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A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater

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Abstract

Decolourisation of wastewater using Fenton (Fe^{2+}/H_2O_2) and Fenton-like (Fe^{3+}/H_2O_2) reactions was investigated and compared to that of a typical azo dye, C.I. Acid Black 1, under neutral conditions. The effects of different system variables namely initial concentration of Fe^{2+} or Fe^{3+}, initial concentration of H_2O_2, initial pH of solution and reaction temperature were studied. Dye degradation in Fenton oxidation was faster initially than Fenton-like oxidation but the extent of degradation achieved for the two systems was similar after 100 min. The kinetics of Fenton oxidation is complex and can be described by a combined pseudo-first-order kinetic model while the Fenton-like reaction follows comparatively simpler, pseudo-first-order kinetics. The apparent reaction orders regarding Fe and H_2O_2 concentrations for the two systems were similar, with values of 3 and 0.7, respectively. The degradation rate was strongly dependent on the initial concentration of Fe^{2+} or Fe^{3+}, the initial concentration of H_2O_2 and initial pH. Maximum degradation rate was achieved at optimum concentrations of Fe and H_2O_2 as well as solution pH. The reaction temperature (15–45 °C) had little effect on overall dye oxidation rate in the Fenton-like reaction.

Keywords: Wet peroxide oxidation; Azo dye; Fenton reagent; Kinetics

1. Introduction

The dyes used in the textile dyeing and printing industries not only can impart colour to water sources but also can cause environmental damage to living organisms by stopping the reoxygenation capacity of water and also blocking sunlight, thereby disturbing the natural growth activity of aquatic life. Azo dyes, which contain at least one azo group (–N=N–), which is attached to at least one aromatic moiety, are commonly used in textile coloration. These dyes are resistant to biodegradation under aerobic conditions. Discharge of azo dyes can cause aesthetic problems and their breakdown products are toxic to aquatic life [1]. Many different approaches have been proposed to remove dyes from aqueous solution such as physical adsorption, electrochemical oxidation, chemical oxidation, chemical coagulation/precipitation, and biological anaerobic/aerobic decomposition [2–4].

Recently, advanced oxidation processes (AOPs) have been proposed as offering promise for wastewater treatment because AOPs are able to oxidise a wide range of compounds that are otherwise difficult to degrade. Among AOPs, oxidation using Fenton's reagent is an attractive treatment for the effective decolourisation and degradation of dyes because of its low cost, the lack of toxicity of the reagents (i.e., Fe^{2+} and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology [5].

The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidising ability to degrade organic pollutants as shown in Eqs. (1)–(4) [6].

$$H_2O_2 + Fe^{2+} \rightarrow OH^\bullet + OH^- + Fe^{3+} \tag{1}$$

$$OH^\bullet + RH \rightarrow R^\bullet + H_2O \tag{2}$$

$$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{3}$$

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$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^- \qquad (4)$$

During reaction, ferric ions are formed which can be reacted to produce ferrous ions. The reaction of hydrogen peroxide with ferric ions is referred to as a Fenton-like reaction, Eqs. (5)–(8).

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\cdots OOH^{2+} + H^+ \qquad (5)$$

$$Fe\cdots OOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \qquad (6)$$

$$H_2O_2 + Fe^{2+} \rightarrow OH\bullet + OH^- + Fe^{3+} \qquad (7)$$

$$OH\bullet + RH \rightarrow R\bullet + H_2O \qquad (8)$$

Many investigations have been conducted into the decolourisation of dyes using Fenton oxidation [1,7–12]. The main drawback of this technique is represented by the cost of the reactants, H_2O_2 and Fe^{2+}. For this reason, various methods have been introduced to use the lower cost Fe^{3+} salts rather than Fe^{2+}salts, which have resulted in photo-Fenton and electro-Fenton techniques [13]. While Fenton-like oxidation should also be effective, little work has been reported on the Fenton-like oxidation of dyes. Several studies have shown that the rate of decomposition of H_2O_2 and the rate of oxidation of organic solutes are much slower using Fe^{3+}/H_2O_2 than Fe^{2+}/H_2O_2, and are optimal at pH 3 [14]. However, as the solution pH in many cases is neutral or alkaline, the necessity to acidify the reaction medium limits the applicability of the Fenton process in environmental technology. Moreover, despite numerous studies of the Fe^{3+}/H_2O_2 system, the chemistry and kinetics of the oxidation of organic compounds by Fe^{3+}/H_2O_2 have not been well elucidated.

In this paper, we report an investigation of the Fenton and Fenton-like oxidations of a typical azo dye under neutral conditions. The dye's degradation rate and efficiency of the two reaction systems were compared and the kinetics of the two reactions was studied. The reaction parameters affecting the decolourisation such as initial concentration of Fe^{2+}, Fe^{3+} and H_2O_2, initial pH of dye solution and reaction temperature were also investigated.

2. Experimental

A commercial azo dye, C.I Acid Black 1, was used in this study (Fig. 1). H_2O_2 (30%) was obtained from Chem-Supply, Australia; ferrous sulfate ($FeSO_4\cdot 7H_2O$) and ferric sulfate ($Fe_2(SO_4)_3$) were obtained from BDH.

All experiments were carried out in a 250 ml batch reactor. Typically, the reactor was charged with 200 ml of dye solution at a temperature of 15–45 °C using 100 rpm stirring. Then, certain amounts of H_2O_2 (30%) and 0.1 M $FeSO_4$ or $Fe_2(SO_4)_3$ solution were added to the dye solution. For most of the experiments, the initial pH was set at 6.3. For the experimental runs at different pH, the values were adjusted using sulphuric acid or sodium hydroxide solutions and measured using a pH meter (PHM 250 Ion analyser). Aliquots were withdrawn from the reactor at selected intervals for spectrophotometric analysis. The concentration of dye in the reaction mixture at different times was obtained by measuring the λ_{max} (618 nm) of the dye and computing the concentration from a calibration curve. A Spectronic 20 Genesis spectrophotometer (USA) was employed for absorbance measurements using quartz cells of 1 cm path length.

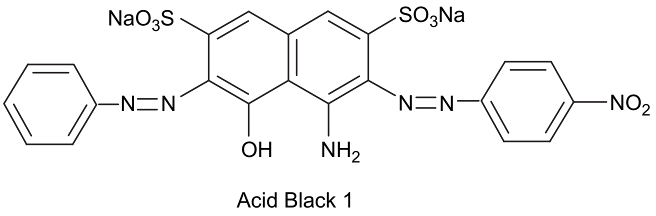

Fig. 1. Chemical structure of Acid Black 1.

3. Results and discussion

3.1. Comparison of Fenton and Fenton-like oxidations

Fig. 2 shows a comparison of the variation of dye decolourisation with Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 at 30 °C from which it is apparent that both Fenton or Fenton-like oxidations were effective in dye decolourisation. The extent of dye degradation was 95% after 100 min. However, decolourisation exhibited different rates for the two systems. The degradation rate in Fenton oxidation was much faster than that of the Fenton-like reaction in the initial stages and the degree of degradation was similar for both systems after 80 min. During the Fenton or Fenton-like reaction, dye decomposition is caused by both hydroxyl and hydroperoxyl radicals. It is known that the hydroperoxyl radical has lower oxidation capability than OH• [11]. Several investigations into the Fenton oxidation of organic compounds have shown that the initial rate of mineralisation is faster with Fenton than with Fenton-like reagents, due

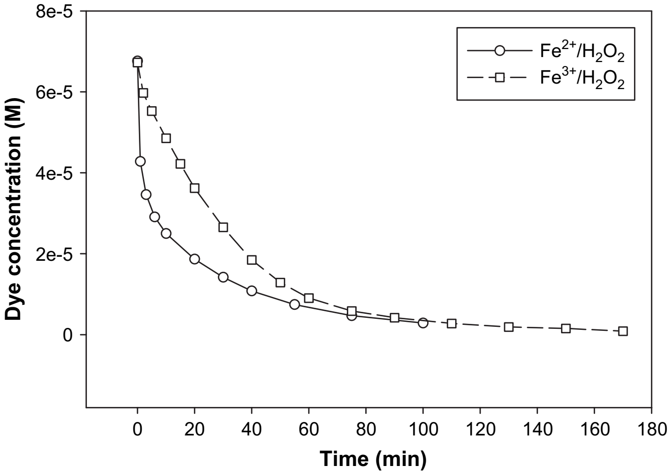

Fig. 2. Comparison of Fenton and Fenton-like reactions for decolouration. Reaction conditions: $[Fe^{2+}]_0 = 3.4 \times 10^{-5}$ M, $[Fe^{3+}]_0 = 3.4 \times 10^{-5}$ M, $[H_2O_2]_0 = 5.4 \times 10^{-4}$ M, pH = 6.3, and $T = 30$ °C.

to the immediate formation of hydroxyl radicals in the case of Fenton reagent [14,15].

3.2. Kinetics of Fenton and Fenton-like oxidations

The Fenton oxidation of the dye can be represented by the following *n*th-order reaction kinetics

$$\frac{dC}{dt} = -kC^n \tag{9}$$

where C represents the dye concentration, n the order of the reaction, k the reaction rate coefficient and t the time. For a first-order reaction, the above equation after integration becomes

$$C = C_0 \exp(-kt) \tag{10}$$

in which C_0 is the initial dye concentration. For a second-order reaction, the integrated equation becomes

$$C = \frac{C_0}{1 + kC_0 t}. \tag{11}$$

In addition, a combined first-order reaction can be described as follows

$$C = C_{10} \exp(-k_1 t) + C_{20} \exp(-k_2 t) \tag{12}$$

where, C_{10} and C_{20} are the initial dye concentrations of two independent first-order reactions and k_1 and k_2 are the reaction rate constants, respectively.

Fig. 3 shows a comparison of three kinetic models for the experimental results and the parameters obtained from the curve fitting are presented in Table 1. The first-order and second-order kinetics do not fit the data very well for the whole Fenton reaction due to the lower regression coefficients (<0.96). The combined first-order rate model fits the results best as evidenced by the high regression coefficient (>0.99). This suggests that two parallel reactions should be responsible for dye degradation. For the Fenton-like reaction, first-order kinetics produces a good fit to the experimental data while the second-order rate shows deviation from the data. From Table 1, it is also seen that the correlation coefficients obtained for the three models are different. The second-order kinetics shows higher correlation than the first-order kinetics in the case of the Fenton reaction, while in the Fenton-like reaction, the correlation coefficient of the first-order kinetics is much better than second-order kinetics. The Fenton reaction has a higher reaction rate than the Fenton-like reaction. Several investigators have found that the Fenton reaction for dye degradation follows pseudo-first-order kinetics [10,15,16], which is different from the results obtained in this work, presumably, because such previous investigations only considered the initial rate of degradation rather than the whole process.

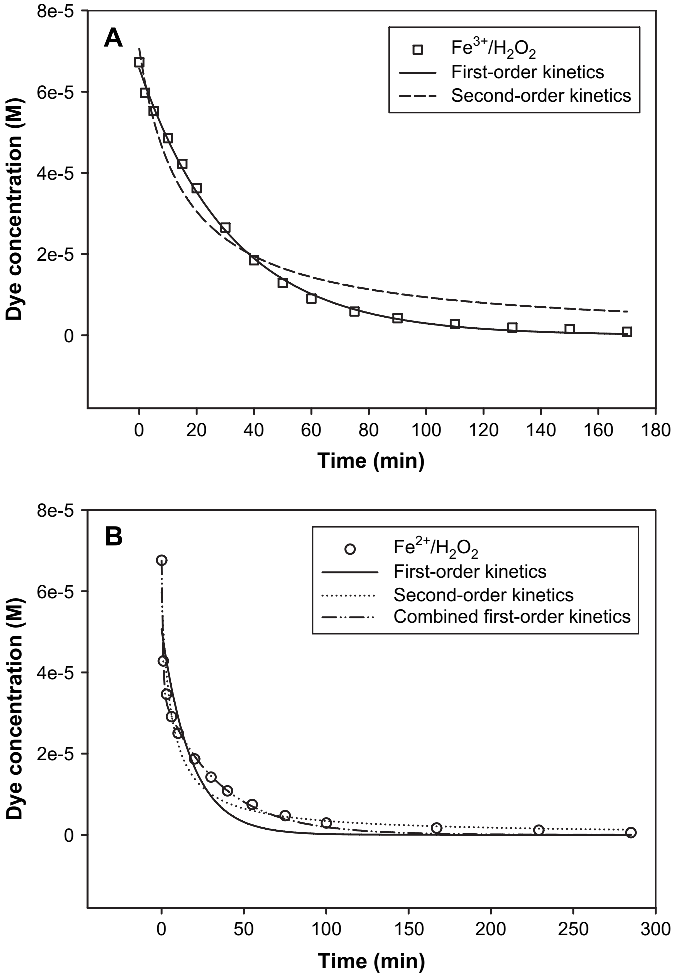

Fig. 3. Comparison of kinetic simulation of Fenton and Fenton-like reactions for decolouration.

During the Fenton reaction, ferrous ions can quickly react with H_2O_2 to produce hydroxyl radicals and ferric ions ($k = 70\ M^{-1}\ s^{-1}$) [6], which will then be reduced by the dye to ferrous ions again. Meanwhile, ferric ions can also react with H_2O_2, producing hydroperoxide radicals which cause a second decomposition process for the dye. Malik and Saha [11] investigated the oxidation of direct dyes via the Fenton reaction and found that the entire degradation reaction could be divided into a two-stage reaction. In the first stage, referred

Table 1
Kinetic parameters for Fenton and Fenton-like oxidations of Acid Black 1

Reaction	First-order		Second-order		Combined first-order		
	k (min^{-1})	R^2	k (L/mol min)	R^2	k_1 (min^{-1})	k_2 (min^{-1})	R^2
Fe^{2+}/H_2O_2/dye	0.0556	0.888	2.76×10^4	0.954	1.2466	0.0292	0.998
Fe^{3+}/H_2O_2/dye	0.0311	0.998	9.29×10^2	0.955			

to Fe^{2+}/H_2O_2 stage, it was considered that the dyes decomposed quickly; the second stage of reaction was referred to as the Fe^{3+}/H_2O_2 stage.

In Fenton-like reaction, ferric ions react with H_2O_2 to produce ferrous ions at very slow rate ($k = 0.001-0.01\ M^{-1}\ s^{-1}$) [6]; few ferrous ions can be formed and thus induce the Fenton reaction. Therefore, only one process with Fe^{3+}/H_2O_2 reaction will dominate.

3.3. Effect of Fe^{2+} and Fe^{3+} concentrations

Fig. 4 shows the effect of Fe ion concentration on dye degradation in both Fenton and Fenton-like reactions. The extent of degradation of the dye increased with increasing Fe ion concentration. In the case of Fenton oxidation, the extent of degradation was very small when the Fe ion concentration was $<1 \times 10^{-5}$ M. When the Fe ion concentration was $>1.0 \times 10^{-4}$ M, the extent of dye degradation was 90% after 10 min. For Fenton-like oxidation, if the Fe ion concentration was $<1 \times 10^{-5}$ M, dye degradation was only 5% after 250 min. By contrast, the extent of degradation was 80% after 10 min at a Fe ion concentration of 7.3×10^{-5} M.

Based on the kinetic model of Fenton and Fenton-like reactions, the reaction order respective to Fe concentration was calculated. Fig. 5 shows the relationship between reaction rate and Fe concentration. For the Fenton reaction, the orders for the first and second reactions were 3.0 and 4.8, respectively. For the Fenton-like reaction, the reaction order for Fe was 3.3, similar to the value of the first stage in Fenton oxidation.

3.4. Effect of H_2O_2 concentration

Fig. 6 shows the relationship between degradation of the dye as a function of time at different initial H_2O_2 concentrations. One can see that flocculation of the dye by Fe^{3+} was not significant. Without H_2O_2, dye decolourisation was only about 15% after 3 h. The results also indicate that the degradation of the dye increased with increasing H_2O_2 concentration. When the H_2O_2 concentration increased to 1×10^{-3} M, 90% decolourisation could be achieved after 1 h in the Fenton reaction; H_2O_2 concentrations $> 1 \times 10^{-3}$ M would not induce significant change in decolourisation. In Fenton-like reaction, 95% decolourisation could be achieved after 1 h when the H_2O_2 concentration was $>1.5 \times 10^{-3}$ M. Several investigations have

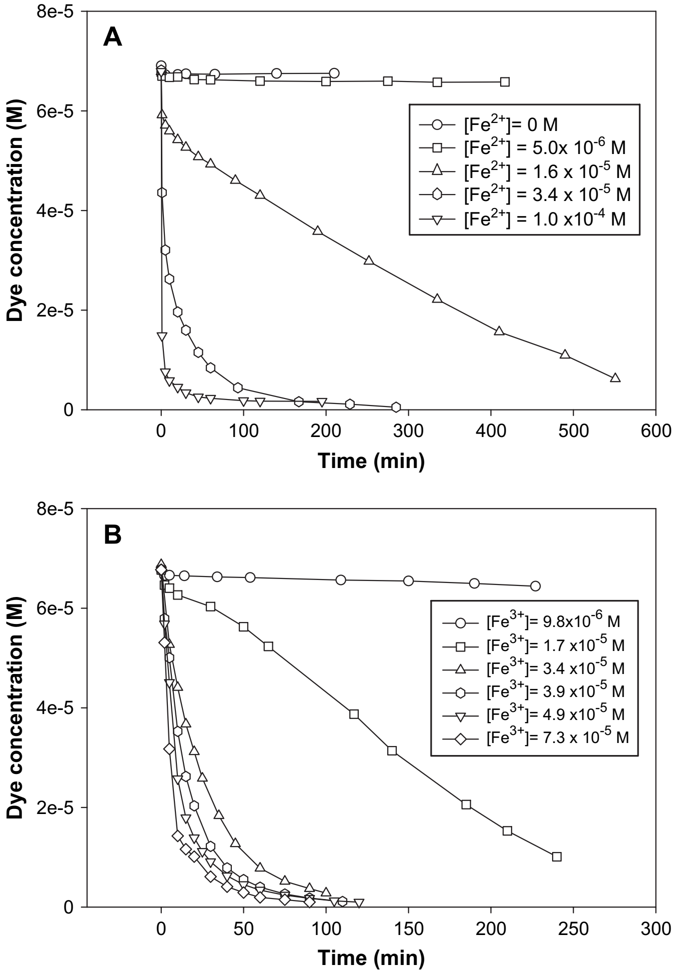

Fig. 4. Effect of initial Fe concentration on colour degradation in Fenton and Fenton-like reactions. Reaction conditions: $[H_2O_2]_0 = 5.4 \times 10^{-4}$ M, pH = 6.3, and $T = 30$ °C; (A) Fenton oxidation (B) Fenton-like oxidation.

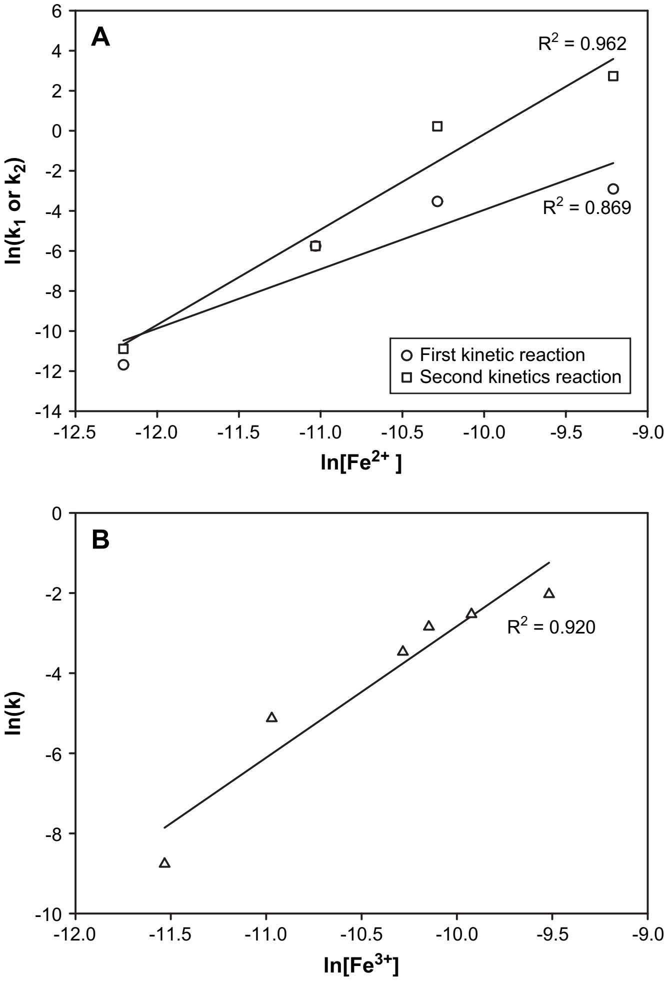

Fig. 5. Reaction rate versus Fe concentration in Fenton and Fenton-like reactions. Reaction conditions: $[H_2O_2]_0 = 5.4 \times 10^{-4}$ M, pH = 6.3, $T = 30$ °C. (A) Fenton oxidation (B) Fenton-like oxidation.

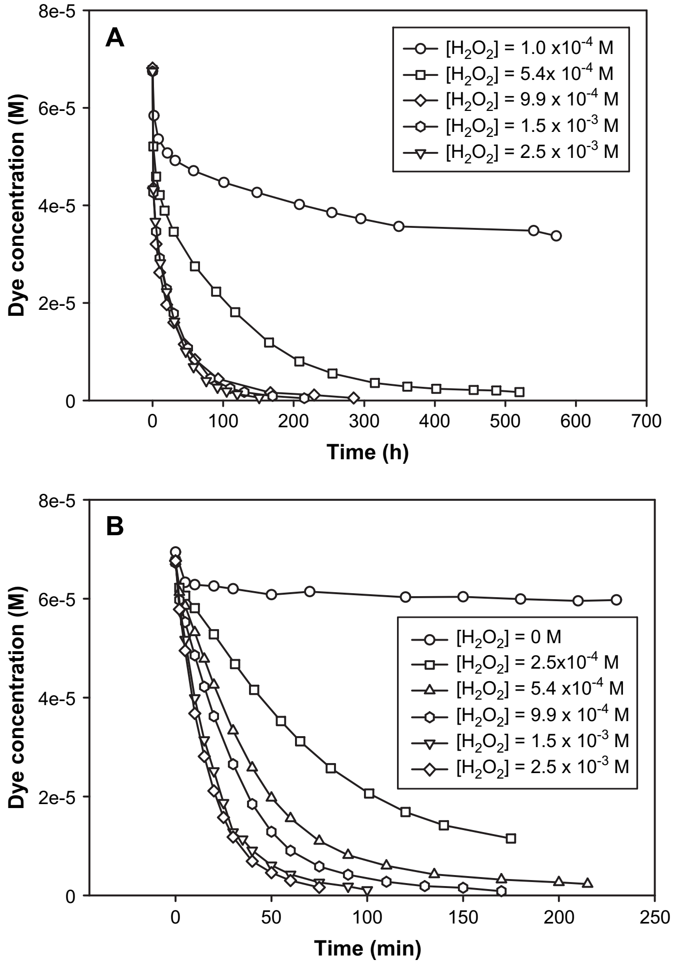

Fig. 6. Effect of initial H_2O_2 concentration on colour degradation in Fenton and Fenton-like reactions. Reaction conditions: $[Fe^{2+}]_0 = 3.4 \times 10^{-5}$ M, $[Fe^{3+}]_0 = 3.4 \times 10^{-5}$ M, pH = 6.3, and $T = 30$ °C; (A) Fenton oxidation (B) Fenton-like oxidation.

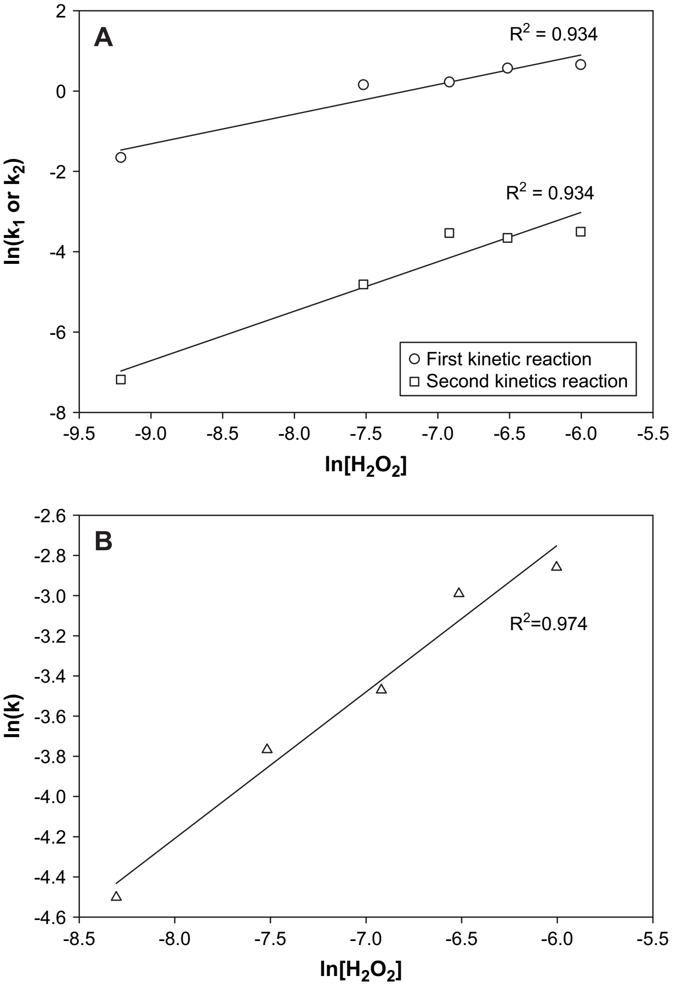

Fig. 7. Reaction rate versus H_2O_2 concentration in Fenton and Fenton-like reactions. Reaction conditions: $[Fe^{2+}]_0 = 3.4 \times 10^{-5}$ M, $[Fe^{3+}]_0 = 3.4 \times 10^{-5}$ M, pH = 6.3, and $T = 30$ °C; (A) Fenton oxidation (B) Fenton-like oxidation.

reported an optimal peroxide concentration in the Fenton oxidation of dyes [8,10]; unreacted H_2O_2 will act as a scavenger of $^{\bullet}OH$ and produces a less potent perhydroxyl radical, resulting in less dye degradation.

Similarly, the order of the Fenton and Fenton-like reactions were also obtained (Fig. 7). The reaction orders respective to H_2O_2 concentration in the Fenton reaction were 0.74 and 1.23 for the first and second-stage reactions, respectively, while for the Fenton-like reaction, the order for H_2O_2 concentration was 0.73, which was also similar to the value in the first stage of Fenton oxidation.

3.5. Effect of pH

Fig. 8 shows that lower pH resulted in higher rates of dye degradation. For the Fenton reaction, 95% decolourisation was achieved in 20 min at a pH < 4.5 and when the pH was further decreased, the degradation rate was similar. However, for the Fenton-like reaction, 70% decolourisation was obtained after 20 min at pH < 4.8. When the pH was lowered to 2.4, degradation was increased and 98% colour degradation could be achieved after 10 min. Hence, the optimum initial pH for either Fenton or Fenton-like oxidation should be <4.5. Several investigations have indicated that the optimum pH for decolourisation is 3 and that the extent of degradation decreases with increasing pH for pH > 3 [7,10,11].

It is considered that more $Fe(OH)^+$ is formed at low pH (2–4) and the activity of $Fe(OH)^+$ is higher than Fe^{2+} in Fenton oxidation [11]. In contrast, ferrous ions are unstable at a pH > 4.0 and they easily form ferric ions, which have a tendency to produce ferric hydroxo complexes. These complexes would form further $[Fe(OH)_4]^-$ when the pH value was >9.0. Besides, hydrogen peroxide is also unstable in basic solution and may decompose to give oxygen and water and lose its oxidation ability. Thus, hydrogen peroxide and ferrous ions have difficulty in establishing an effective redox system and their decolourisation is also less effective [7].

3.6. Effect of temperature

Fig. 9 shows the extent of degradation of the dye as a function of time at different temperatures. For the Fenton reaction,

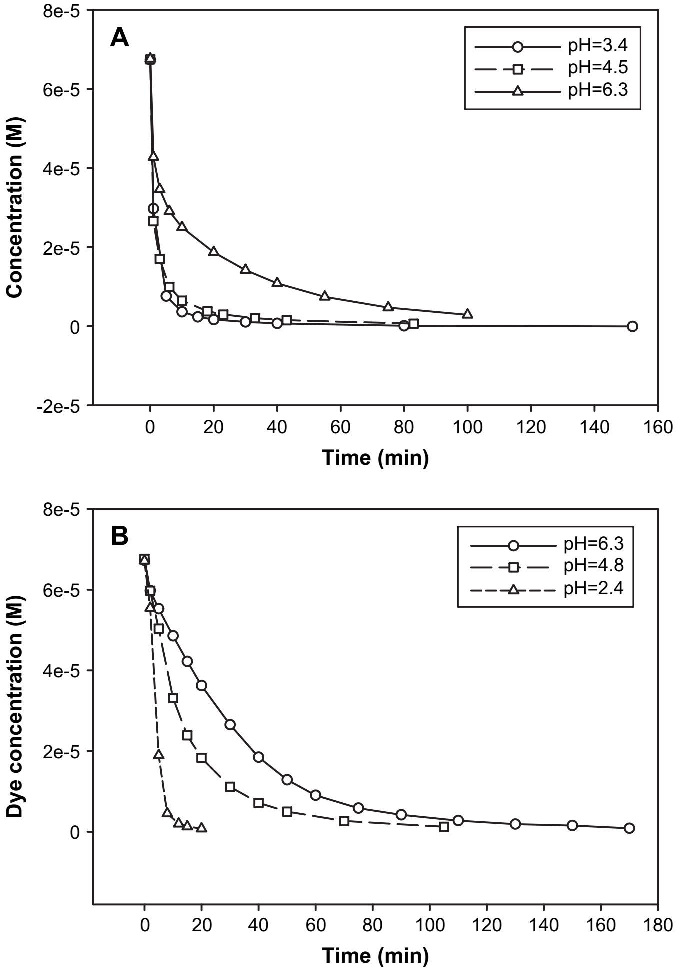

Fig. 8. Effect of initial pH of solution on colour degradation in Fenton and Fenton-like reactions. Reaction conditions: $[Fe^{2+}]_0 = 3.4 \times 10^{-5}$ M, $[Fe^{3+}]_0 = 3.4 \times 10^{-5}$ M, $[H_2O_2]_0 = 5.4 \times 10^{-4}$ M, and $T = 30$ °C; (A) Fenton oxidation (B) Fenton-like oxidation.

the rate of dye degradation was lower at low temperature and the extent of degradation was higher at 20–30 °C before 100 min. Dye degradation rate decreased when the temperature was >30 °C due to decomposition of H_2O_2 at higher temperature. Table 2 shows the dye degradation rate constants for the two oxidation systems from which it is clear that the rate constant in the first reaction was higher than that in the second reaction for Fenton oxidation. The reaction rate constants at different temperatures were similar except at 44 °C. In this case, the rate constants for the first and second reactions were similar. At 15.8 °C the rate constant for the second reaction was much lower compared with the values at other temperatures. These results suggest that the first reaction plays a dominant role for overall dye degradation at low temperatures and that the role of the second reaction in dye degradation will increase with increasing temperature.

For the Fenton-like reaction, the dye degradation rates show some variation with temperature but no clear trend can be obtained. From the results in Table 2, one can see that the reaction rate constants are very similar at different temperatures.

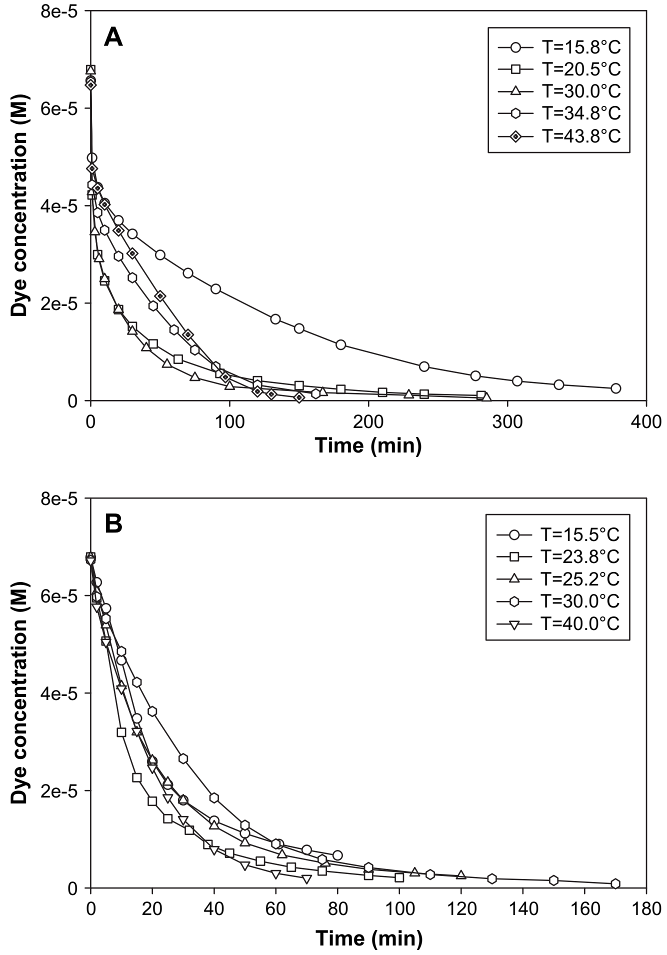

Fig. 9. Effect of reaction temperature on colour degradation in Fenton and Fenton-like reactions. Reaction conditions: $[Fe^{2+}]_0 = 3.4 \times 10^{-5}$ M, $[Fe^{3+}]_0 = 3.4 \times 10^{-5}$ M, $[H_2O_2]_0 = 5.4 \times 10^{-4}$ M, and pH = 6.3; (A) Fenton oxidation (B) Fenton-like oxidation.

4. Conclusions

Fenton and Fenton-like oxidations effectively decolourise C.I. Acid Black 1 in aqueous solution under neutral conditions. The degradation of the dye in the initial stages of the Fenton oxidation was faster than in the Fenton-like oxidation, although the extent of dye degradation in the two processes was very similar after 100 min. Fenton oxidation can be

Table 2
Kinetic parameters for Fenton and Fenton-like reaction at different temperatures

Temperature (°C)	Fe^{2+}/H_2O_2/Dye		Temperature (°C)	Fe^{3+}/H_2O_2/Dye
	k_1 (min^{-1})	k_2 (min^{-1})		k (min^{-1})
15.8	1.25	0.00752	15.5	0.0413
20.5	1.09	0.0200	23.8	0.0623
30.0	1.25	0.0292	25.5	0.0475
34.8	2.30	0.0187	30.0	0.0311
43.8	0.0220	0.0219	40.0	0.0503

Reactions conditions: $[Fe^{2+}]_0 = 3.4 \times 10^{-5}$ M, $[Fe^{3+}]_0 = 3.4 \times 10^{-5}$ M, $[H_2O_2]_0 = 5.4 \times 10^{-4}$ M, and pH = 6.3.

described by combined first-order kinetics while Fenton-like oxidation follows simpler first-order kinetics. The reaction orders in terms of Fe and H_2O_2 concentrations for both Fenton and Fenton-like oxidations were similar at values of 3 and 0.75, respectively. For the two oxidation systems, dye degradation depends on initial Fe and H_2O_2 concentrations and pH, but temperature has little influence on overall dye degradation in the range 15–45 °C.

References

[1] Meric S, Kaptan D, Tunay C. Removal of color and COD from a mixture of four reactive azo dyes using Fenton oxidation process. Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering 2003;38:2241–50.

[2] Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology 2001;77:247–55.

[3] Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewaters: a review. Environment International 2004;30:953–71.

[4] Hao OJ, Kim H, Chiang PC. Decolorization of wastewater. Critical Reviews in Environmental Science and Technology 2000;30:449–505.

[5] Aplin R, Waite TD. Comparison of three advanced oxidation processes for degradation of textile dyes. Water Science and Technology 2000; 42:345–54.

[6] Neyens E, Baeyens J. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials 2003; 98:33–50.

[7] Kuo WG. Decolorizing dye waste-water with Fenton reagent. Water Research 1992;26:881–6.

[8] Lin SH, Peng CF. Treatment of textile waste-water by Fenton's reagent. Journal of Environmental Science and Health Part A-Environmental Science and Engineering & Toxic and Hazardous Substance Control 1995;30:89–98.

[9] Solozhenko EG, Soboleva NM, Goncharuk VV. Decolourization of azodye solutions by Fenton's oxidation. Water Research 1995;29:2206–10.

[10] Dutta K, Bhattacharjee S, Chaudhuri B, Mukhopadhyay S. Chemical oxidation of CI Reactive Red 2 using Fenton-like reactions. Journal of Environmental Monitoring 2002;4:754–60.

[11] Malik PK, Saha SK. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. Separation and Purification Technology 2003;31:241–50.

[12] Kim TH, Park C, Yang JM, Kim S. Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. Journal of Hazardous Materials 2004;112:95–103.

[13] Minero C, Lucchiari M, Vione D, Maurino V. Fe(III)-enhanced sonochemical degradation of methylene blue in aqueous solution. Environmental Science and Technology 2005;39:8936–42.

[14] Gallard H, De Laat J. Kinetic modelling of Fe(III)/H_2O_2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. Water Research 2000;34:3107–16.

[15] Ince NH, Tezcanli G. Treatability of textile dye-bath effluents by advanced oxidation: preparation for reuse. Water Science and Technology 1999;40:183–90.

[16] Swaminathan K, Sandhya S, Sophia AC, Pachhade K, Subrahmanyam YV. Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system. Chemosphere 2003;50: 619–25.