
DECOLOURISATION OF REACTIVE DYESTUFF USING FENTON'S REAGENT

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Abstract: The behaviour of Fenton's Reagent (FR) system in decolourising Reactive Black 5 (RB5) was investigated. It was observed that the system is capable to decolourise 0.2 mM RB5 within a reasonable time with most decolourisation occurred in the first minute. The performance of the process is greatly affected by the reagent dosage. The best dosages of peroxide and Fe²⁺ were 7 mM and 1 mM, respectively. The best H₂O₂:Fe²⁺:dye molar ratio was 35:5:1. The dye was also found to enhance the decomposition of the peroxide. This suggests the possibility of Fe³⁺/Fe²⁺ 'redox-recycled' as experienced in a Hamilton-like system favouring the use of FR process for the degradation of the dye.

Keyword: *Fenton's Reagent; Reactive Dyestuff; Dyeing Wastewater*

Abstrak: Kajian telah dijalankan untuk menyiasat kelakuan sistem Reagen Fenton (FR) untuk menyahwarna bahan pewarna Reactive Black 5 (RB5). Hasil kajian menunjukkan bahawa sistem ini mampu untuk menyahwarnakan 0.2 mM RB5 dalam tempoh yang agak singkat. Hampir kesemua warna dapat disingkirkan dalam masa 1 minit. Keberkesanan proses dipengaruhi oleh dos reagen yang digunakan. Dos peroksida dan Fe²⁺ yang terbaik adalah 7 mM dan 1 mM, masing-masing. Nisbah molar terbaik bagi H₂O₂:Fe²⁺:pewarna adalah 35:5:1. Pewarna juga didapati mempertingkatkan penguraian peroksida. Ini mencadangkan kemungkinan wujudnya 'kitaran-redoks' Fe³⁺/Fe²⁺ sebagaimana yang dialami di dalam sistem Hamilton. Ia juga memberi petunjuk tentang kelebihan penggunaan proses FR dalam menguraikan bahan pewarna RB5.

Katakunci: *Reagen Fenton; Pewarna Reaktif; Airsisa Pewarnaan Tekstil*

1.0 Introduction

Biological treatment systems have traditionally been very popular in treating wastewaters. They are cheaper than other treatment systems and are capable of treating a wide variety of pollutants. With the emergence of new technologies to fulfil the ever-increasing needs of the society, new synthetic chemicals have been developed and introduced into the waste stream. Unfortunately, these chemicals, which can be found in wastewater from industries such as textile, are not amenable to biological treatment due to their toxicity, stability, or refractory characteristics (Clarkson *et al.*, 1993; Dutta *et al.*, 2001). The chemicals are

released into the water bodies since they are not removed by the treatment process, thus could damage their ecosystem (Cooper, 1995; Kennedy *et al.*, 1999).

In order to deal with these types of wastewater, different treatment systems have been developed as alternatives. These include physico-chemical treatments such as coagulation-flocculation-sedimentation, adsorption, ion-exchange, membrane separation and air stripping. These processes have been proven effective in removing refractory pollutants from the wastewater stream (Koprivanac *et al.*, 1993; Gahr *et al.*, 1994; Vandevivere *et al.*, 1998; Bottino *et al.*, 2001). Nevertheless, instead of destroying the pollutants, they are actually transferring them from one phase to another, and thus require additional treatment, handling and disposal. Furthermore, some processes which utilise trapping media such as activated carbon and ion-exchange require the media to be regenerated or replaced once they are exhausted. These incur additional costs on the processes and make them attractive only for dilute wastewaters.

In recent years, a lot of research activities in water and wastewater treatment have been devoted to the application of a new class of chemical oxidation process termed as Advanced Oxidation Processes (AOPs). Although making use of different reacting systems (Table 1), the processes are all characterised by the same chemical feature, i.e. production and application of hydroxyl radicals (HO^\bullet), as the oxidising agent. The HO^\bullet has oxidation potential much higher than its nearest competitor, ozone and is also characterised by unselective attack of pollutants making it suitable for wastewater treatment application (Andreozzi *et al.*, 1999).

Table 1: List of typically reported Advanced Oxidation Processes

Type of System	Example
Ozone-based	O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$, O_3/OH^- , $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$, $\text{O}_3/\text{solid catalyst}$
H_2O_2 -based	$\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, $\text{H}_2\text{O}_2/\text{Fe}^{3+}$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$, $\text{H}_2\text{O}_2/\text{Fe}^{3+}/\text{UV}$
Photocatalyst	UV/TiO_2 , $\text{UV}/\text{TiO}_2/\text{H}_2\text{O}_2$

In this study, a specific focus has been given to one of the AOPs, namely Fenton's Reagent (FR). It is apparently a simple process which generates HO^\bullet through the reaction of hydrogen peroxide with ferrous ion under acidic condition (pH 3 to 5). The aim of the study is to provide insight on the behaviour of the FR system in decolourising a common reactive diazo type dyestuff, Reactive Black 5 (RB5) or also known as Remazol Black B. In particular, the effect of H_2O_2 and Fe^{2+} dosage on RB5 decolourisation behaviour and the effect of RB5 and the reagent dosage on H_2O_2 decomposition were investigated. The latter was also compared against H_2O_2 decomposition in the presence of other compounds with different chemical structure, i.e. chloroform (CHCl_3) and ethylene-diamine-tetraacetic acid (EDTA).

Reactive Black 5 (Figure 1) was chosen as a representative dye model due to its low biodegradability and relatively high rate of use in the textile industry (European IPPC Bureau, 2001). Dye concentrations varying from 10 mg l^{-1} to 7 g l^{-1} have been reported in studies dealing with treating textile effluent (Koprivanac *et al.*, 1993; Pierce, 1994; Gahr *et al.*, 1994; Vandevivere *et al.*, 1998; O'Neill *et al.*, 1999). Such variation is mainly due to the variations in the dyeing processes and the number and types of dyestuff used. Within this wide range, an initial concentration of 200 mg l^{-1} (0.2 mM) of RB5 was chosen in this study. This concentration corresponds to those values reported by Gahr *et al.* (1994) and Meric *et al.* (2004) and stands in about the middle of the range reported by earlier studies. This study differs from the previously published FR works with RB5 in terms of experimental approach and reagent dosage. In addition, the effect of RB5 on the decomposition of H_2O_2 has yet to be sufficiently explored.

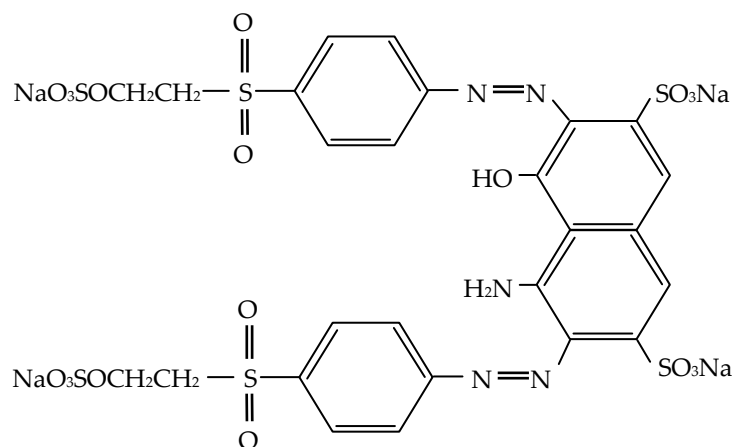


Figure 1: The chemical structure of Reactive Black 5

2.0 Methodology

2.1 Materials and Analysis

The chemicals used were of analytical grade and were supplied by either BDH or Aldrich. Deionised water, generated by an Elgastat Spectrum deioniser was used throughout the experiment. Stock solutions of titanium sulphate for H_2O_2 analysis, enzyme catalase for H_2O_2 destruction, and RB5 were prepared and stored below 4°C .

The performance of the FR process was examined based on two parameters, namely colour and residual H_2O_2 . Colour was analysed based on absorbance at a wavelength of 597 nm (as recommended by the dye manufacturer) using Perkin Elmer Lamda 10 UV/vis spectrophotometer. The destruction of H_2O_2 to quench the reactions at the time of sampling was done by mixing the sample with an appropriate amount of catalase (bovine liver origin) solution immediately after the

sample was taken. The concentration of H_2O_2 was analysed using Titanium Sulphate Spectrophotometric Method (Mendham *et al.*, 2000). This was carried out based on the absorbance value at wavelength of 410 nm.

2.2 Experimental Procedure

A commonly used matrix approach was employed to determine the effect of reagent dosage on the FR process in decolourising RB5. As shown in Table 2, a 5×4 matrix of Fe^{2+} and H_2O_2 dosages ranging from 0.1 mM to 3 mM and 3 mM to 10 mM, respectively were used. These correspond to $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratios of 1 to 100. While there was no economic consideration in choosing these dosages, they were in the range commonly reported in the literature. The experimental runs were labelled as “Rx_y” where x and y refer to the concentration of Fe^{2+} and H_2O_2 in mM, respectively. Control experiments which ran with only H_2O_2 (R0_10) or Fe^{2+} (R3_0) were also carried out.

Table 2: Decolourisation of RB5 dye using different H_2O_2 and Fe^{2+} dosages

		H_2O_2 (mM)				
		0	3	5	7	10
Fe^{2+} (mM)	0	-	-	-	-	*R0_10
	0.1	-	R0.1_3	R0.1_5	R0.1_7	R0.1_10
	0.2	-	R0.2_3	R0.2_5	R0.2_7	R0.2_10
	0.5	-	R0.5_3	R0.5_5	R0.5_7	R0.5_10
	1	-	R1_3	R1_5	R1_7	R1_10
	3	*R3_0	R3_3	R3_5	R3_7	R3_10

*Controlled run

The experiments were conducted batch-wise in a 1 L beaker. Mixing in the vessel was achieved using a magnetic stirrer. As mentioned in section 1.0, a dye solution of 0.2 mM (200 mg l⁻¹), was used in the experimental runs. The solution was freshly prepared from the stock solution prior to each experiment. The temperature of the solution was raised and maintained at $25 \pm 1^\circ\text{C}$ throughout the experiment using the heating plate available within the stirrer unit. The pH of the solution was carefully adjusted to 3.0 using 1:1 (concentrated acid:deionised water) H_2SO_4 . An appropriate dosage (Table 2) of ferrous sulphate (FeSO_4 being the source of Fe^{2+}) was then added into the solution. A sample of the solution was then taken representing sample for colour at $t = 0$ minute. The experimental run started with the addition of the appropriate dosage of H_2O_2 . Subsequently, two different sets of sample, i.e. 5 ml and 100 μl for colour and H_2O_2 concentration analyses, respectively were drawn from the beaker at certain intervals up to 60 minutes. The sample for colour analysis was immediately mixed with the catalase to quench the reactions. The samples were then analysed for colour and H_2O_2 residual using the procedures described in section 2.1.

As H_2O_2 is immediately decomposed by the Fe^{2+} once it is added into the dye solution, separate experiments were conducted to determine the peroxide initial concentrations. This was done by adding the appropriate dosage of peroxide into a well mixed 1-L beaker of deionised water. After at least 5 minutes, to ensure a complete mixing, sample was withdrawn from the beaker and analysed for H_2O_2 .

Two additional sets of experiments were carried out to explore the effect of RB5 on H_2O_2 decomposition. The first set basically repeats the three previous experimental runs but was conducted in the absence of RB5. At certain intervals, samples were taken and analysed for H_2O_2 residual concentration. The second set of experiments was carried out based on the work by Namkung (2002). In this experiment, 0.1 mM RB5 was treated with 1 mM of Fe^{2+} and 1 mM of H_2O_2 . The ionic strength of the solution was adjusted to 0.1 M using NaNO_3 and the solution was bubbled with N_2 gas throughout the experiment. After a 30-minute reaction, another similar dose of H_2O_2 was added to the solution. Samples were taken at certain intervals, up to 60 minutes, and analysed for H_2O_2 . Similar experiments were repeated but RB5 was replaced with 0.5 mM CHCl_3 and 0.5 mM EDTA for comparison. These compounds were chosen as they are structurally different from RB5 (Figure 2).

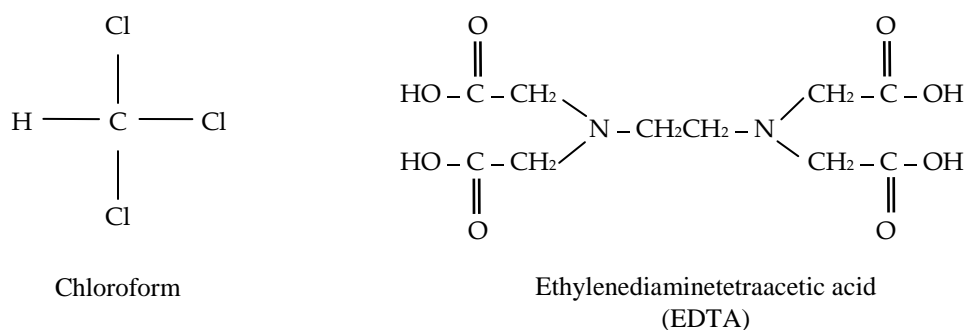


Figure 2: The chemical structure of chloroform and EDTA

3.0 Results and Discussion

3.1 General Overview

A typical decolourisation profile of RB5 by FR is shown in Figure 3 along with the profile of the control runs. With the exception of the control runs, between 90% and 95% decolourisation were achieved by all runs within 5 and 15 minutes, respectively. After 60 minutes, the solution was more than 99% decolourised in almost all runs. Nevertheless, the end product remained yellowish (light to cloudy brownish depending on the amount of Fe^{2+} added) which may be due to the presence of ferric complexes (Kang *et al.*, 1999).

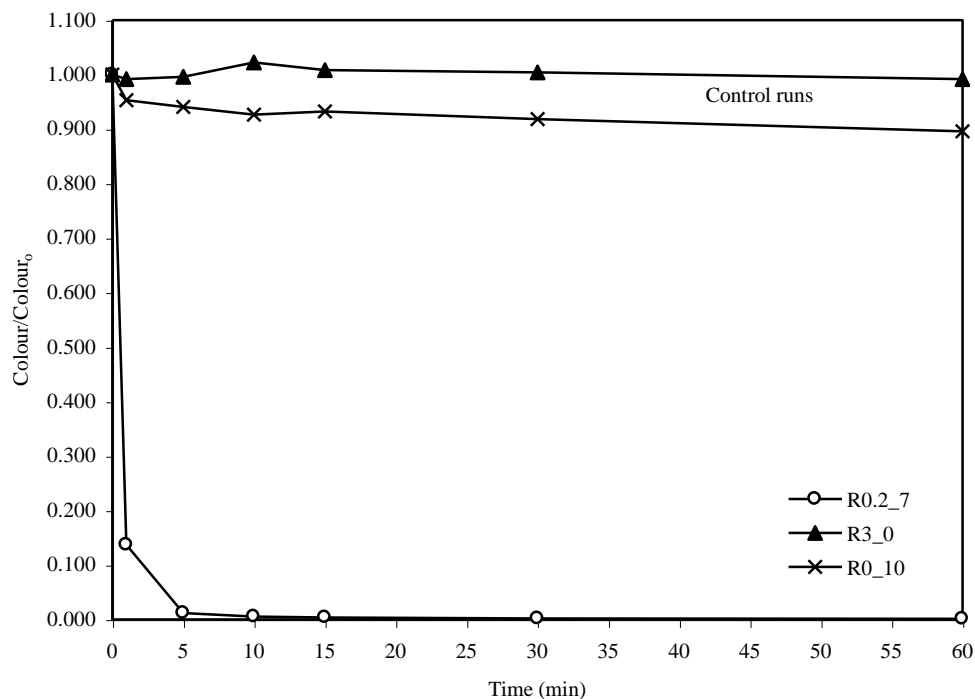


Figure 3: A typical decolourisation profile of RB5

After 60 minutes of reaction, decolourisation by either H_2O_2 only (R0_10) or Fe^{2+} only (R3_0) was insignificant. This indicates the role of HO^\bullet in the process as represented by the following reactions.



The results of the study are consistent with those observed by Sun and Pignatello (1993) and Lu *et al.* (1999). Three main stages can be observed throughout the reaction; the first which is very fast, completed over the first minute of reaction, the second which is slower, took place between 1 and 10 minutes, and the third which is the slowest, took place after approximately 10 minutes of reaction. Such a pattern is expected due to the fast Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) at the beginning, followed by a much slower Fenton-like reaction ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) (Aris, 2004).

Attempts were made to characterise the order of the reaction (as 0th, 1st, or 2nd order) with respect to RB5 decolourisation and H_2O_2 decomposition. However,

as the reactions were characterised by three distinct rates, a fit could not be obtained based on the data collected during the 60-minute reaction. For most of the experimental runs, the reactions showed a 2nd order reaction behaviour with respect to colour (absorbance at 597 nm is taken as closely equivalent to dye concentration) and also a 2nd order reaction behaviour with respect to H₂O₂ (absorbance at 410 nm is taken as closely equivalent to peroxide concentration) decomposition, based on the first 10 minutes of reaction.

Due to the rapid decolourisation and decomposition of the dye and H₂O₂ at Fe²⁺ concentration of 3 mM, the fitting was only valid for the first minute. With respect to the dyestuff, the 2nd order reaction behaviour observed in this study seems to be different from the pseudo 1st order reaction characterised by Solozhenko *et al.*, (1995) and Swaminathan *et al.*, (2003). This could be due to the complex nature of the reactions involved in the FR process which are dependent on many factors such as pH, reagent dosage, temperature, and contaminant structure.

3.2 Effect of Reagent Dosage

Extensive studies have been carried out to determine the optimum reagent dosage in the FR process for various pollutant compounds. Different optimum dosages and ratios have been reported by different researchers (Kuo, 1992; Oliveros *et al.*, 1997; Chen *et al.* 2001). Some reported the existence of a maximum or an optimum value while others did not. The values seem to vary depending on factors such as reaction conditions (e.g. pH, temperature, presence of scavengers), type of target pollutants, strength of the pollutants and range of dosage used.

The effects of Fe²⁺ and H₂O₂ dosage on the initial decolourisation rate (i.e. fitted second order rate constant over first 10 minutes) of RB5 are illustrated in Figures 4 and 5. In general, the initial decolourisation rate increases with the increase of Fe²⁺ and H₂O₂ dosage. The existence of optimum reagents dosage as observed by some researchers seems to depend on the dosage of the reagents. For example, at H₂O₂ dosage of 7 mM, increasing the Fe²⁺ dosage from 0.1 mM to 1 mM increases the initial decolourisation rate from 2.45 A⁻¹ min⁻¹ to 4.1 × 10² A⁻¹ min⁻¹. As the Fe²⁺ dosage was increased to 3 mM, the rate dropped to 2.17 × 10² A⁻¹ min⁻¹. While a similar pattern was observed for the runs with H₂O₂ dosage of 10 mM, it was not observed for the run using 5 mM of H₂O₂ where the initial decolourisation rate continues to increase with the Fe²⁺ dosage. At low H₂O₂ dosage (3 mM), increasing the Fe²⁺ dosage has no significant effect on the reaction rate.

With respect to the H₂O₂ dosage, increasing the reagent dosages from 3 mM to 7 mM has increased the rate of the reaction. For Fe²⁺ dosages of 1 mM and 3 mM, increasing the H₂O₂ dosage further to 10 mM has reduced the reaction rate. At lower Fe²⁺ dosage, the influence of H₂O₂ is less significant. The H₂O₂ effect seems to be strongly influenced by the dosage of Fe²⁺.

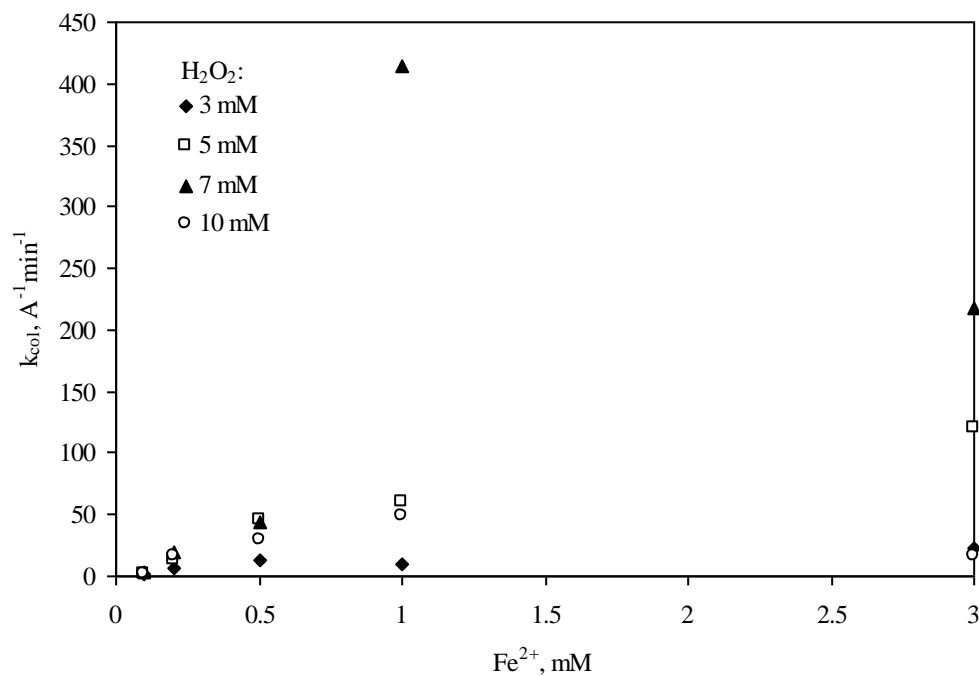


Figure 4: Effect of Fe^{2+} to initial decolourisation rate of RB5

Sufficient H_2O_2 and Fe^{2+} are required to generate HO^\bullet for the degradation of RB5. On the other hand, when their concentrations are too high, they will become competitors to RB5 for HO^\bullet (Eqns. 5 and 6) which eventually reduces the efficiency of the process (Sychev and Isak, 1995). When a high concentration of HO^\bullet is produced, they will react with each other and generating less reactive species (Eqn. 7).

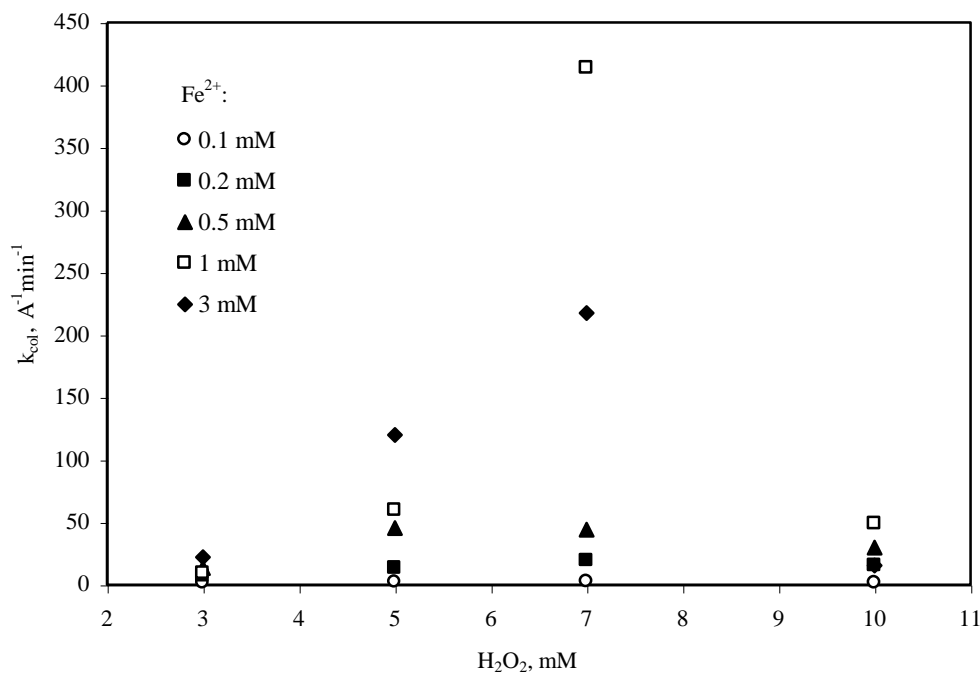


Figure 5: Effect of H₂O₂ dosage to initial decolourisation rate of RB5



Furthermore, at high concentrations, Fe²⁺ apparently forms complexes which contribute to the end colour of the solution (Kang *et al.*, 1999) and adds to the cost of the process in term of quantity of sludge for disposal. As for the initial decolourisation rate, the best dosages for H₂O₂ and Fe²⁺ in this study are 7 mM (238.1 mg L⁻¹) and 1 mM (55.9 mg L⁻¹), respectively. However, further detail studies are needed to verify these values.

A maximum decolourisation rate was achieved at H₂O₂/Fe²⁺ molar ratio of 7:1 (Figure 6). The effects of H₂O₂/Fe²⁺ molar ratio on the efficiency of FR process were also observed by others (e.g. Sychev and Isak, 1995; Namkung, 2002; Neyens and Baeyens, 2003). This has been attributed to the changing balance of reactions pathways that occur at different ratios which are closely linked to the radical scavenging phenomenon.

With respect to the dyestuff and its initial concentration used in this study, the best initial decolourisation rate was found at the H₂O₂:Fe²⁺:RB5 molar ratio of 35:5:1. Under this condition, more than 99% decolourisation was achieved within

1 minute of reaction while 100% decolourisation was achieved within 10 minutes. For economic reasons, other options are also available for consideration. For a 10-minute reaction, H_2O_2 and Fe^{2+} dosages as low as 3 mM (102.0 mg L^{-1}) and 0.2 mM (11.2 mg L^{-1}), respectively, are sufficient for about 99% decolourisation. With 3 mM of H_2O_2 , a Fe^{2+} dosage of 0.1 mM (5.6 mg/L) is sufficient to decolourise 99% of the RB5 within 60 minutes. Nonetheless, although reducing the reagent dosage will lower the operating cost of the process, increasing reaction time will result in additional volume of the reactor and thus, the capital cost of the process. Therefore, an economic analysis is needed to balance between these two costs in choosing the best possible option.

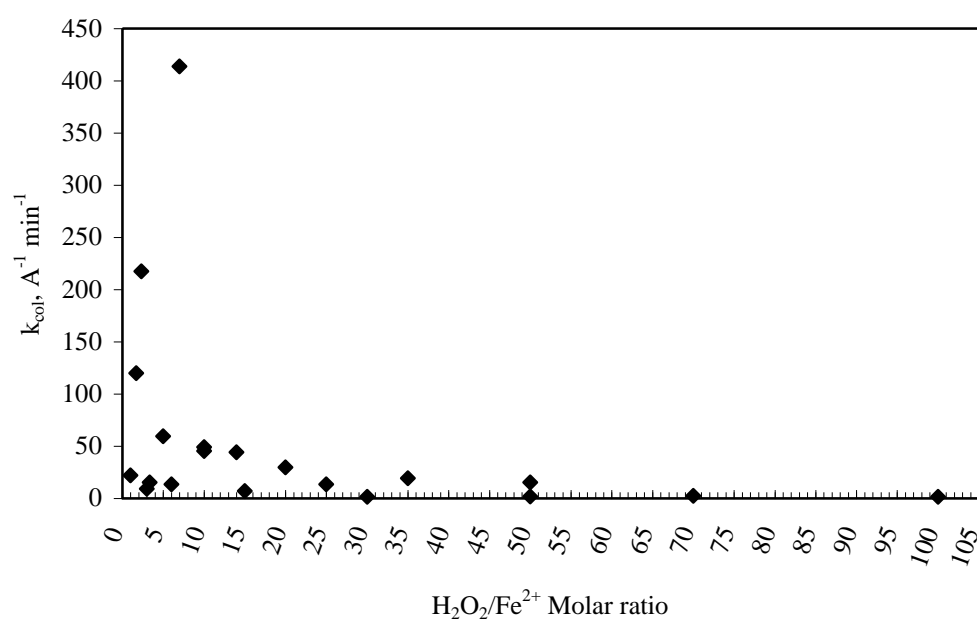


Figure 6: Effect of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio on initial decolourisation rate

3.3 Hydrogen Peroxide Decomposition

The decomposition of 10 mM H_2O_2 with time as a function of Fe^{2+} dosage is shown in Figure 7. Figure 8 illustrates the fitted initial 2nd order decomposition rate constant of the peroxide as a function of Fe^{2+} dosage. It is obvious that the decomposition of H_2O_2 is strongly affected by the Fe^{2+} and H_2O_2 dosages. The higher the Fe^{2+} dosage, the higher is the initial H_2O_2 decomposition rate and the extent of the decomposition. Conversely, the higher the peroxide dosage, the lower is its initial decomposition rate constant.

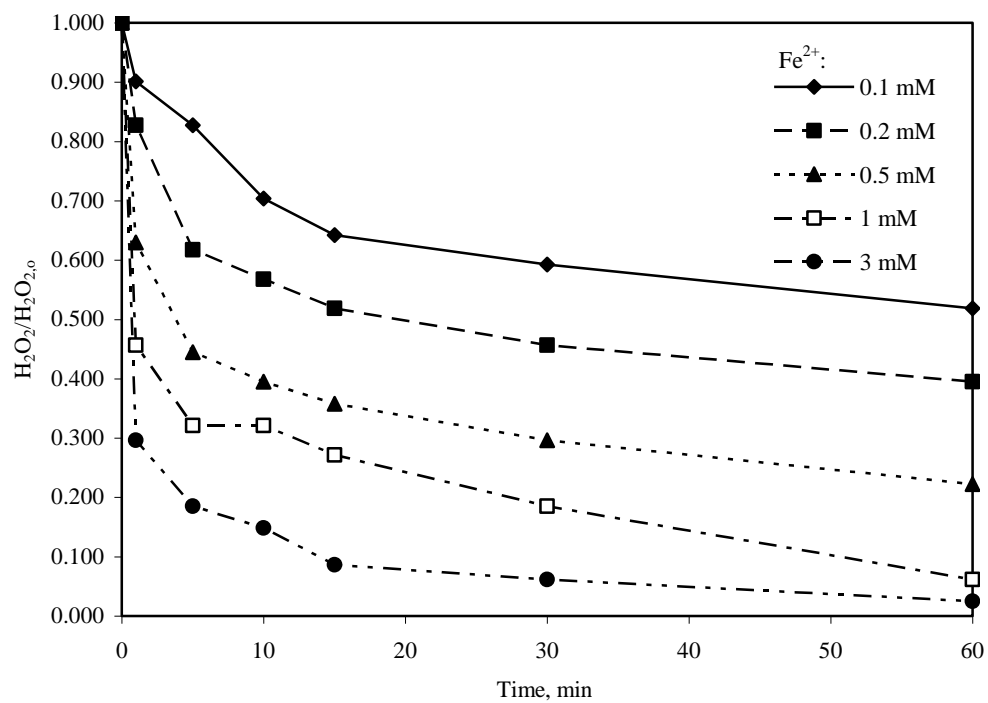


Figure 7: Decomposition of H_2O_2 under different Fe^{2+} initial concentrations (H_2O_2 : 10 mM)

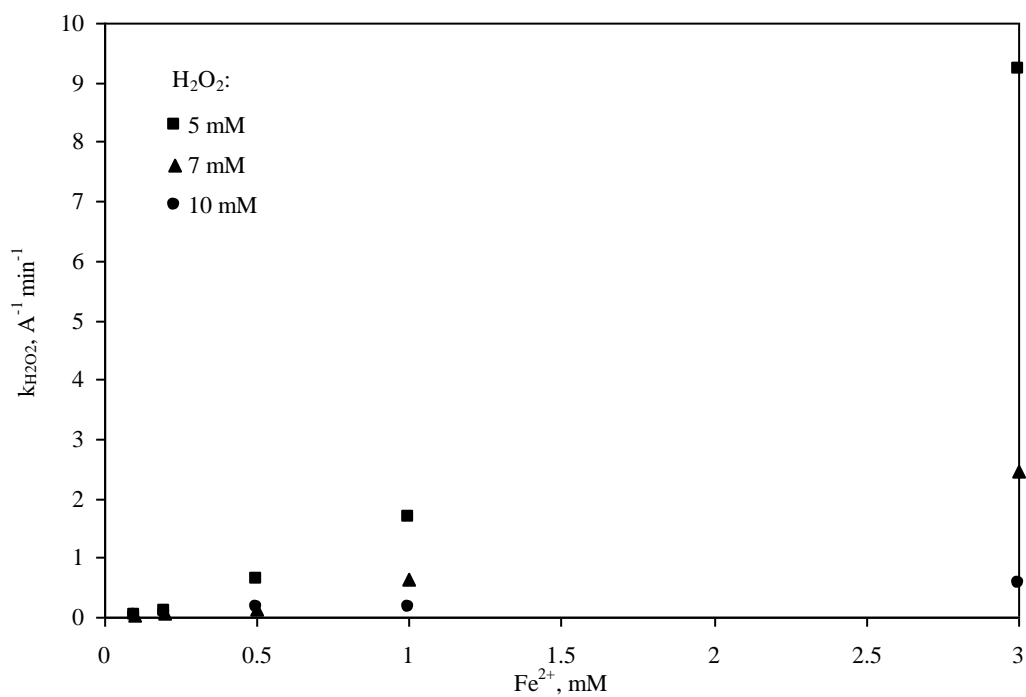


Figure 8: Initial decomposition rate of H_2O_2 under different Fe^{2+} and H_2O_2 dosage

The profile of H_2O_2 decomposition also seems to follow that of RB5 decolourisation. The decomposition was faster in the first few minutes and became slower after about 10 minutes. The initial H_2O_2 concentration was apparently in excess and reacted with Fe^{2+} to produce HO^\bullet . The degradation slowed down when Fe^{2+} had been transformed to Fe^{3+} . Since H_2O_2 is decomposed by Fe^{2+} to form HO^\bullet in the FR system, the decomposition of the peroxide can be correlated to the production of HO^\bullet and can possibly be used as a qualitative indicator on the generation of HO^\bullet .

As mentioned earlier, experiments were also conducted to determine the effect of RB5 on the decomposition of H_2O_2 . Two sets of experiments were conducted. The first set compared the decomposition of H_2O_2 in the absence and presence of RB5 while the second compared the degradation of H_2O_2 in the presence of RB5 and in the presence of CHCl_3 and EDTA. Figure 9 illustrates the effect of RB5 on H_2O_2 decomposition. Based on the three pairs of comparative runs, RB5 was found to substantially increase the decomposition of H_2O_2 . Besides, the extent of peroxide decomposition increased with the increase of RB5 initial concentration (Figure 10) although the initial decomposition rate was not greatly affected.

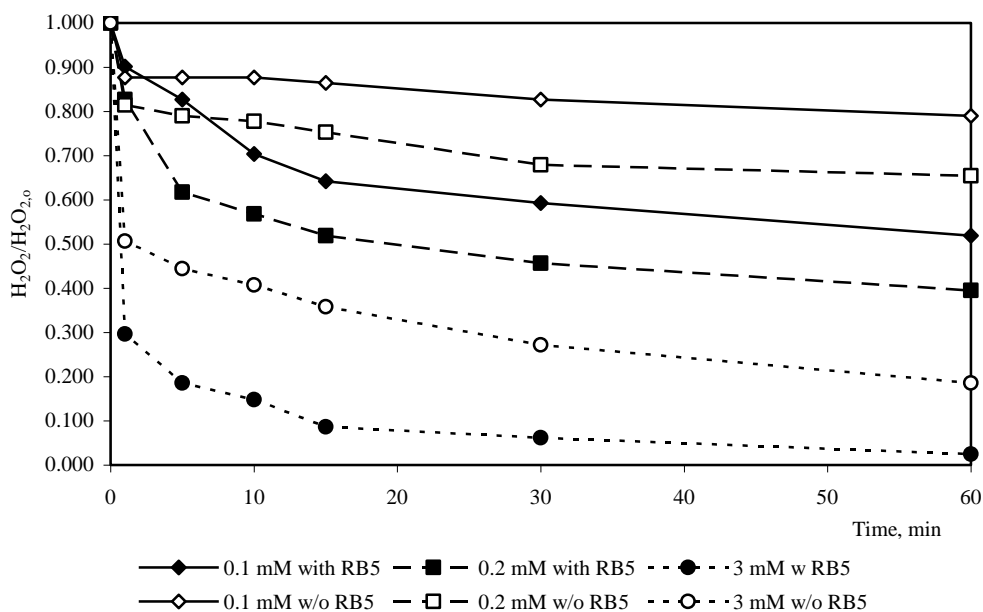


Figure 9: Decomposition of H_2O_2 under different Fe^{2+} dosages (0.1, 0.2, 3 mM) with RB5 (solid) and without RB5 (hollow) (H_2O_2 : 10 mM)

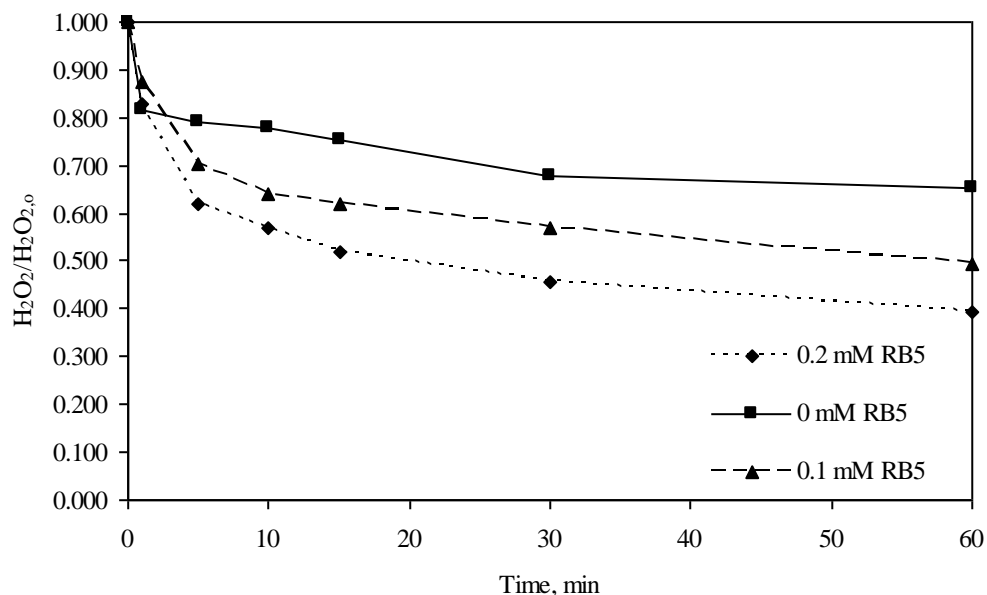


Figure 10: Decomposition of H₂O₂ under different RB5 initial concentrations (H₂O₂: 10 mM; Fe²⁺: 0.2 mM)

In the second experiment, the three compounds, i.e. RB5, CHCl₃ and EDTA have resulted in different rates of H₂O₂ decomposition (Figure 11). The presence of RB5 caused rapid degradation of the peroxide while the decomposition was relatively slower with CHCl₃ and EDTA. This was also observed when second dosage of H₂O₂ was added at 30 minutes of reaction.

The considerable differences in H₂O₂ decomposition rate for the different compounds might be due to the differences in their structure. The rapid decomposition of H₂O₂ in the presence of RB5 was comparable to that observed by Namkung (2002) in the presence of 4-chlorophenol. Since both compounds contain aromatic groups, it is anticipated that the reactions which took place in the Fenton-RB5 system is similar to those of Hamilton-like systems during Fenton oxidation (Hamilton *et al.*, 1966; Rodriguez *et al.*, 2001; Namkung and Sharratt, 2001). In these systems, the aromatic compounds seem to cause reduction of Fe³⁺ to Fe²⁺ leading to an enhanced HO[•] formation during the Fenton reaction. While more study is needed to understand the role of RB5 in the Fenton-RB5 system, the current observations appear to favour the use of FR in degrading the dye. If such a Fe³⁺/Fe²⁺ 'redox cycle' phenomenon exists in the Fenton-RB5 system, it will then reduce the iron requirement which is an advantage to the process.

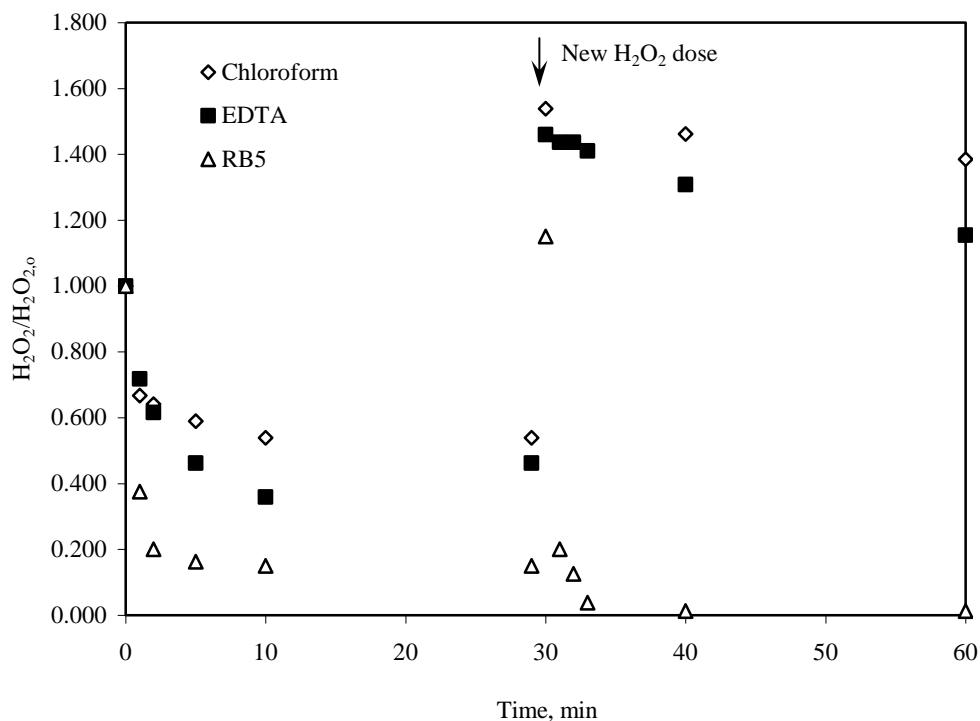


Figure 11: The profile of H_2O_2 in the presence of RB5, CHCl_3 and EDTA (H_2O_2 : 1 mM; Fe^{2+} : 0.5 mM; RB5: 0.1 mM; CHCl_3 : 0.5 mM; EDTA: 0.5 mM)

Figure 12 correlates the initial decomposition rate constant of H_2O_2 to the initial decolourisation rate constant of RB5 at two different H_2O_2 dosages. In general, the initial decolourisation rate of RB5 increases with the increase of initial H_2O_2 decomposition rate. This implies that as more peroxide is decomposed, more HO^\cdot is formed, thus enhancing the decolourisation rate of RB5. However, the behaviour of the correlation seems to depend on the dosage of H_2O_2 . At H_2O_2 dosage of 10 mM, a small increase in the initial peroxide decomposition rate causes substantial increase in the initial rate of decolourisation initially. As the initial peroxide decomposition rate increases further, the initial decolourisation rate drops. At peroxide dosage of 5 mM, the initial decolourisation rate increase gradually with the initial increase in the peroxide decomposition rate. A maximum in the initial H_2O_2 decomposition rate (as with the 10 mM peroxide dosage) is not observed but the extent in the increase of the decolourisation rate reduces as the peroxide decomposition rate increases.

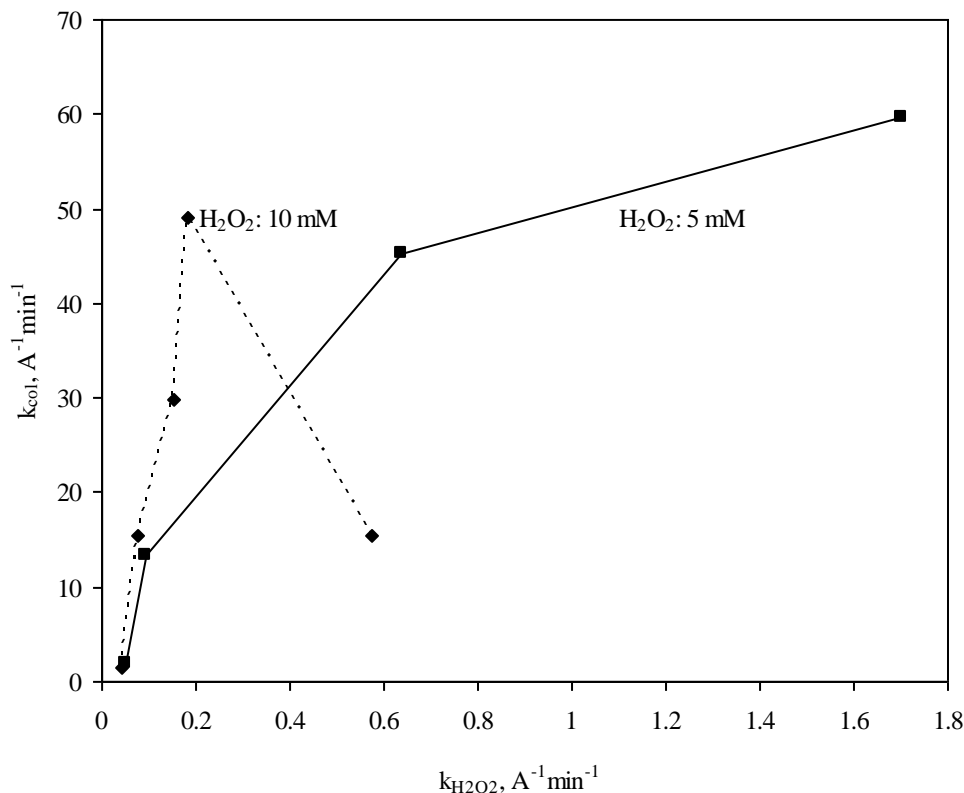


Figure 12: Relationship between initial H_2O_2 decomposition rate and initial RB5 decolourisation rate (Fe^{2+} : 0.1 – 3 mM)

As H_2O_2 decomposition rate is influenced by the reagent dosage, these observations again indicate the importance of applying correct H_2O_2 and Fe^{2+} dosage and ratio. Incorrect dosage may lead to insufficient or excessive concentration of radicals (generated from the peroxide decomposition) which reduces the efficiency of the FR process. The results also suggest that the decomposition of H_2O_2 could not be used directly as a gauge to determine the efficiency of the FR process. While it may qualitatively indicate the production of HO^\bullet , its use in assessing the process efficiency is complicated by the scavenging activity of the radical.

4.0 Conclusion

Several conclusions could be derived from the experimental work carried out in this study:

- i. Within the experimental conditions of the study, Fenton's reagent is capable to decolourise 0.2 mM RB5 within a reasonable time. Most of the decolourisation occurred in the first minute of the reaction.

- ii. The effectiveness of the process depends on the reagents dosage. The initial decolourisation rate increases with the increase of H_2O_2 and Fe^{2+} dosages, but only to a certain level. Further increase would result in reduction of process efficiency. This is possibly caused by the scavenging of the radical by the reagents. For this study, the best dosages of H_2O_2 and Fe^{2+} (based on the initial decolourisation rate) were 7 mM (238.1 mg l^{-1}) and 1 mM (55.9 mg l^{-1}), respectively. The best $\text{H}_2\text{O}_2:\text{Fe}^{2+}:\text{dye}$ molar ratio was 35:5:1 for 0.2 mM RB5.
- iii. The profile of peroxide decomposition is similar to that of decolourisation. The decomposition of H_2O_2 is dependent on the dosage of Fe^{2+} and H_2O_2 . The higher the Fe^{2+} dosage, the higher is the rate and the extent of the decomposition and the reverse is true for the peroxide dosage.
- iv. H_2O_2 decomposes faster in the presence of RB5. The rate and extent of the decomposition also increase as the initial concentration of RB5 increases. The peroxide decomposition in the presence of RB5 is the fastest compared with the presence of CHCl_3 or EDTA. These observations suggest the possibility of $\text{Fe}^{3+}/\text{Fe}^{2+}$ 'redox-recycled' system as in a Hamilton-like system, thus favour the use of FR process for the degradation of the dye.
- v. The initial decolourisation rate of RB5 correlates well with the initial decomposition rate of H_2O_2 . The nature of the correlation, however, depends on the reagents dosage and the relationship is rather complex, possibly due to the radical scavenging phenomenon.

References

- Andreozzi, R., Caprio, V., Insola, A. and Marotta, R. (1999) Advanced oxidation processes (AOP) for water purification and recovery. *Catalysis Today*, 53: 51-59.
- Aris, A. (2004) *Fenton's Reaction System for the Treatment of Textile Dyeing Wastewater*. Ph.D Thesis, University of Manchester Science and Technology, Manchester, 253pp.
- Bottino, A., Capannelli, G. and Tocchi, G. (2001) Membrane separation processes tackle textile wastewater treatment. *Membrane Technology*, 130: 9-11.
- Chen, G., Hoag, G. E., Chedda, P., Nadim, F., Woody, B. A. and Dobbs, G. M. (2001) The mechanism and applicability of in situ oxidation of trichloroethylene with Fenton's reagent. *Journal of Hazardous Materials*, B87:171-186.
- Clarkson, W. W., Yang, C. P. and Harker, A. R. (1993) 4-D degradation in monoculture biofilm reactors. *Water Research*, 27: 1275-1284.
- Cooper, P. E. (1995) *Colour in Dyehouse Effluent*. Society of Dyers and Colourists
- Dutta, K., Mukhopadhyay, S., Bhattacharjee, S. and Chaudhuri, B. (2001) Chemical oxidation of methylene blue using a Fenton-like reaction. *Journal of Hazardous Materials*, B84: 57-71.
- European IPPC Bureau (2003) *Reference Document on Best Available Techniques for the Textile Industry (Draft D2)*, Seville : Institute for Prospective Technological Studies.
- Gahr, F., Hermanutz, F. and Oppermann, W. (1994) Ozonation - an important technique to comply with new German laws for textile wastewater treatment. *Water Science and Technology*, 30: 255-263.

- Hamilton, G. A., Hanifin, J. W. and Friedman, J. P. (1966) The hydroxylation of aromatic compounds by hydrogen peroxide in the presence of catalytic amounts of ferric ion and catechol. Product studies, mechanism, and relation to some enzymatic reaction. *Journal of the American Chemical Society*, 88: 5269-5272.
- Kang, S. F., Liao, C. H. and Hung, H. P. (1999) Preoxidation treatment of dye manufacturing wastewater in the presence of ultraviolet light and ferrous ions. *Journal of Hazardous Materials*, B65: 317-333.
- Kennedy, J. C., Morris, G. and Croxford, A. (1999) The impact of the textile industry on the water environment. *Proceedings of International Conference Water and Textiles*. University of Huddersfield.
- Koprivanac, N., Bosanac, G., Grabaric, Z. and Papic, S. (1993) Treatment of wastewaters from dye industry. *Environmental Technology*, 14: 385-390.
- Kuo, W. G. (1992) Decolourizing dye wastewater with Fenton's Reagent. *Water Research*, 26: 881-886.
- Lu, M. C., Chen, J. N. and Chang, C. P. (1999) Oxidation of dichlorvos with hydrogen peroxide using ferrous ion as catalyst. *Journal of Hazardous Materials*, B65: 277-288.
- Mendham, J., Denny, R. C., Barnes, J. D. and Thomas, M. J. K. (2000) *Vogel's Quantitative Chemical Analysis*. Prentice Hall
- Meric, S., Kaptan, D. and Olmez, T. (2004) Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. *Chemosphere*, 54: 435-441.
- Namkung, K. C. and Sharratt, P. N. (2001) Experimental and modelling study of a Fenton system with 4-chlorophenol. *Proceedings of the 15th International Ozone Association World Congress*. London.
- Namkung, K. C. (2002) *Experimental and Modelling Studies of Fenton Reaction Systems*. Ph.D Thesis, University of Manchester Science and Technology, Manchester.
- Neyens, E. and Baeyens, J. (2003) A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, B98: 33-50.
- O'Neill, C., Hawkes, F. R., Hawkes, D. L., Lourenco, N. D., Pinheiro, H. M. and Delee, W. (1999) Colour in textile effluents - sources, measurement, discharge consents and simulation: a review. *Journal of Chemical Technology and Biotechnology*, 74: 1009-1018.
- Oliveros, E., Legrini, O., Hohl, M., Muller, T. and Braun, A. M. (1997) Large scale development of a light-enhanced Fenton reaction by optimal experimental design. *Water Science Technology*, 35: 223-230.
- Pierce, J. (1994) Colour in textile effluents - the origins of the problem. *Journal of the Society of Dyers and Colourist*, 110: 131-133.
- Rodriguez, J., Parra, C., Contreras, D., Freer, J. and Baeza, J. (2001) Dihydroxybenzenes driven Fenton reactions. *Water Science and Technology*, 44: 251-256.
- Solozhenko, E. G., Soboleva, N. M. and Goncharuk, V. V. (1995) Decolourization of Azodye solutions by Fenton's oxidation. *Water Research*, 29: 2206-2210.
- Sun, Y. and Pignatello, J. J. (1993) Photochemical reactions involved in the total mineralization of 2,4-D by $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$. *Environmental Science Technology*, 27: 304-310.
- Swaminathan, K., Sandhya, S., Sophia, A. C., Pachhade, K. and Subrahmanyam, Y. V. (2003) Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide. *Chemosphere*, 50: 619-625.
- Sychev, A. Y. and Isak, V. G. (1995) Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O_2 and H_2O_2 and of the oxidation of organic substrates. *Russian Chemical Reviews*, 64: 1105-1129.
- Vandevivere, P. C., Bianchi, R. and Verstraete, W. (1998) Treatment and reuse of wastewater from textile wet-processing industry: review of emerging technologies. *Journal of Chemical Technology and Biotechnology*, 72: 289-302.