_2$  concentrations ( $\geq 0.1 \text{ mol dm}^{-3}$ ),  $\text{H}_2\text{O}_2$  decomposes into  $\text{O}_2$  and  $\text{H}_2\text{O}$ , and this results in a rapid increase in solution temperature, decreasing in effect the oxidative power of the Fenton-like reagent because of large decrease in the concentration of  $\text{H}_2\text{O}_2$  (Centi et al., 2000).

#### 4.6. 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 and potassium nitrate on the rate and the extent of the oxidative decolorization 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  $\text{Fe}^{3+}$ . Fig. 4 shows the effects of these salts on the rate of decolorization, and it was observed that the presence of halide salts at the same concentration level substantially decreased the rate and the extent of decolorization, whereas for nitrate salt, there is an increase in the extent of dye decolorization. Halide salts reduced the rate of conversion of the dye due to the interaction of the electronegative chloride anion with the hydroxyl radical that inhibited the rate of the decolorization reaction (Ming-Chun et al., 2005). While in the presence of nitrate salts, it is not clear why the rates of decolorization were increased; it might be due to the availability of soluble  $\text{Fe}^{3+}$  ions (From ferric nitrate) concentration for catalyzing was increased.



**Figure 4** Effect of added electrolytes on the conversion of  $1.5 \times 10^{-5} \text{ mol dm}^{-3}$  Malachite green in water with  $0.02 \text{ mol dm}^{-3}$   $\text{H}_2\text{O}_2$  and  $3.0 \times 10^{-4} \text{ mol dm}^{-3}$   $\text{Fe}^{3+}$ : (▲) 0.5% NaCl, (◇) 0.5% KCl, (◆) 1% NaCl, (□) 1% KCl, (●) 0.5%  $\text{KNO}_3$ , and (△) 1%  $\text{KNO}_3$ .

#### 4.7. Effect of temperature on the decolorization of the examined dyes

Experiments were conducted at four different temperatures between 298 and 328 K to investigate the effect of temperature on the decolorization kinetics of aqueous dye solutions. The results are shown in Table 1. An increase in the extent of decolorization of the dye was observed when the reaction temperature was raised. There was practically no difference in the rate and extent of decolorization of the reaction in the temperature between 323 and 328 K. At higher reaction temperature more than 328 K, the rates of decolorization were decreased. This might be due to 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.

The activation parameters were calculated for all dyes at 303 K and are shown in Table 1. The values of free energy of activation  $\Delta G^\ddagger$  indicate the independence of  $\Delta G^\ddagger$  on the structural of the dyes used.

#### 4.8. Determination of the order of decolorization

The kinetic analysis was done for those experiments in which the dye concentration, ferric ion concentration and hydrogen peroxide concentration were varied in the optimum ranges.

The initial rate of decolorization of the dyes is given by:

$$-R_{A_0} = k[A_0]^m[B_0]^n[C_0]^p \quad (10)$$

where  $[A_0]$ ,  $[B_0]$  and  $[C_0]$  are respectively, the initial concentrations of dye,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$ ,  $m$ ,  $n$  and  $p$  the respective orders, and  $k$  the rate constant. Keeping  $[B_0]$  and  $[C_0]$  constant, the initial dye concentration was varied and the initial rates were determined from the concentration versus time profile. A plot of  $\log(-R_{A_0})$  against  $\log[A_0]$  was found to be linear, whence the slope of the line yielded the order ( $m$ ) with respect to the dye. Similarly, the effects of varying  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  concentrations on the initial rates of decolorization were assessed whence  $n$  and  $p$  were evaluated. The results showed that all values of  $m$ ,  $n$  and  $p$  are around 1 for decolorization of the studied dyes, which indicate the first-order with respect to each reactant.

#### 4.9. Mineralization of all studied dyes

It is known that reaction intermediates can form during the oxidation of studied dyes and some of them could be long-lived and even more toxic than the parent compounds. Therefore, it is necessary to realize the mineralization of these dyes simultaneously although we focus our study on the decolorization. To quantitatively characterize the mineralization of the studied dyes in the solution, the TOC removal ratio is used in the study, which is defined as follows:

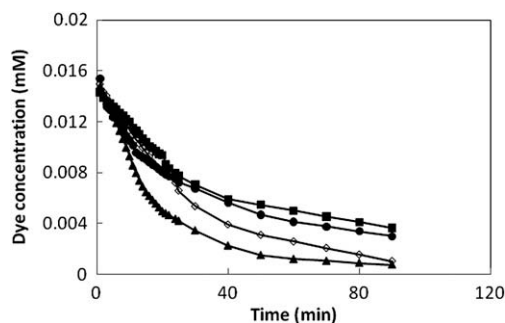
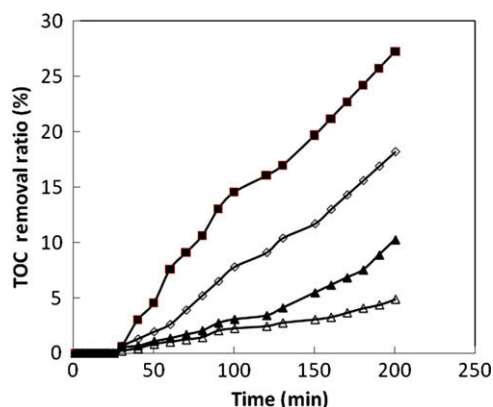
$$\text{TOC removal ratio} = (1 - \text{TOC}_t/\text{TOC}_0) \times 100\% \quad (11)$$

where  $\text{TOC}_t$  and  $\text{TOC}_0$  are the TOC values at reaction time  $t$  and 0, respectively.

Figs. 5 and 6 present the concentration degradation and TOC removal ratio of the studied dyes as a function of time at pH 3.5. As we can see in Fig. 5, dye decolorization signifi-

**Table 1** Effect of temperature on the rate constants of decolorization of the examined dyes and the calculated activation parameters.

Dye	$10^4 k$ (S <sup>-1</sup> )				$\Delta E^\ddagger$ KJ mol <sup>-1</sup>	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta S^\ddagger$ e.u
	298 K	303 K	313 K	323 K				
MG	4.01	6.14	20.1	44.1	79.52 ± 1.2	76.99 ± 1.1	93.425 ± 1.0	-54.22 ± 2.0
RB	4.83	8.83	26.5	56.81	79.716 ± 1.3	77.187 ± 1.2	93.425 ± 1.0	-53.59 ± 1.0
MB	5.6	11.5	30.0	70.0	79.75 ± 1.3	77.22 ± 1.2	93.425 ± 1.0	-53.45 ± 1.1
CV	2.50	5.10	15.0	30.1	79.73 ± 1.1	77.20 ± 1.1	93.425 ± 1.0	-53.53 ± 1.0

**Figure 5** The change of concentration of the dyes as a function of reaction time: (■) CV, (●) Rb, (◇) MG and (▲) MB.**Figure 6** The change of TOC removal ratio of the dyes as a function time: (◆) CV, (◇) Rb, (▲) MG and (△) MB.

cantly increased with increasing reaction time for all dyes. After 30 min of reaction time, dye decolorization was 53%, 55%, 64% and 77% for CV, RB, MG and MB respectively. However, Fig. 6 shows almost no TOC removal efficiency for the first 30 min. It demonstrates that intermediates form by oxidation of dyes during the first 30 min reaction. After then, TOC removal efficiency increases slowly even though a complete dye decolorization is achieved. Meanwhile, at 200 min reaction time, all of the TOC removal ratios reach to about 27%. Compared with the results of decolorization and TOC removal ratio, it can be seen that the decolorization of the studied dyes undergoes a fast reaction rate than the mineralization under the same conditions.

## 5. Conclusions

The kinetics of oxidative decolorization of four commercial dyes, namely, Malachite green (MG), Rhodamine B (RB), Methylene blue (MB) and Crystal violet (CV) were studied

using a Fenton-like reagent. The optimum concentrations of Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> were, respectively, 6.0 × 10<sup>-4</sup> mol dm<sup>-3</sup> and 0.04 mol dm<sup>-3</sup> for the decolorization of a 1.5 × 10<sup>-5</sup> mol dm<sup>-3</sup> dye solution at 298 K. The rate of decolorization of the dye was found to be very rapid in the initial period of reaction. The solution pH strongly influences the decolorization reaction rate. The optimum pH range is between 3 and 4. Dissolved electrolytes such as halides suppressed the rate of decolorization, possibly due to the interaction of the anions with the hydroxyl radical. The rate of decolorization was found to be practically dependent on temperature in the range of 298–323 K. The initial rate of decolorization could be expressed in terms of a power-law equation as follows:  $-R_{A_0} = k[A_0]^m[B_0]^n[C_0]^p$ , where,  $m$ ,  $n$  and  $p$  are the obtained orders with respect to dye, Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> respectively. It was also found that the decolorization of the dyes undergoes a fast reaction than the mineralization.

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