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Chapter 5

COMBINED SONOHOMOGENEOUS AND HETEROGENEOUS OXIDATION OF DYES FOR WASTEWATER TREATMENT

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ABSTRACT

Dyestuff in water introduces several environmental problems and should be removed for clean water system. Fenton oxidation can be as an effective technique for the water treatment. In this report, homogeneous and heterogeneous catalysis in Fenton oxidation was examined for two dyes with acidic (Naphthol blue-black, NBB) and basic (Methylene Blue, MB) properties. The behaviour of these dyes under different experimental conditions (temperature, pH, peroxide concentration, Fe concentration) was studied using Fenton (Fe^{2+}) and Fenton-like (Fe^{3+}) reactions for the following processes: 1) normal Fenton oxidation, 2) Fenton oxidation combined with sonication effect, 3) Fenton oxidation combined with a solid catalyst (activated carbon). The main Fenton oxidation reactants, Fe^{2+}, Fe^{3+} and H_2O_2 were used in small quantities in order to observe closely the reaction kinetics for decolourisation of these dyes. It was found that both sonication and heterogeneous catalysis offer improvements to the Fenton oxidation under optimised conditions, with Fe^{2+} being faster than Fe^{3+} initially but Fe^{3+} ending up with a higher overall efficiency. 90-95% decolourisation was achieved in some optimised runs after 2 hours; however the general decolourisation was completed for all batch runs after a period of 24 hours, except in conditions where the reaction did not proceed at all. Chemical oxygen demand (COD) removal also occurred during the decolourisation process of both dyes, in maximum efficiencies of about 80% after 48 hours. Methylene blue also showed greater decolourisation efficiency in comparison with Naphthol blue-

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black for most of the experimental runs under the same experimental conditions. The reaction kinetics was mainly pseudo-first order for majority of the homogeneous reaction, as determined by non-linear regression or a combination of first order kinetics for heterogeneous reactions.

1 INTRODUCTION

Wastewater from textile and dyeing industries contains dye stuff, suspended solids, and other soluble substances. Currently several types of dyes such as acid, basic, azo, reactive, dispersive dyes are widely employed in textile and other industries. The textile industry in many countries has to meet with local and national regulations regarding the purification of water from dyeing processes before the treated wastewater can be released into the environment. Dyestuff in waters affects the colour and hence the transparency and light penetration, as well as gas solubility in water, which will cause environmental damage to the biosystem. Also, several commonly used dyes have been reported to be carcinogenic and mutagenic for aquatic life [1].

Many methods of dye removal have been researched, some of which are currently in use. Physical adsorption using activated carbon has been employed as effective method to remove dyes from aqueous solution [2]. However, this method can not destroy the dyestuff. Chemical removal will be an effective alternative technology. The main chemical processes currently used on a large scale are the advanced oxidation processes (AOPs) which involve the generation of the hydroxyl (OH•) radical. Common AOPs involve Fenton (Fe^{2+}/H_2O_2, R1) and Fenton-like (Fe^{3+}/H_2O_2, R2) processes, ozonation, photochemical and electrochemical oxidation, photolysis with H_2O_2 and O_3, high voltage electrical discharge (corona) process, TiO_2 photocatalysis, radiolysis, wet oxidation, water solutions treatment by electronic beams or γ-beams and various combinations of these methods [3]. Compared with other oxidation processes, processes using the Fenton type reagent are relatively cheap, easily operated and maintained, especially for Fenton-like reaction. However, previous investigations always employed high Fe and H_2O_2 concentrations, which resulted in higher cost and large amount of sludge. Thus, using low dosage of Fenton reagent is highly demanded.

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

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

In recent years, considerable interest has been shown on the application of ultrasound (US) as an advanced oxidation process for the treatment of hazardous contaminants in water. Ultrasonic irradiation of aqueous solutions induces acoustic cavitation, which can be defined as the cyclic formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small intervals of time and releasing large quantities of energy over a small location [4]. During the sonolysis of water and in the presence of oxygen, reactive radicals such as ${}^{\bullet}OH$, ${}^{\bullet}O$ and ${}^{\bullet}OOH$ are produced through a series of reactions and may participate in the decomposition reactions of target contaminants [5].

$$H_2O +)))) \rightarrow OH^{\bullet} + H^{\bullet} \quad (3)$$

$$OH^{\bullet} + H^{\bullet} \rightarrow H_2O \tag{4}$$

$$2OH^{\bullet} \rightarrow H_2O_2 \tag{5}$$

where)))) refers to the application of ultrasound.

In the presence of oxygen

$$O_2 \rightarrow 2\ O^{\bullet} \tag{6}$$

$$O_2 + O^{\bullet} \rightarrow O_3 \tag{7}$$

$$O_2 + H^{\bullet} \rightarrow HO_2^{\bullet} \tag{8}$$

$$2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2^{\bullet} \tag{9}$$

The combinations of US and other advanced oxidation processes have also been investigated. The coupling of US with H_2O_2, ozone, and UV irradiation resulted in higher degradation efficiencies of phenols and chlorinated phenols, as compared to each treatment alone. Humic and fulvic acid mineralisation was enhanced by the combination of sonication with H_2O_2 and with ozone [6]. For dye degradation, some investigations employing US [7-9], US/ozonation [10, 11], UV/US [12] UV/H_2O_2/US [13] have been reported. However, few work has been done on US/Fenton combination [14, 15] for dye degradation. Abdelsalam and Birkin [14] investigated sonoelectrochemical degradation of meldola blue employing Fenton's reagent. The effect of adding Fe^{2+} to the rate of dye degradation was measured and demonstrated to be significant. Joseph et al. [15] conducted a sonochemical degradation of azo dyes (methyl orange, o-methyl red, and p-methyl red) at 500 kHz and 50 W, under air, O_2, or Ar saturation at 15 °C. The acceleration of the sonochemical bleaching and the mineralisation process upon addition of Fe^{2+} was also investigated in Ar-saturated methyl orange solutions. A 3-fold increase in the reaction rate was observed at optimal Fe^{2+}.

In previous investigations, most of reports focus on Fenton oxidation of dyes, few investigations have been reported on the degradation of dyes using Fenton-like oxidations [16-19]. In addition, it is known that different types of dyes will exhibit quite different degradation behaviour. Dutta et al. firstly conducted a systematic investigation on chemical oxidation of methylene blue using Fenton-like reaction [17]. Hsueh et al. [18] investigated Fenton and Fenton-like reactions at low iron concentration ($< 1.78 \times 10^{-4}$ M) to oxidise three commercial azo dyes, namely Red MX-5B, Reactive Black 5 and Orange G. Their results reveal that both of these methods can remove the colour of these dyes completely. Recently, Ntampegliotis et al. reported the decolourisation kinetics of three commercially used Procion H-exl dyes using a Fenton-like reagent [19]. But the Fenton reagent concentration is too high.

As stated above, there are other contaminated matters such as ions and solids in textile wastewater and these contaminants will affect the Fenton reaction. However, few investigations have been reported in this aspect. De Laat et al. [20, 21] investigated the effect of chloride, sulfate and nitrate ions on the efficiency of the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 systems and reported a negative effect of chloride ion. Ashraf et al. [22] studied the effect of other salts that are normally present in textile waste streams. They used 10 different salt solutions to investigate the effect on Fenton degradation of methyl red and found that some of the ions tested enhanced the rate and extent of degradation of the dye, whereas some had an inhibitory effect. On the other hand, no investigation has been reported on the effect of solid materials based on our knowledge. Solid materials in wastewater could play a positive or negative role in Fenton oxidation. Activated carbon is an excellent adsorbent showing high adsorption capacity in various metal ions and organics. The presence of activated carbon with Fenton reagent could combine adsorption and catalytic oxidation together. In this paper, we report an investigation of Fenton and sonic promoted Fenton reaction at very low Fe and H_2O_2 concentrations for dye degradation. We employed two types of dyes, azo and basic dyes, and investigated the dye degradation efficiency and kinetics using the combination of sonolysis and Fenton reaction. In addition, we report an investigation of Fenton oxidation with or without activated carbon to study the effect of activated carbon on dye degradation during Fenton oxidation.

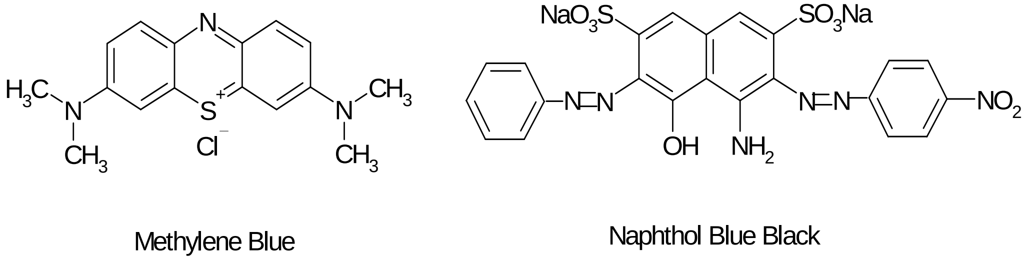
2 EXPERIMENTAL

2.1. Chemicals

Naphthol blue-black ($C_{22}H_{14}N_6Na_2O_9S_2$, NBB) and methylene blue ($C_6H_{18}ClN_3S^{\cdot}2H_2O$, MB) were selected as corresponding typical type of azo and basic dyes, respectively. Figure 1 shows their chemical structure. These two dyes were obtained from Ajax Chemicals. Other chemicals, sulphuric acid was obtained from BDH Chemicals, sodium hydroxide and hydrogen peroxide (30%) was from Redox Chemicals, and ferrous sulfate and ferric sulphate were obtained from Sigma Chemicals. All chemicals were used as supplied without further treatment. Activated carbon was obtained from BDH Chemicals.

2.2. Reaction Tests

All homogeneous system experiments were carried out in a 1000 ml batch reactor in a controlled temperature environment using a water bath at 30 ± 0.5 ^{o}C unless otherwise stated. The solution pH was adjusted using sulphuric acid or sodium hydroxide solutions and measured with a pH meter (PHM 250 Ion analyser). For all tests, only the initial pH was monitored. In some tests, the final pH was also measured. The addition of sulphuric acid or sodium hydroxide had no effect on the dye solution in terms of precipitation or colouration. The dye (MB and NBB) and the ferrous or ferric iron solutions were firstly prepared and pre-mixed in the reactor. The reaction time was recorded when H_2O_2 was added into the mixture. The reacting solution homogeneity was ensured by stirring at a rate of 40 rpm. All iron solutions needed for the experiments were prepared daily and all experiments were carried out at pH 2 ± 0.02 unless otherwise stated. Absorbance measurements were carried out in the visible region using a spectrophotometer (Spectronic 20 Genesys Spectrophotometer, USA) at a λ_{max} of 665 nm for MB and 618 nm for NBB, respectively. The concentration was determined based on calibration curves obtained for both dyes at these λ_{max} values. The experiments were carried out for 120 min continually.



Methylene Blue

Naphthol Blue Black

Figure 1. Chemical structure of tested dyes.

The sonication experiments were carried out by an ultrasonic bath (40 Hz, 300W, FXP14M, Unisonics, Australia). Various runs of a 1000 ml dye solution with different combination of varying of H_2O_2, Fe^{2+} and Fe^{3+} concentrations at pH 2 were conducted. Samples were taken out at varying time for absorbance measurement and the reactions were also carried out for 120 min continually.

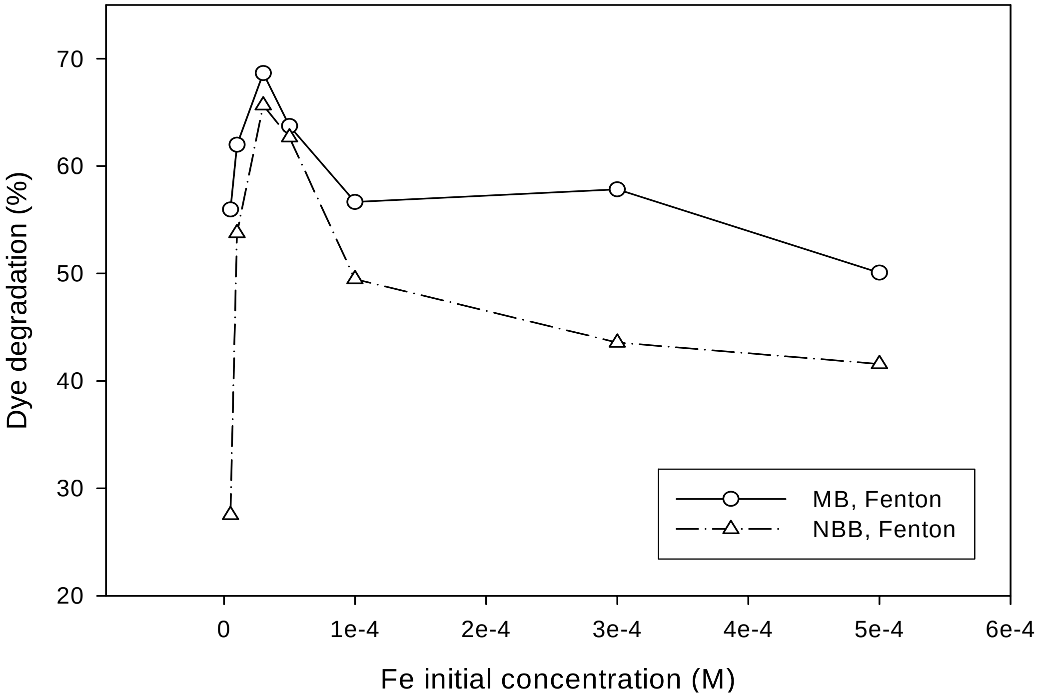


Figure 2. Effect of initial Fe2+ concentration on dye degradation.

The adsorption of dye using activated carbon (AC) was performed in an orbital shaker (Thermoline Scientific Orbital shaker incubator). A bottle with 250 ml filled with 200 ml of dye solution and some amount of solids was put in the shaker run at a speed of 100 rpm at 30 °C. At a certain time intervals, the dye solution was drawn from the bottle and measured with a spectrophotometer (Spectronic 20 Genesys Spectrophotometer, USA) at a wavelength (λ_{max}) of 665 nm for MB and 618 nm for NBB. Dye concentration was then determined using a calibration curve. Fenton oxidation with the presence of activated carbon was carried out similarly to the Fenton oxidation but at 200 ml solution and with varying H_2O_2 concentration, carbon content and initial solution pH.

3 RESULTS AND DISCUSSION

3.1. Dye Degradation in Fenton Reaction

It has been known that several parameters influence the reaction rate. In this investigation, the effects of Fe^{2+} concentration, H_2O_2 concentration, solution pH and temperature were studied.

3.1.1. Effect of Fe^{2+} Concentration

Figure 2 illustrates the overall efficiency of dye degradation at 120 min with the variation of Fe^{2+} initial concentration while keeping H_2O_2 concentraion at 5 x10^{-5} M, pH 2 and temperature at 30 °C. For Fenton reactions, no degradation was observed for both dyes in the absence H_2O_2. When a small amount of Fe^{2+} at concentration of 5 x 10^{-6} M was added in the solution, dye degradation was remarkably observed. For MB and NBB, the decolourisation efficiencies at 28 and 55% could be achieved. If Fe^{2+} concentration is further increased, the rate of dye decolourisation increases and reaches an optimum of 70% at Fe^{2+} concentration of 3 x 10^{-5} M. However, at higher Fe^{2+} concentrations, dye degradation appears to decrease. This might be due to the limited concentration of H_2O_2 in solution. When H_2O_2 is consumed during the reaction, higher Fe^{2+} concentration will not produce further dye degradation. On the contrary, unreacted H_2O_2 will act as a scavenger of $^{\bullet}OH$ and produces a less potent perhydroxyl radicals (R10), resulting in less dye degradation. Thus, the optimum Fe^{2+}/H_2O_2 ration will be around 1: 1. For two dyes, it is also seen from the Figure that MB degradation is generally higher than NBB.

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (10)$$

Several investigations on dye degradation in Fenton reaction have reported the effect of Fe^{2+}. Dutta et al. [17] observed that methylene blue degradation increased with the increasing Fe^{2+} concentration and would be constant at higher Fe^{2+}concentration. Hsueh et al. [18] also found that degradation of several azo dyes would increase with increasing Fe concentration and no improvement would be obtained if more Fe^{2+} is in the solution. The different behaviour of dye degradation observed in this research with others is probably due to the higher H_2O_2 concentration (> 4.4 x 10^{-4} M) employed in those investigations.

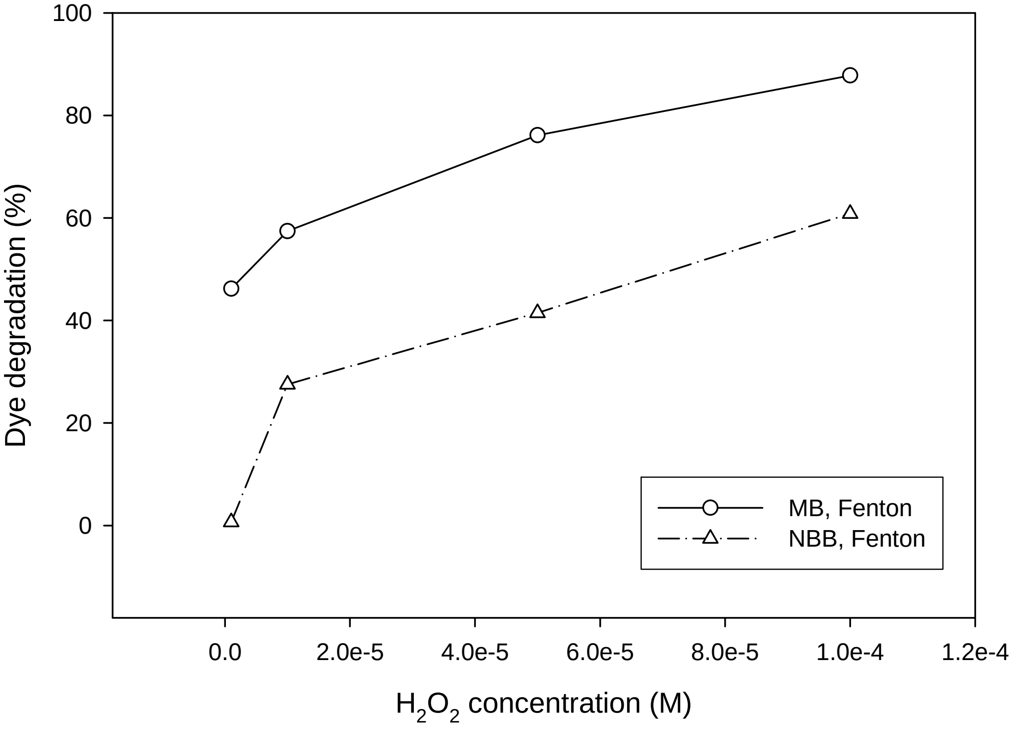


Figure 3. Effect of H_2O_2 initial concentration on dye degradation.

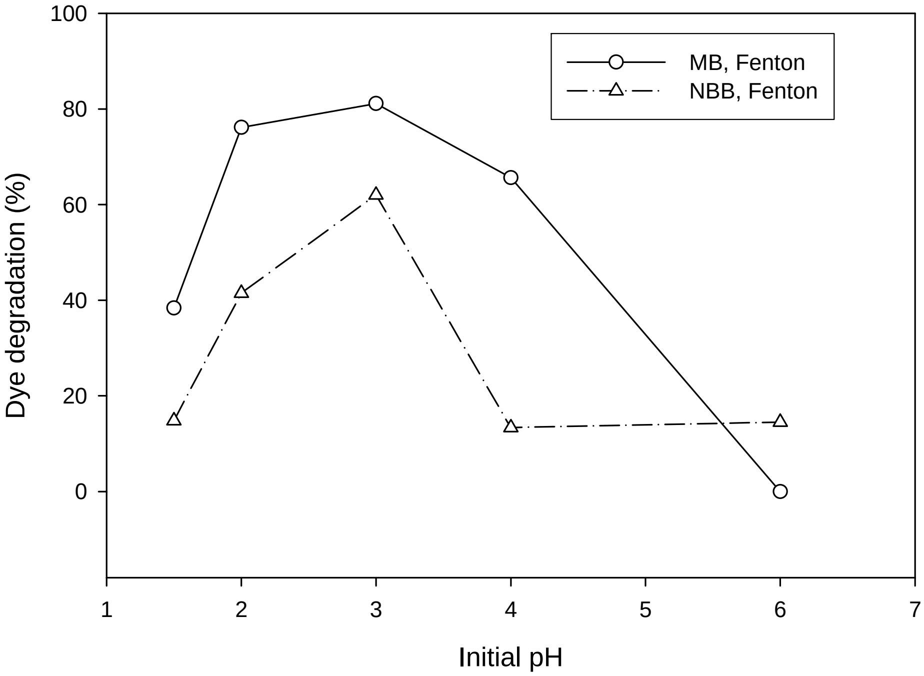


Figure 4. Effect of initial pH on dye degradation.

3.1.2. Effect of H_2O_2 Concentration

The effect of H_2O_2 was studied by increasing the peroxide concentration from 5 x 10^{-6} M to 1 x 10^{-4} M while maintaining all other conditions the same. Figure 3 shows the effect of H_2O_2 on dye degradation. The use of peroxide in the absence of Fe^{2+} showed little or no improvement in dye degradation. However, it was observed that the rate of degradation increased with increase in peroxide concentration. At H_2O_2 concentration of 1 x 10^{-4} M, dye degradation will be 85% and 60% for MB and NBB, respectively.

Some studies [16-18] have reported an optimal peroxide concentration in Fenton oxidation of dyes. Dutta et al. [17] found that at initial $[Fe^{2+}] = 3.58\times10^{-5}$ M and initial $[H_2O_2] < 4.14\times10^{-4}$ M, the rate of decolourisation of methylene blue increased with increasing the initial concentration of hydrogen peroxide. The rate remained almost same for initial H_2O_2 concentration of $4.14\times10^{-4} – 2.94\times10^{-2}$ M. Others reported similar results for different dyes [16, 18, 23]. In our investigation, it is seen that dye degradation keeps increasing as H_2O_2 concentration increases, which is somewhat different from previous observations. In fact, the difference is probably due to the different range of H_2O_2 concentration. The maximum H_2O_2 concentration investigated in this work is much lowers than that of previous reports.

3.1.3. Effect of Solution pH

It is known that H_2O_2 becomes unstable and loses its oxidising potential in alkaline medium. Thus the pH values in this investigation were varied between 1.5 and 6 and Figure 4 presents the effect of pH on dye degradation. As seen that the highest degradation efficiency was observed at pH 3 for both dyes. For MB, dye decolourisation is little at pH 6 while NBB still shows some decolourisation at pH 6.

Many other studies [16, 18, 24-26] also report similar range between 2.5 and 3.5 for maximum dye degradation; hence this pH range seems suitable for the formation of hydroxyl ions, irrespective of what organic compound is being purified. The low performance at higher and lower pH values is attributed to a number of reasons. For pH < 2, 'scavenging effect' [18] play an important role due to the reaction of $^{\cdot}OH$ and H^+ ions and less reactivity of oxonium ion $[H_3O_2]^+$ formed at low pH values. In addition, the formation of complex species $[Fe(H_2O)_6]^{2+}$ at low pH which reacts slower with peroxide than $[Fe(OH)H_2O]^{2+}$ also result in the reduced efficiency [26]. Above pH 3, the reduction in degradation efficiency can be attributed to the hydrolysis of Fe^{3+} into $Fe(OH)_3$ and in this form, iron decomposes H_2O_2 into oxygen and water hence the degradation rate decreases because less hydroxyl radicals are available [14].

3.1.4. Effect of Reaction Temperature

Tests at temperatures varying between 21 and 60 ^{o}C for both dyes were conducted and the results show that an increase in temperature leads to an increase in dye decolourisation up to 60 ^{o}C (Figure 5). At 21 ^{o}C, degradation efficiency was very low, and this increased as the temperature was increased. For two dyes, the effect of temperature on dye degradation seems to be different. For NBB, the increase in temperature led to an increase in degradation efficiency to 94% at 60 ^{o}C. For MB, a maximum efficiency was observed at 40 ^{o}C. At 50 and 60 ^{o}C, no improvement was observed in the overall efficiency; in fact a bit decline was observed at 60 °C, which can be attributed to the thermal decomposition of H_2O_2 into oxygen and water at high temperatures.

Dutta et al. [17] conducted chemical oxidation of methylene blue using a Fenton reaction. A substantial increase in the extent of degradation of the dye was also observed when the reaction temperature was raised from 8 to 26 °C. A further increase in the reaction temperature from 26 to 40 °C resulted in the decrease in the extent of degradation of the dye. Malik and Saha reported that the extent of degradation of direct dyes, Blue 2B (B54) and Red 12B (R31), increases with increase in temperature from 20 to 40 °C. A further increase in the reaction temperature up to 50 °C results in small increase in the extent of dye degradation [23]. Our results are similar to these investigations.

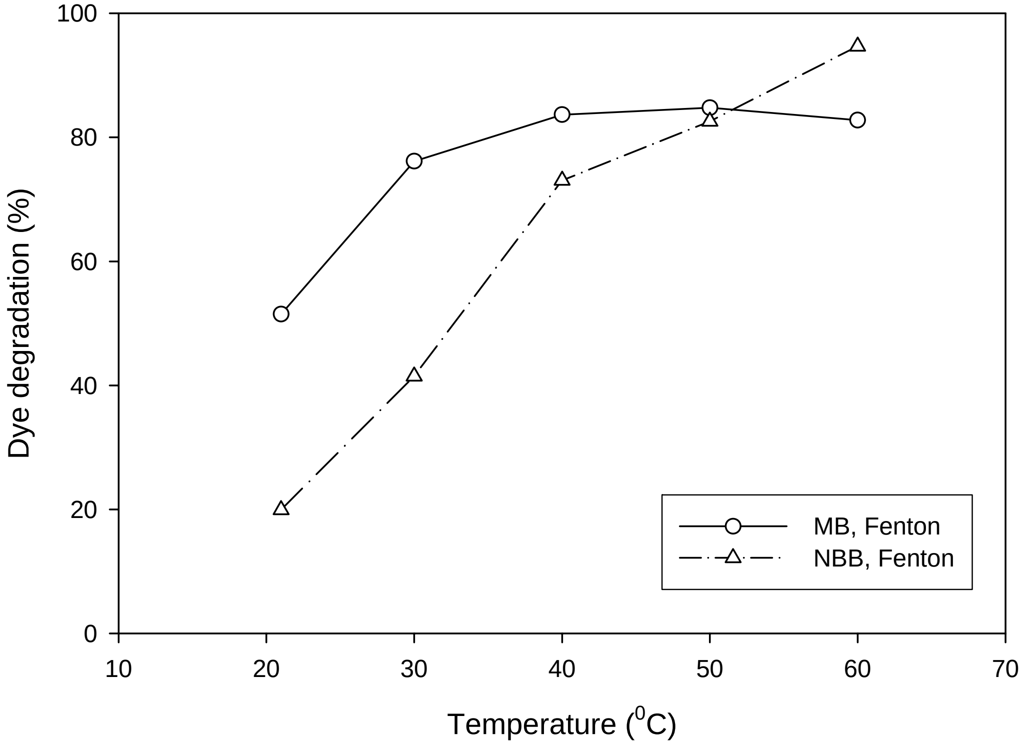


Figure 5. Effect of reaction temperature on dye degradation.

3.2. Comparison of Fenton and Sono-Fenton Reactions for Decolourisation

Figure 6 shows a comparison of decolourisation of MB and NBB under various reactions, sonolysis, Fenton and sono-Fenton reactions. The lowest degradation performances were observed under non-sonic conditions using either H_2O_2 or Fe^{2+} but not with both reactants. Using only H_2O_2, however, yielded better degradation efficiency than using Fe^{2+} and this was observed for both dyes. Using only sonication without Fenton oxidation yielded better results than the two previous processes. This can be attributed to the presence of hydroxyl ions formed during sonication. Sonication of an aerated aqueous solution can yield $^{\bullet}OH$ upon the reactions (3) and following reactions [28].

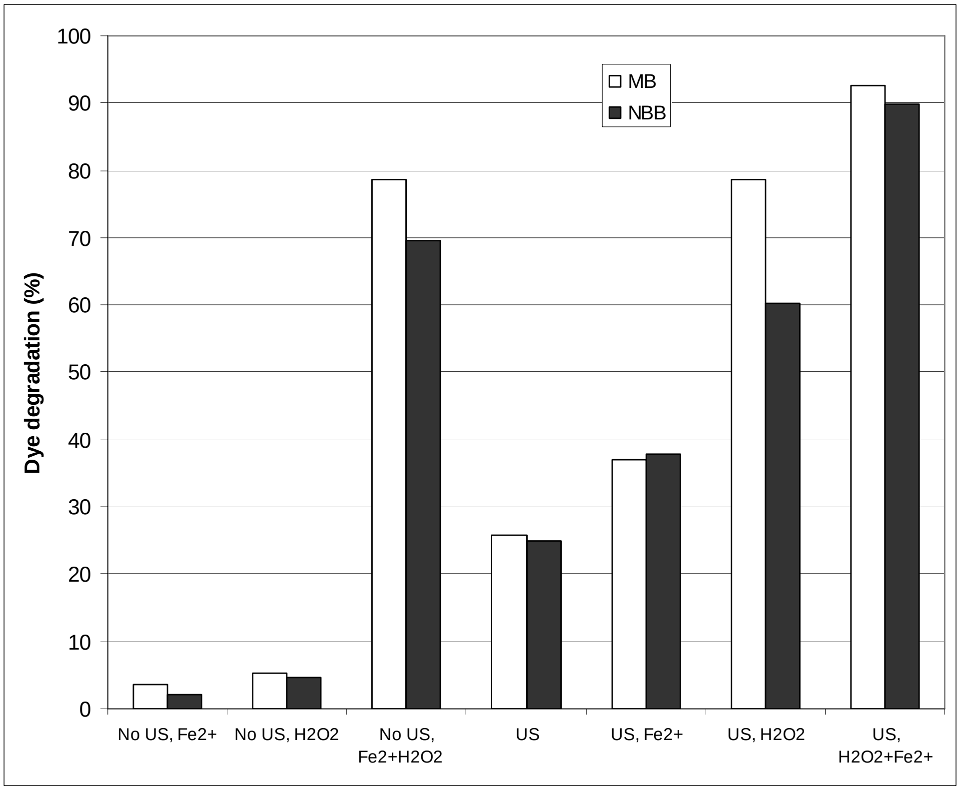


Figure 6. Comparison of dye degradation under different reactions.

$$H_2O_2 + H^{\bullet} \longrightarrow H_2O + OH^{\bullet} \qquad (11)$$

$$H_2O + O \ )))\!\longrightarrow 2\ {}^{\bullet}OH \qquad (12)$$

Degradation efficiency was further increased by combining sonic effect with the presence of either H_2O_2 or Fe^{2+} in solution. The improvements observed on addition of Fe^{2+} to sonication could be attributed to the occurrence of Fenton's oxidation under sonication. For this to happen, H_2O_2 needs to be made available since both Fe^{2+} and H_2O_2 are needed for Fenton's oxidation. This formation of H_2O_2 is made possible via reaction 5. On the other hand, the combined effects of sonication and H_2O_2 are possibly due to enhanced formation of hydroxyl radicals. Again, sonication with only H_2O_2 proved more efficient compared with sonication with only Fe^{2+}.

For Fenton oxidation without sonication, dye decolourisation is much higher than those with the presence of Fe or H_2O_2. The removal efficiencies for two dyes are 80% and 70%, respectively. The combined effects of sonication and Fenton oxidation proved to be the most efficient process. The dye degradation can reach 90% for two dyes. The improvements in decolourisation of combined sonication and Fenton's reaction over Fenton oxidation were 15 and 24 % for MB and NBB, respectively.

3.3. Kinetics of Dye Degradation

Figure 7 shows the dynamic variation of dye degradation during Fenton and sono-Fenton reactions. As seen that the sono-Fenton reaction shows faster reaction rates than the Fenton reaction. For two dyes, decolourisation efficiency in Fenton oxidation is only about 70 % and 43 %, while in sono-Fenton oxidation the efficiency will reach 89% and 84% in 60 min for MB and NBB, respectively. After 2 h, the decolourisation efficiency will be 93% and 90%. Further investigations indicate that dye decolourisation will be completely achieved after 6 h for both dyes. Hsueh et al. [18] investigated Fenton and Fenton-like reactions at low iron concentration (10 mg/L) to oxidise azo dyes and found that 96% decolourisation would be achieved in 1 h. Our results indicate that using sonic-Fenton oxidation, similar efficiency could be obtained at even lower Fenton reagent concentration.

The Fenton oxidation of the dye can be represented by the following nth order reaction kinetics

$$\frac{dC}{dt} = -kC^n \tag{13}$$

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

$$C = C_0 \exp(-k_1 t) \tag{14}$$

in which C_0 is the initial dye concentration and k_1 is the first-order reaction rate constant. For a second-order reaction, the integrated equation becomes

$$C = \frac{C_0}{1 + k_2 C_0 t} \tag{15}$$

and k_2 is the second-order rate constant.

The kinetic parameters calculated from the above two models are presented in Table 1. Figure 7 also shows the first-order kinetic curves for the Fenton and sono-Fenton reactions. It is seen that the first-order kinetics will produce better results than that of the second-order kinetics evidenced from the regression coefficients. The reaction rate for sono-Fenton reaction is always higher than the Fenton reaction. Also the reaction rate for MB is generally higher than that of NBB.

Several investigations on dye degradation in Fenton reactions have demonstrated that reaction kinetics of Fenton oxidation follows a pseudo-first order plot [16, 29, 30]. Wang et al. [7] investigated sonochemical degradation kinetics of methyl violet in aqueous solutions and found the reaction to be the first-order and the degradation rate coefficient is 1.35×10^{-2} min^{-1}. Lall et al. [10] also reported a first-order kinetics for decolourisation of reactive blue 19 in ozonation, ultrasound, and ultrasound-enhanced ozonation processes.

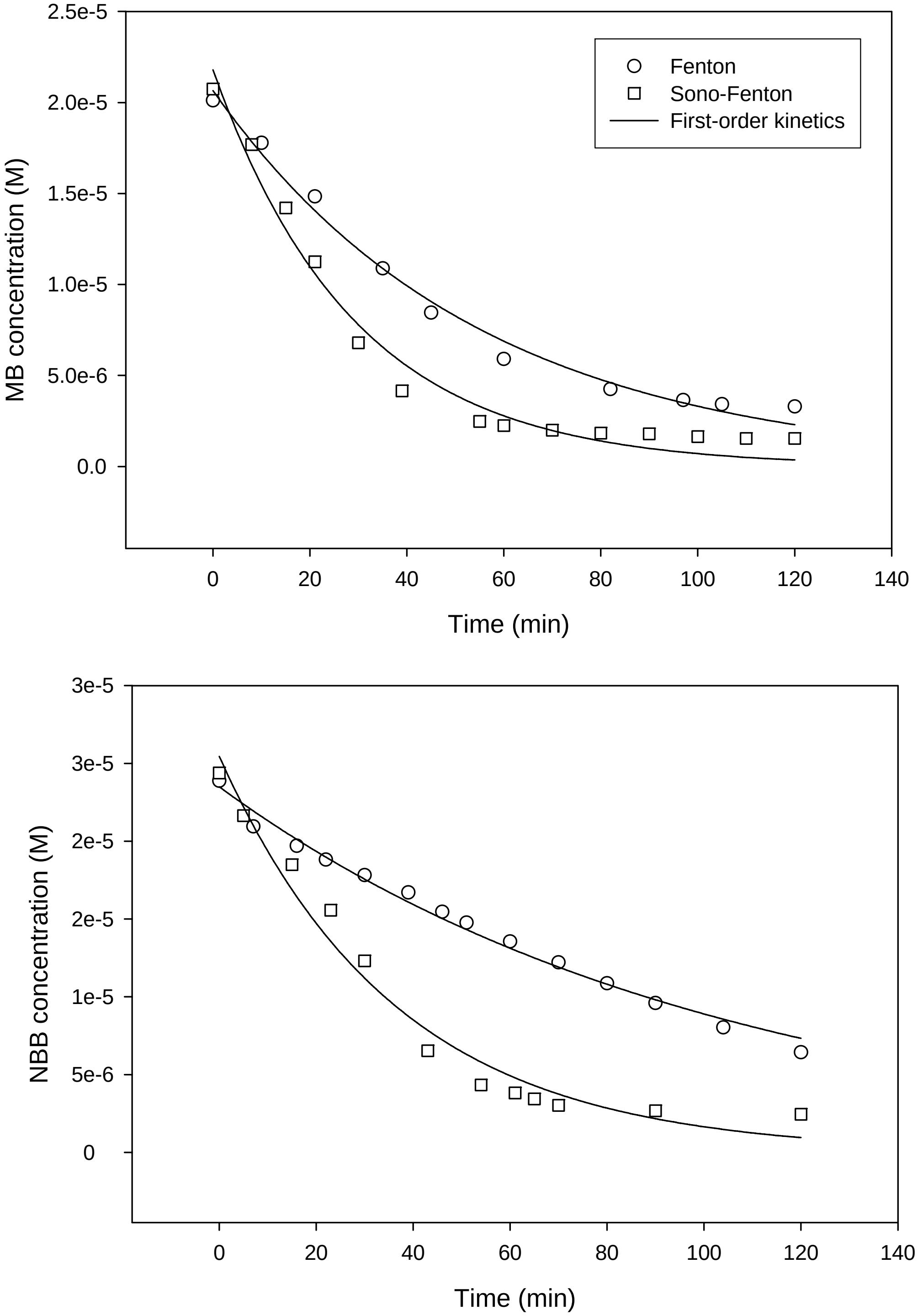


Figure 7. Kinetics of dye degradation in Fenton and sono-Fention reactions.

Table 1. Kinetic parameters of dye degradation in Fenton and sono-Fenton reactions

System	Dye	First-order kinetics			Second-order kinetics		
		C_0 (M)	k_1(min^{-1})	R^2	C_0 (M)	k_2 (M^{-1}min^{-1}	R^2
Fenton	MB	2.06 x10^{-5}	0.0183	0.989	2.16 x10^{-5}	1.59 x10^{3}	0.947
Sonic Fenton	MB	2.18 x10^{-5}	0.0343	0.978	2.27 x10^{-5}	3.12 x10^{3}	0.911
Fenton	NBB	2.35 x10^{-5}	9.70 x10^{-3}	0.989	2.44 x10^{-5}	6.08 x10^{2}	0.956
Sonic Fenton	NBB	2.54 x10^{-5}	0.0274	0.976	2.64 x10^{-5}	2.01 x10^{3}	0.906

3.4. Dye Degradation in Fenton-like Reactions

As in the Fenton oxidation several parameters including Fe^{3+} concentration, H_2O_2 concentration, solution pH and temperature influence the reaction rate and decolourisation efficiency and were also investigated.

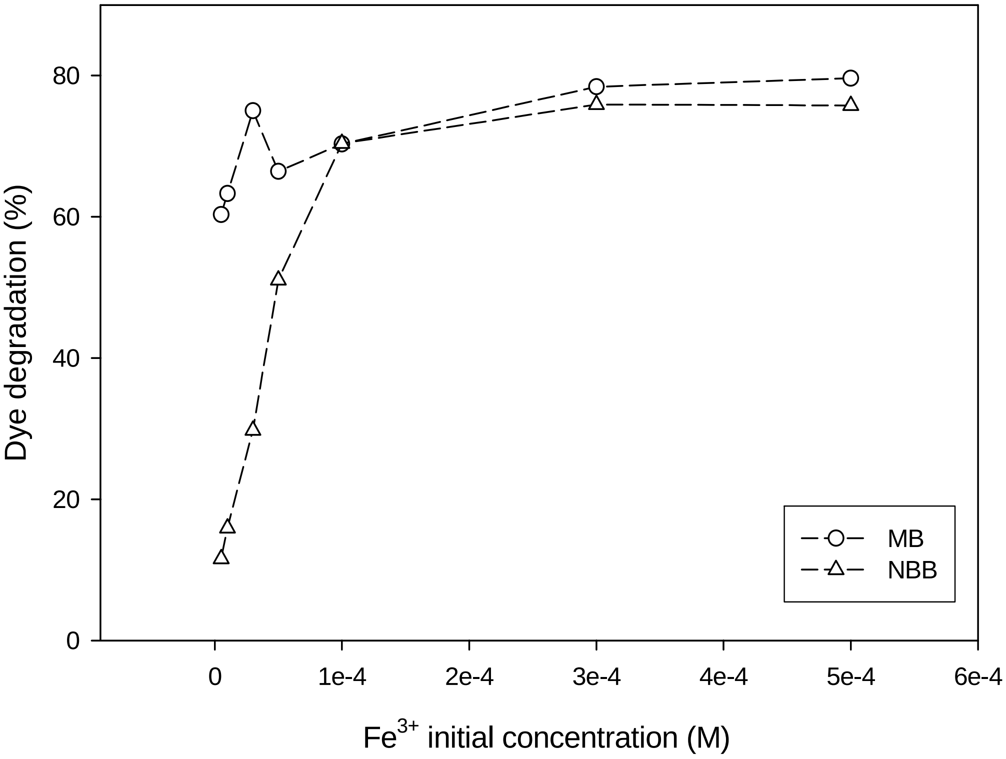


Figure 8. Effect of initial Fe^{3+} concentration on dye degradation.

3.4.1. Effect of Fe^{3+} Concentration

Figure 8 illustrates the overall efficiency of dye degradation at 120 min with the variation of Fe^{3+} initial concentration. For Fenton-like reactions, little degradation was observed for both dyes in the absence of H_2O_2. When Fe^{3+} is present, dye degradation is significant. From the Figure it is seen that the rate of dye decolourisation increases with the increasing Fe concentration and reaches equilibrium of 75% and 70% for MB and NBB, respectively, at Fe^{3+} concentration of 3×10^{-4} M. At even higher Fe^{3+} concentration, little improvement is achieved in decolourisation efficiency. This is attributed to the limited availability of H_2O_2. For two dyes, it is also seen that MB degradation is generally higher than NBB.

3.4.2. Effect of H_2O_2 Concentration

The effect of H_2O_2 on decolourisation efficiency was studied by increasing the peroxide concentration between 5×10^{-6} M and 1×10^{-4} M while maintaining all other conditions the same. Figure 9 shows the effect of H_2O_2 on dye degradation. The use of peroxide in the absence of Fe^{3+} showed little or no improvement in dye degradation. However, it was observed that the rate of degradation increased with increase in peroxide concentration. For NBB, the increase in H_2O_2 concentration seems to have less effect on dye degradation. The colourisation efficiency is only 18% at 1×10^{-4} M H_2O_2 concentration while for MB, the decolourisation efficiency is 80%. Some studies [16, 18] reported an optimal peroxide concentration, above which degradation efficiency was reduced due to scavenging effect. In Fenton reaction, H_2O_2 could act as a scavenger of $^{\bullet}OH$ and produce a less potent perhydroxyl radical ($HO_2^{\bullet}$) as shown in R10 [18].

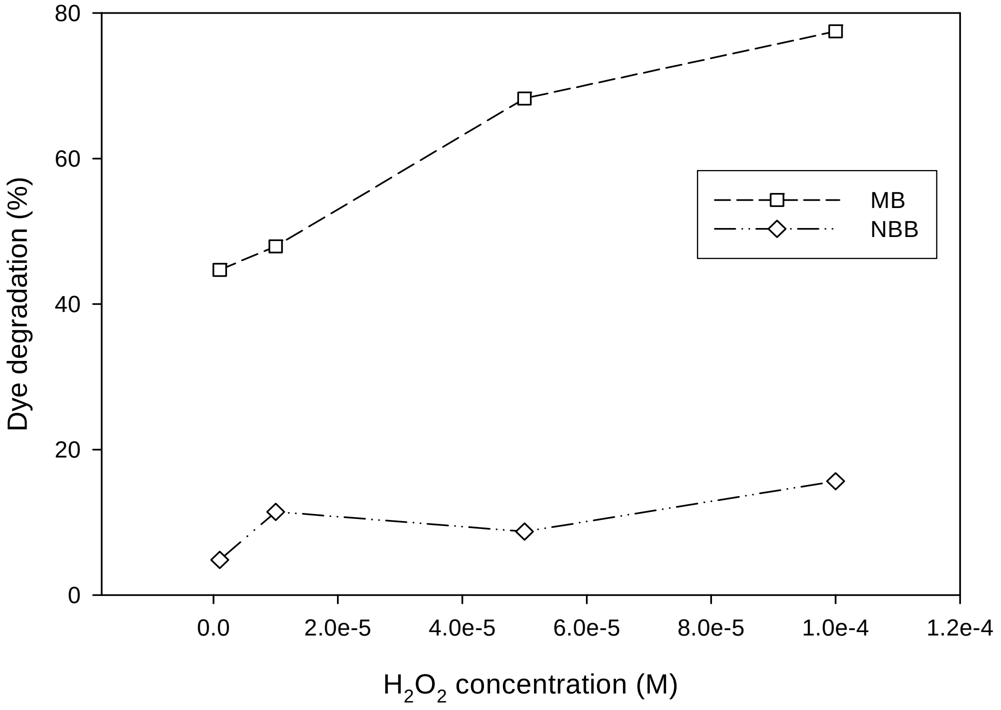


Figure 9. Effect of H_2O_2 concentration on dye degradation.

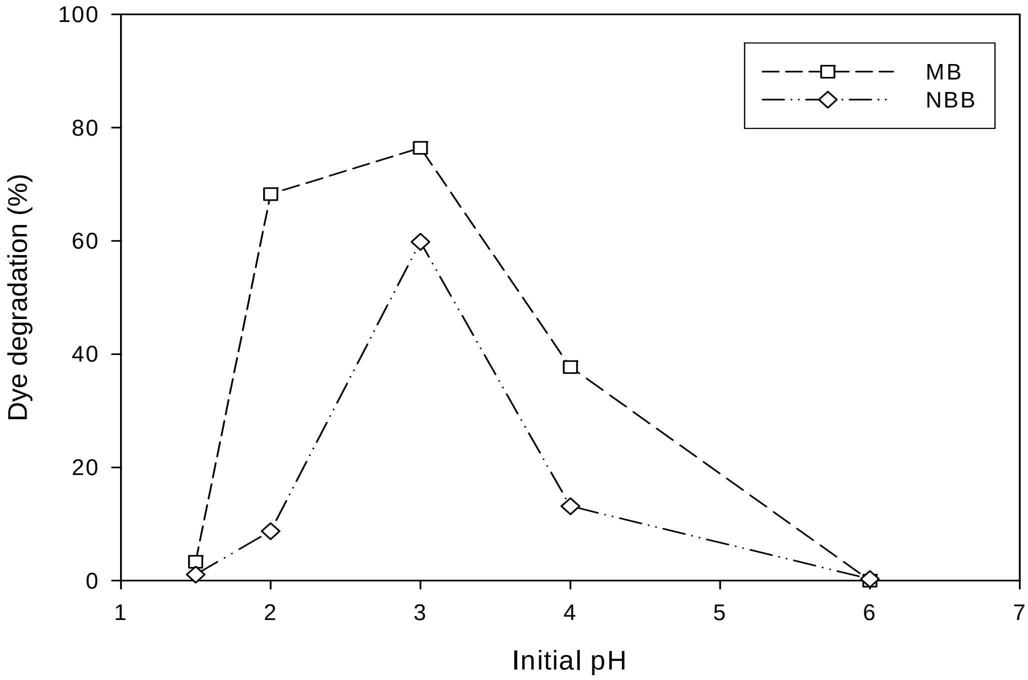


Figure 10. Effect of initial pH on dye degradation.

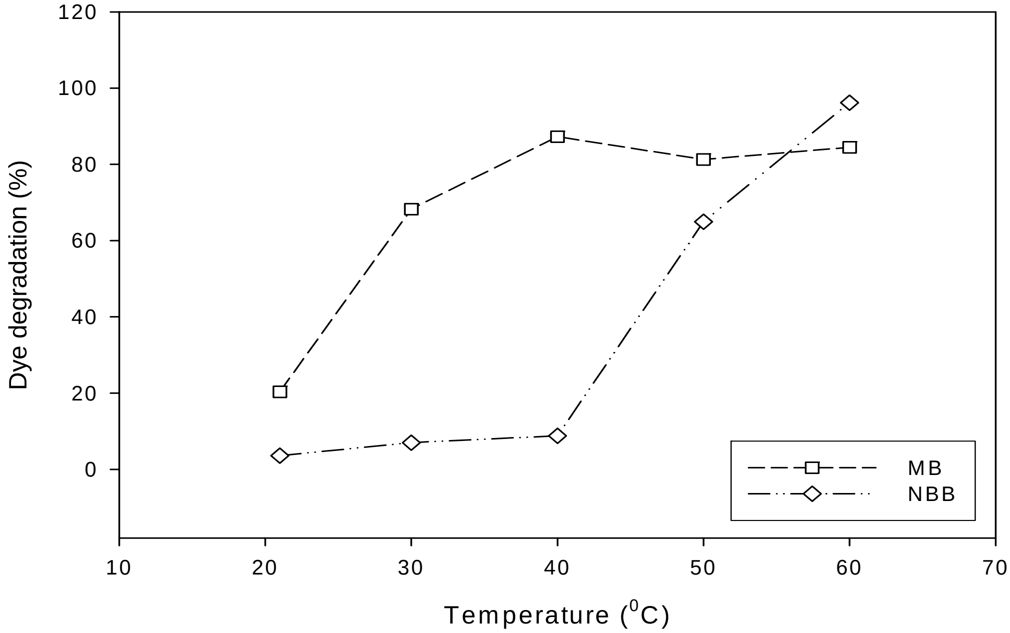


Figure 11. Effect of reaction temperature on dye degradation.

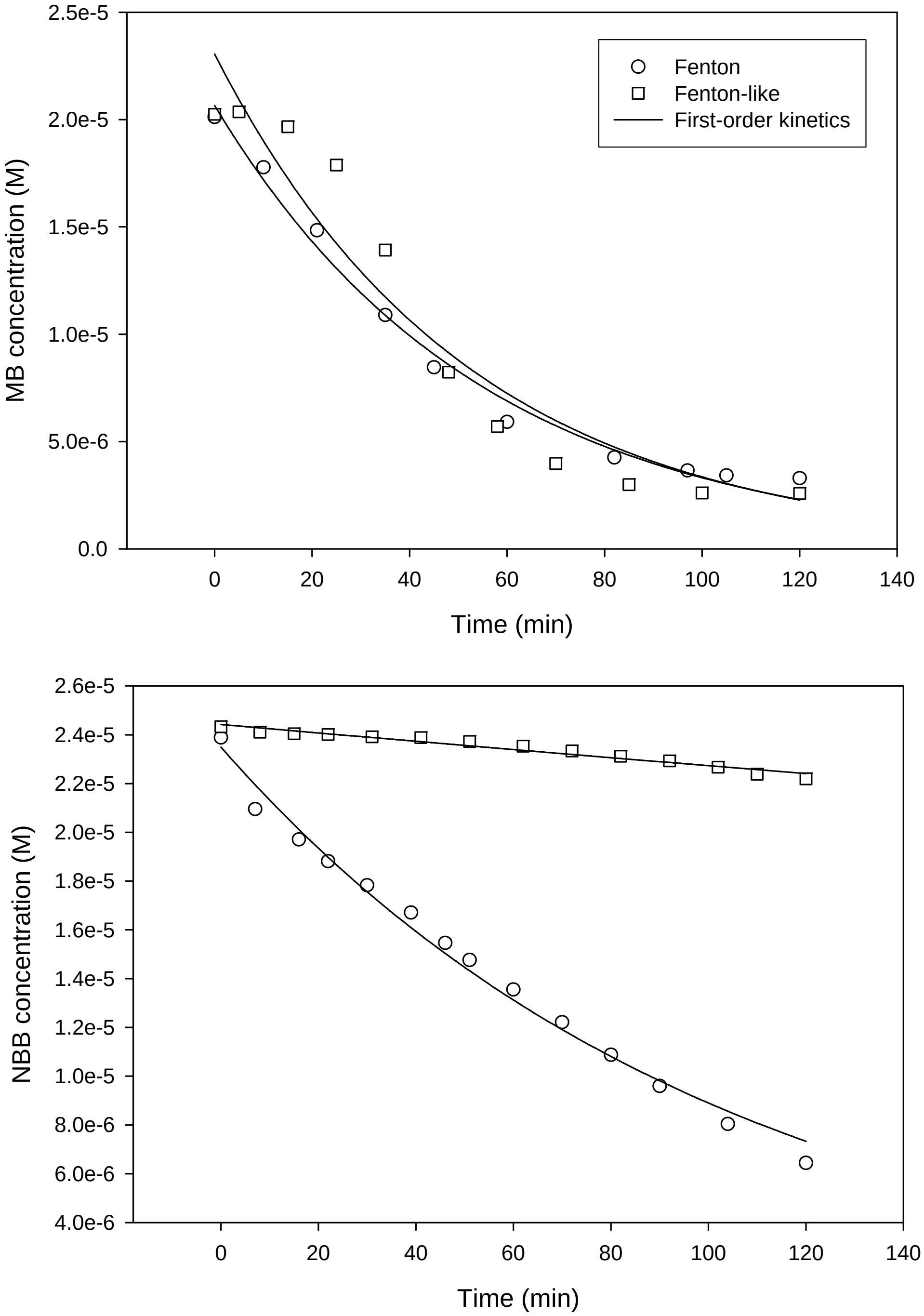


Figure 12. Dynamic dye degradation in Fenton and Fenton-like reactions.

3.4.3. Effect of Solution pH

Figure 10 presents the effect of pH between 1.5 and 6 on dye degradation. As seen that the highest degradation efficiency was observed at pH 3 for both dyes. Lower or higher pH will not favour dye degradation. At pH 6, dye decolourisation is almost zero for two dyes.

Many studies [14-19] also report similar range between 2.5 and 4 for various organic compounds in Fenton and Fenton-like reactions. For pH < 2, $^{\cdot}OH$ will react with H^+ ions present in acidic conditions, playing the ‘scavenging effect’ [18], and oxonium ion $[H_3O_2]^+$ is also formed at low pH, which shows reduced reactivity. In addition, H_2O_2 is stabilised at low pH and this inhibits the production of the intermediate ion HO_2^-, which reacts with Fe^{3+} to produce $Fe\text{-}OOH^{2+}$. At high pH, decolorisation efficiency is reduced because of the reduction in the solubility of Fe^{2+} and Fe^{3+} and the formation of $Fe(OH)_3$ and $Fe_2O_3{\cdot}nH_2O$, resulting in the decrease in Fe^{3+} ions in the solution and subsequently in a reduction in the concentration of Fe^{2+} ions, which are more efficient than Fe^{3+} ions because they directly produce $OH\cdot$ [19]. Also, if the pH is too high, the iron precipitates as $Fe(OH)_3$ and catalytically decomposes the H_2O_2 to oxygen, which reduces its concentration in the solution, potentially creating a hazardous situation [20].

3.4.4. Effect of Reaction Temperature

Figure 11 shows the dye decolorisation efficiency at varying temperatures between 21 and 60 ^{o}C. As shown that temperature is usually presenting a positive effect and an increase in temperature results in an increase in dye decolourisation up to 60 ^{o}C. At 21 ^{o}C, degradation efficiency is very low at 20% and 3% for MB and NBB, respectively. For two dyes, the effect of temperature on dye degradation seems to be different. For NBB, colourisation efficiency shows lower changes at temperatures below 40 ^{o}C but increases significantly at higher temperatures. The degradation efficiency will reach 96% at 60 ^{o}C. For MB, a maximum efficiency can be observed at 40 ^{o}C. At 50 and 60 ^{o}C, no improvement in the overall efficiency is observed; in fact a bit decline is observed at 50 - 60 ^{o}C, which can be attributed to the thermal decomposition of H_2O_2 into oxygen and water at high temperatures.

3.5. Comparison of Fenton and Fenton-like Oxidation for Decolourisation

Figure 12 shows the dye degradation as a function of time in Fenton and Fenton-like oxidation. For MB, the initial dye degradation rate in Fenton oxidation is faster than that of Fenton-like oxidation. However, the dye decolourisation efficiency after 2 h is almost the same, reaching 84% and 87% for Fenton and Fenton-like oxidation, respectively. For NBB, dye degradation in two reactions is quite different. Dye degradation rate and efficiency are much higher in Fenton reaction. The efficiencies for two oxidations are 73% and 9%, respectively, all lower than MB.

It has been known that Fenton-like reaction rate is usually lower than that of Fenton reaction, which is also proven in this investigation. However, the dye decolourisation efficiency for MB shows the similar results. Hsueh et al. [18] investigated Fenton and Fenton-like reactions for degradation of azo dyes and reported the similar phenomenon. In the initial stage of reaction (< 30 min), the dye decolorisation rate of Fenton reaction exceeds than that of Fenton-like one. However, when the reactions time over 60 min, there shows almost no difference of the dye decolorisation efficiencies between Fenton and Fenton-like reaction. The reason is that almost all of Fe^{2+} was converted to Fe^{3+} at this time. Ntampegliotis et al. [19] compared the decolorisation kinetics of three commercially used Procion H-exl dyes and reported that use of Fenton reagent is more efficient than the use of Fenton-like reagent. Regarding decolorisation efficiency after a 10 min reaction time, the two methods achieve nearly identical decolorisation efficiencies in the pH range between 3 and 5. The Fenton reagent gives better results at a pH equal to 2 and at a pH higher than 5. At pH 3, decolourisation efficiencies are about 84% for both methods, while at pH 2, decolourisation efficiencies are 94 and 100% for the Fenton-like and Fenton processes, respectively. All these results suggest that decolourisation efficiency would be achieved for Fenton and Fenton-like reactions for some types of dyes.

3.6. Comparison of Fenton-like and Sono-Fenton-like Reactions for Decolourisation

Figure 13 shows a comparison of decolourisation of MB and NBB under various reactions, sonolysis, Fenton-like and sono-Fenton-like reactions. The lowest degradation performances were observed under non-sonic conditions using either H_2O_2 or Fe^{3+}. The degradation efficiencies for two dyes are lower than 5%. Using only H_2O_2, however, yielded better degradation efficiency than using Fe^{3+} for both dyes. Using only sonication without Fenton oxidation yielded further better results than the two previous processes. The degradation efficiency is above 20% for MB and NBB. This can be attributed to the presence of hydroxyl ions formed during sonication. Sonication of an aerated aqueous solution can yield $^{\bullet}OH$ upon the reactions (3) and following reactions [21].

It is noted that degradation efficiency was further increased by combining sonic effects with either H_2O_2 or Fe^{3+} in solution. The decolourisation efficiency is significant under sonolysis combined with H_2O_2 and the efficiencies for MB and NBB are 80% and 60%, respectively. The improvements to sonication observed on addition of Fe^{3+} could be attributed to the occurrence of Fenton-like oxidation under sonication. For this to happen, H_2O_2 needs to be made available since both Fe^{3+} and H_2O_2 are needed for Fenton-like oxidation. On the other hand, the combined effects of sonication and H_2O_2 are due to enhanced formation of hydroxyl radicals. Again, sonication with only H_2O_2 proved more efficient compared to sonication with only Fe^{3+}. From the Figure, it is seen that the removal efficiencies for two dyes are 68% and 9%, respectively, in Fenton-like reaction. The combined effect of sonication and Fenton-like oxidation produces the highest efficiency for dye decolourisation. The dye degradation can reach 93% for two dyes. The improvements in decolourisation of combined sonication and Fenton-like reaction over Fenton-like only oxidation is 37% for MB, but 10 times higher for NBB.

3.7. Kinetics of Dye Degradation in Sonolysis and Sono-Fenton-like Reaction

Figure 14 shows the dynamic variation of dye degradation during sonolysis and combined sonolysis with Fenton and Fenton-like reactions. As seen that the combined sonolysis with Fenton reagents, Fe^{2+} or Fe^{3+}, produced similar reaction rate and decolourisation efficiency for two dyes. Sonolysis with H_2O_2 exhibits better reaction rate and efficiency than sono-Fe combination. Sono-Fenton and sono-Fentonlike also present similar reaction rate and decolourisation efficiency. After 1 h, decolourisation with two systems can arrive at 90% for two dyes.

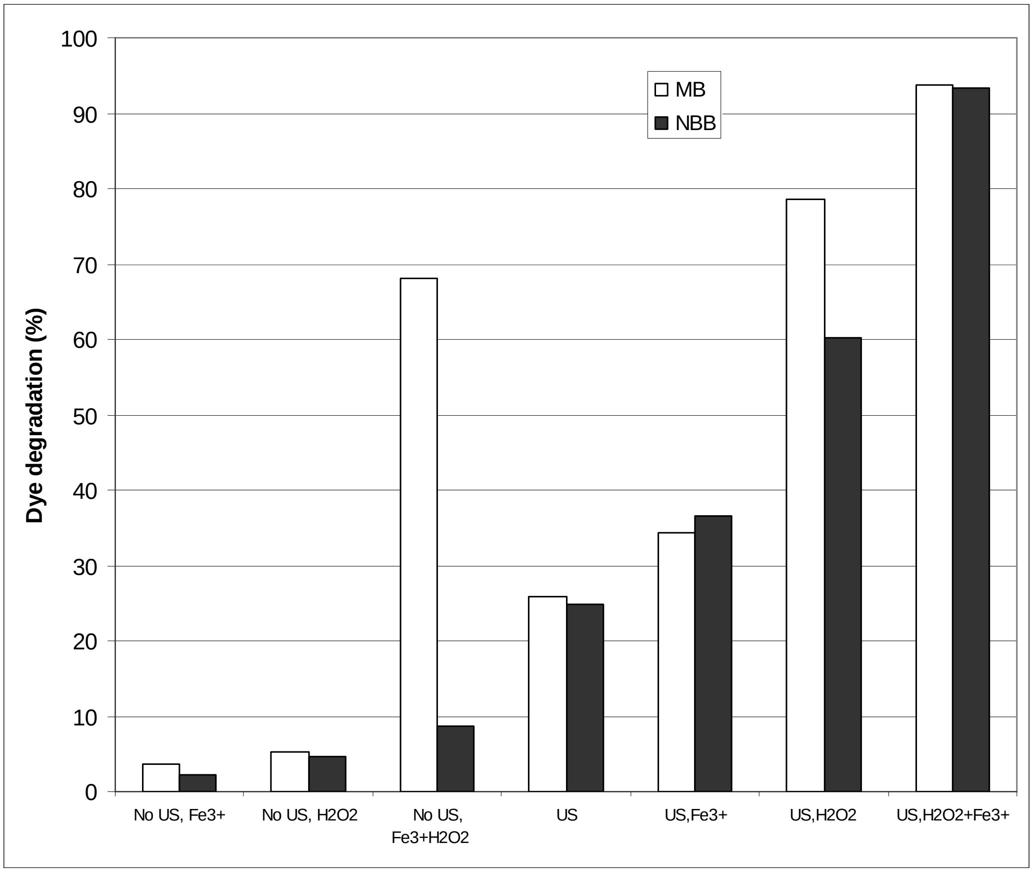


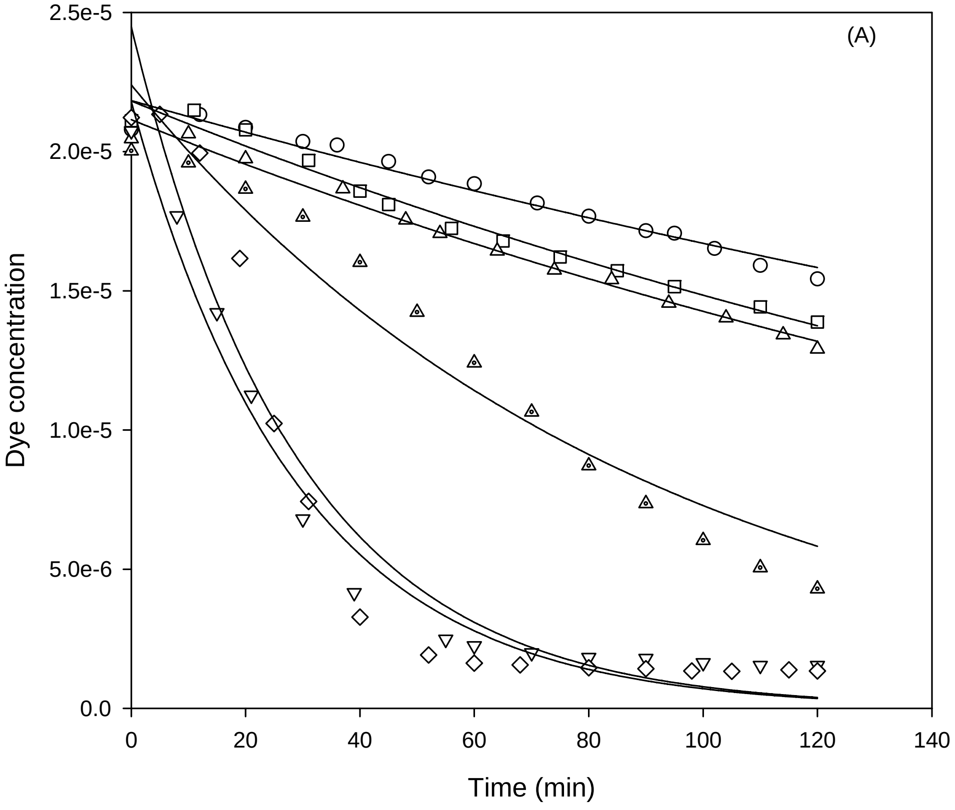
Figure 13. Comparison of dye degradation under none sonic and sonic promoted reactions.

The kinetic parameters calculated from the first-order and second-order kinetic models are presented in Table 2. Figure 14 also shows the first-order kinetic curves for the sono-Fenton and sono-Fentonlike reactions. It is seen that the first-order kinetics will produce better results than that of the second-order kinetics evidenced from the regression coefficients. The reaction rate constants for sono-Fe^{2+} and sono-Fe^{3+} are close each other and the rate constants for sono-Fenton and sono-Fenton-like reaction are also much similar. The order of reaction rate for all sonic based reactions is sonolysis < sono-Fe^{3+} ≈ sono-Fe^{2+} < sono-H_2O_2 < sono-Fenton-like ≈ sono-Fenton. From the table, one can also see that the reaction rate constant for MB is generally higher than that of NBB.

Several investigations on dye degradation in Fenton reactions have demonstrated that reaction kinetics of Fenton oxidation follows a pseudo-first order plot [16, 22, 23]. Wang et al. [7] investigated sonochemical degradation kinetics of methyl violet in aqueous solutions and reported the first-order kinetics with the degradation rate coefficient of 1.35×10^{-2} min^{-1}. Lall et al. [10] also found a first-order kinetics for decolourisation of reactive blue 19 in ozonation, ultrasound, and ultrasound-enhanced ozonation processes. Thus, our results are similar to the previous investigations.

Table 2. Kinetic parameters of dye degradation in Fenton and sono-Fenton reactions

System	Dye	First-order kinetics			Second-order kinetics		
		C_0 (M)	k_1(min^{-1})	R^2	C_0 (M)	k_2 (M^{-1} min^{-1})	R^2
Sonolysis	MB	2.18×10^{-5}	2.68×10^{-3}	0.964	2.19×10^{-5}	140.5	0.949
Sono-Fe^{2+}	MB	2.11×10^{-5}	3.94×10^{-3}	0.989	2.27×10^{-5}	228.2	0.977
Sono-Fe^{3+}	MB	2.18×10^{-5}	3.85×10^{-3}	0.980	2.21×10^{-5}	215.8	0.976
Sono-H_2O_2	MB	2.24×10^{-5}	0.0112	0.944	2.27×10^{-5}	756.2	0.859
Sono-Fenton	MB	2.18×10^{-5}	0.0343	0.978	2.27×10^{-5}	3.12×10^{3}	0.911
Sono-Fenton-like	MB	2.45×10^{-5}	0.0345	0.941	2.49×10^{-5}	2.73×10^{3}	0.840
Sonolysis	NBB	2.24×10^{-5}	2.19×10^{-3}	0.972	2.25×10^{-5}	111.2	0.980
Sono-Fe^{2+}	NBB	2.42×10^{-5}	4.25×10^{-3}	0.970	2.47×10^{-5}	222.3	0.988
Sono-Fe^{3+}	NBB	2.45×10^{-5}	3.95×10^{-3}	0.985	2.48×10^{-5}	200.4	0.994
Sono-H_2O_2	NBB	2.55×10^{-5}	6.51×10^{-3}	0.968	2.59×10^{-5}	341.5	0.934
Sono-Fenton	NBB	2.55×10^{-5}	0.0274	0.976	2.64×10^{-5}	2.01×10^{3}	0.906
Sono-Fenton-like	NBB	2.70×10^{-5}	0.0252	0.973	2.80×10^{-5}	1.71×10^{3}	0.885



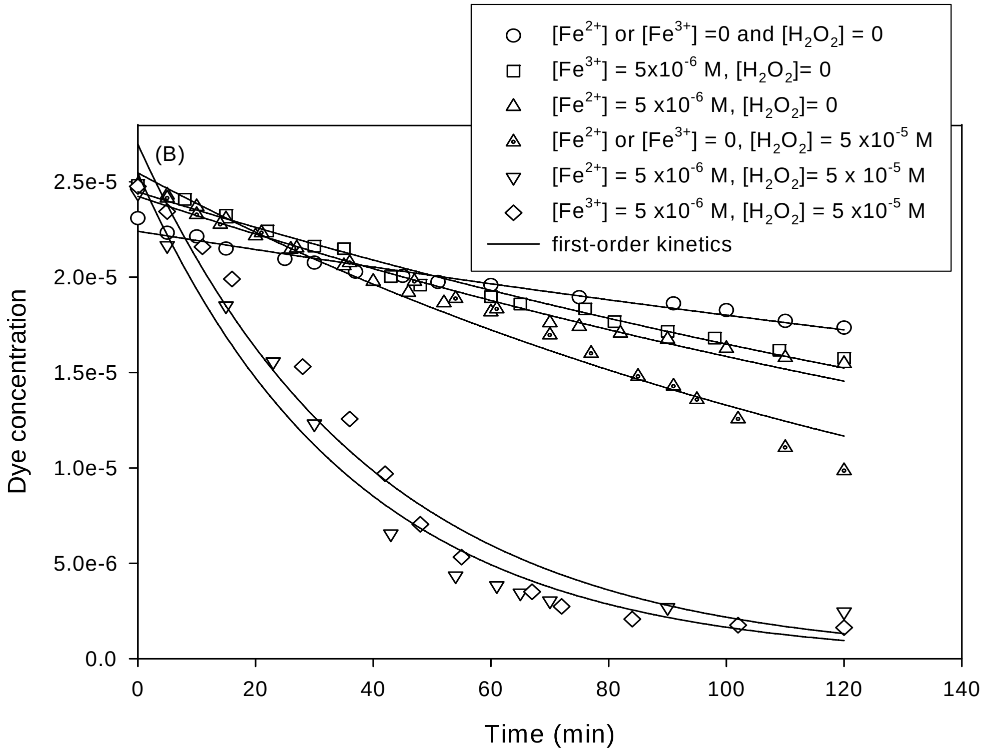


Figure 14. Kinetics of dye degradation in sonolysis, sono-Fenton, and son-Fentonlike reactions.

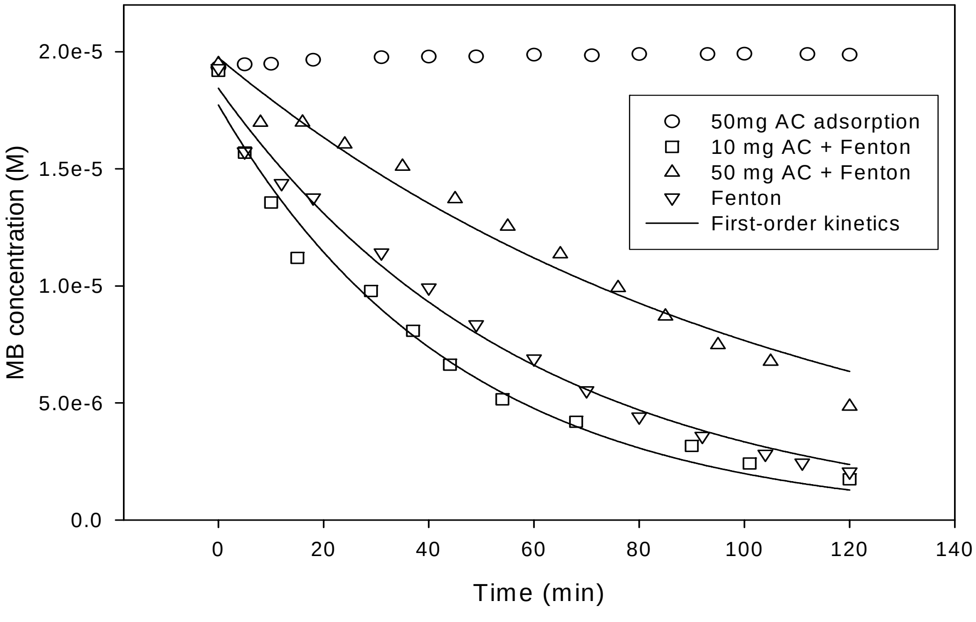


Figure 15. MB decolourisation in adsorption, Fenton oxidation, and combined adsorption with Fenton oxidation.

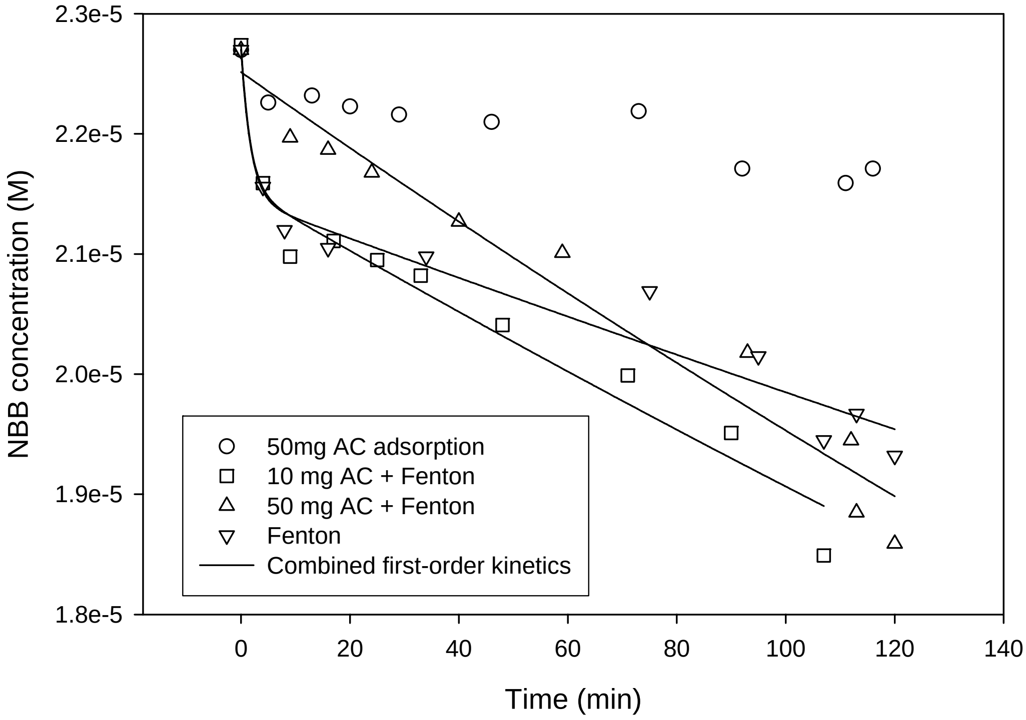


Figure 16. NBB decolourisation in adsorption, Fenton oxidation, and combined adsorption with Fenton oxidation.

3.8. Effect of Activated Carbon in Fenton Oxidation on Dye Degradation

Figure 15 presents MB decolourisation with time in carbon adsorption, Fenton oxidation, and combined adsorption and Fenton oxidation. As seen that dye concentration does not show any changes during 120 min when only activated carbon is present in the solution. This suggests that no adsorption of MB occurs on activated carbon during the period of time. On the other hands, dye concentration will significantly decrease during Fenton oxidation. After 120 min, dye degradation efficiency will achieve at 89%. If activated carbon is present with Fenton reagents in the solution, dye degradation rate is different depending on the amount of activated carbon. For low amount of activated carbon, dye degradation rate is increased and the efficiency is slight higher at 91% after 120 min. For the higher load of activated carbon, dye degradation is, however, decreased and the degradation efficiency is significantly reduced to 75% at 120 min.

Figure 16 illustrates NBB decolourisation with time in carbon adsorption, Fenton oxidation, and combined adsorption and Fenton oxidation. It is seen that NBB degradation is quite different from MB. Unlike the case of MB, activated carbon shows a faster adsorption at initial stage and continuous adsorption with dye decolourisation of 5% at 120 min. Fenton oxidation can also result in dye degradation and the efficiency is greater than carbon adsorption. But compared with MB, decolourisation rate and efficiency of Fenton oxidation are all lower. At 120 min, dye degradation efficiency is 15%. When activated carbon is present with Fenton reagents, dye degradation presents similar behaviour to MB. At 10 mg activated carbon, decolourisation rate and efficiency are all enhanced somewhat and the efficiency is 19% at 120 min. At 50 mg activated carbon, decolourisation rate is reduced but efficiency shows an increase at 18% after 120 min.

The presence of activated carbon in Fenton oxidation will produce two effects. One is adsorption of organic compounds and metal ions in the solution on activated carbon and the other is catalytic reaction of carbon with H_2O_2. It is well known that activated carbon has high adsorption capacity for Fe ions. Also it has been reported that carbon is a catalyst for H_2O_2 decomposition [31-33]. This process can be decsribed in the following equations.

$$\text{AC-OH} + H^+OOH^- \rightarrow \text{AC-OOH} + H_2O \tag{16}$$

$$\text{AC-OOH} + H_2O_2 \rightarrow \text{AC-OH} + H_2O + O_2 \tag{17}$$

During the process, the surface hydroxyl groups on activated carbon react with a hydrogen peroxide anion to produce carbon surface peroxide, which has an increased oxidation potential, and then is further reacted with another H_2O_2, causing H_2O_2 decomposition to release oxygen and regeneration of the carbon surface [31]. Thus, this process results in the consumption of H_2O_2 in the solution.

On the other hand, activated carbon and H_2O_2 can react to produce free radicals via the Haber–Weiss mechanism. AC is believed to function as an electron-transfer catalyst with AC and AC^+ as the oxidised and reduced catalyst states[31]:

$$AC + H_2O_2 \rightarrow AC^+ + OH^- + OH\bullet \tag{18}$$

$$AC^+ + H_2O_2 \rightarrow AC + HO_2\bullet + H^+ \tag{19}$$

In this process, the produced free radicals, $OH\bullet$ and $HO_2\bullet$, will favour the organic decomposition. Therefore, in Fenton oxidation of dyes, the presence of activated carbon will in one way play adsorption role by adsorbing Fe^{2+} or Fe^{3+} on carbon surface, inhibiting the homogeneous Fenton oxidation of dye. On the other hand, activated carbon can either produce hydroxide free radicals via reactions with H_2O_2 (Eqs. (18) and (19)), which will promote homogeneous Fenton oxidation of dyes, or consume H_2O_2 to produce O_2 (Eqs. (16) and (17)), inhibing oxidation of dye. These two effects will compensate each other. At the case of low loading of activated carbon in solution, the adsorption rate is slow and thus most of Fe^{2+}/Fe^{3+} ions are still presence in the solution, making the homogeneous Fenton oxidation dominates the dye oxidation process. In addition, activated carbon can induce additional formation of hydroxide radicals enhancing the dye decolourisation rate and efficiency. However, when more amount of activated carbon is present in the solution, adsorption of Fe ions on activated carbon will be significant, resulting in lower concentration of Fe ions and thus slower reaction rate of homogeneous Fenton oxidation. Even though the adsorbed Fe ions on activated carbon can induce heterogeneous Fenton oxidation, however, the rate is usually much slow compared with homogeneous Fenton reaction. Meanwhile, the rate of H_2O_2 decomposition to radicals is slow and can not compensate the loss of rate in Fenton oxidation, leading to reduced dye decolourisation rate. Georgi and Kopinke [31] investigated the interaction of adsorption and catalytic reactions in water decontamination processes using

AC and H_2O_2 and reported that sorption on AC has an adverse effect on the oxidation of organic compounds via $OH\bullet$ radicals, even though the radicals are formed directly on the AC surface, i.e. in close proximity to the sorbed organic compounds.

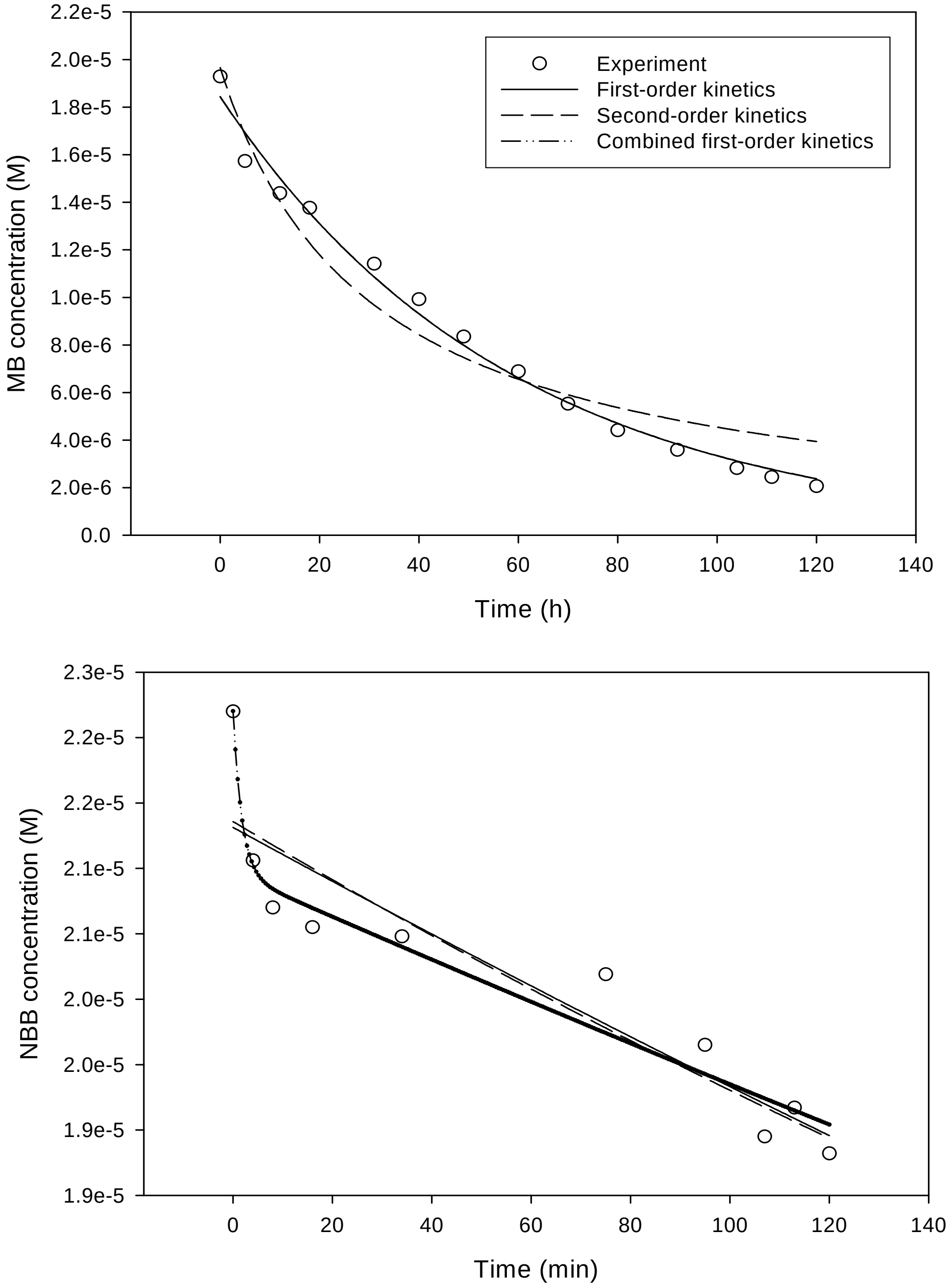


Figure 17. Comparison of kinetics of dye degradation in Fenton oxidation.

3.8.1. Decolourisation Kinetics of Fenton Reaction under Activated Carbon

Two kinetic models, the first-order and second-order kinetics will be evaluated for the dynamic decolourisation of two dyes, which have been discussed before. In addition, a combined first-order reaction can be described as follows

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

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. This model describes parallel reactions occurring at the same time.

Figure 17 shows a comparison of three kinetic models for the experimental results of Fenton oxidation of two dyes. The parameters obtained from the curve fitting are presented in Table 3. For MB, the first-order kinetics will show better fitting results than the second-order kinetics and the combined first-order kinetics is the same as the first-order kinetics. However, for NBB, the first-order and second-order kinetics are much similar and the combined first-order rate model will be the best in simulation of experimental results.

The kinetics of dye degradation in Fenton oxidation has been reported in some investigations. Several investigators have found that the Fenton reaction for dye degradation follows the pseudo first-order kinetics [16, 32, 33]. However, Malik and Saha [26] investigated the oxidation of direct dyes in Fenton reaction and found that the entire degradation reaction could be divided into a two-stage reaction. In the first stage, dyes were decomposed quickly, referred to Fe^{2+}/H_2O_2 stage. The second stage of the reaction may be referred to as the Fe^{3+}/H_2O_2 stage.

Table 4 compares the kinetic results of dye decolourisation using Fenton oxidation without activated carbon and in the presence of activated carbon in solution. It is seen from the values of kinetic rate constant that MB decolourisation rate constant is 0.0171, 0.0219 and 0.0946 min^{-1} for Fenton oxidation, 10 mgAC+Fenton, and 50 mgAC+Fenton, respectively. For NBB, the decolourisation kinetics for Fenton and 10 mgAC+Fenton can be described by the combined first-order kinetics and the rate constants are also higher in case of 10 mgAC+Fenton. However, the two rate constants for 50 mgAC+Fenton are the same, which suggests that it can be simplified to first-order kinetics.

Table 3. Kinetic parameters for dye degradation in Fenton oxidation

Dye	First-order			Second-order			Combined first-order				
	C_0 (M)	k_1 (min^{-1})	R^2	C_0 (M)	k_2 (M^{-1} min^{-1})	R^2	C_{01} (M)	k_1 (min^{-1})	C_{02} (M)	k_2 (min^{-1})	R^2
MB	1.84×10^{-5}	0.0171	0.990	1.96×10^{-5}	1.70×10^{3}	0.947	8.67×10^{-6}	0.0171	9.76×10^{-6}	0.0171	0.990
NBB	2.18×10^{-5}	9.52×10^{-4}	0.850	2.18×10^{-5}	47.5	0.850	1.24×10^{-6}	0.559	2.15×10^{-5}	7.81×10^{-4}	0.957

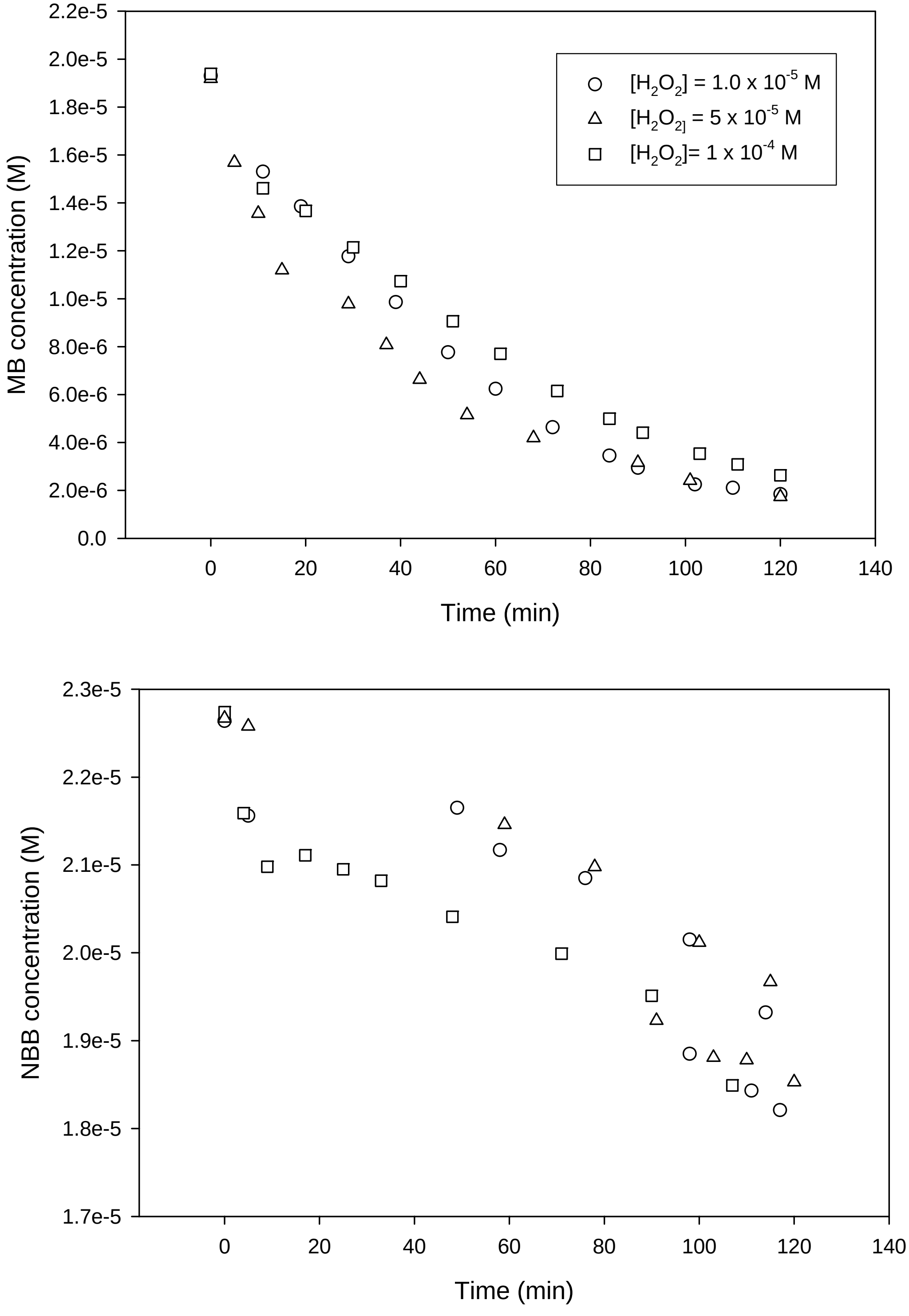


Figure 18. Effect of H_2O_2 concentration on decolourisation.

Table 4. Comparison of kinetic parameters of decolourisation in different activated carbon loading

Dye	AC loading	First-order			Combined first-order				
		C_0 (M)	k (min^{-1})	R^2	C_{01} (M)	k_1 (min^{-1})	C_{02} (M)	k_2 (min^{-1})	R^2
MB	0	$1.84x\ 10^{-5}$	0.0171	0.990					
	10 mg	$1.77x10^{-5}$	0.0219	0.982					
	50 mg	$1.97x10^{-5}$	0.00946	0.970					
NBB	0				$1.24x10^{-6}$	0.559	$2.15x10^{-5}$	$7.81x10^{-4}$	0.957
	10 mg				$1.19x10^{-6}$	0.600	$2.16x10^{-5}$	$1.22x10^{-3}$	0.961
	50 mg				$9.85x10^{-6}$	$1.42x10^{-3}$	$1.27x10^{-5}$	$1.42x10^{-3}$	0.958

3.8.2. Effect of H_2O_2

It has been known that H_2O_2 is an important parameter for Fenton oxidation. Figure 18 presents the effect of H_2O_2 on decolourisation of two dyes at the case of 10 mgAC+Fenton. For the basic dye, decolourisation rate will be increased when H_2O_2 concentration is increased from 1.0 x 10^{-5} to 5 x 10^{-5} M. However, further increasing H_2O_2 concentration to 1 x 10^{-4} M will result in a decrease in decolourisation rate. The decreasing rate of dye decolourisation is attributed to unreacted H_2O_2 acting as a scavenger of $^{\bullet}OH$ and producing a less potent perhydroxyl radicals[18] (Eq.10). For azo dye, decolourisation is similar for H_2O_2 concentration at 1.0 x 10^{-5} to 5 x 10^{-5} M and will increase when H_2O_2 concentration is increased to 1 x 10^{-4} M.

Several investigations in wastewater decolourisation using Fenton oxidation have been conducted and reported an optimal peroxide concentration in Fenton oxidation of dyes [16-18]. Dutta et al. [17] found that at initial [Fe^{2+}] = 3.58×10^{-5} M and initial [H_2O_2] < 4.14×10^{-4} M, the rate of decolourisation of methylene blue increased with increasing initial concentration of hydrogen peroxide. The rate remained almost same for initial H_2O_2 concentration of 4.14×10^{-4} – 2.94×10^{-2} M. Others reported similar results for different dyes [16, 18, 23].

3.8.3. Effect of pH

Solution pH is also important for Fenton oxidation of dyes. Previous investigations show that the optimum pH for Fenton oxidation is 2 – 4 [16, 18]. Low or high pH will reduce the oxidation rate. Figure 19 shows the decolourisation of two dyes at different pH for 10 mgAC+Fenton system. As shown that high pH at 6 will significantly reduce the decolourisation efficiency. For MB, decolourisation efficiency is almost zero while for NBB the decolourisation is only 4% compared with 19% at pH 2. Above pH 4, the reduction in degradation efficiency can be attributed to the hydrolysis of Fe^{3+} into $Fe(OH)_3$, which helps to decompose H_2O_2 into oxygen and water. Therefore, the degradation rate will be decreased because less hydroxyl radicals are available [23].

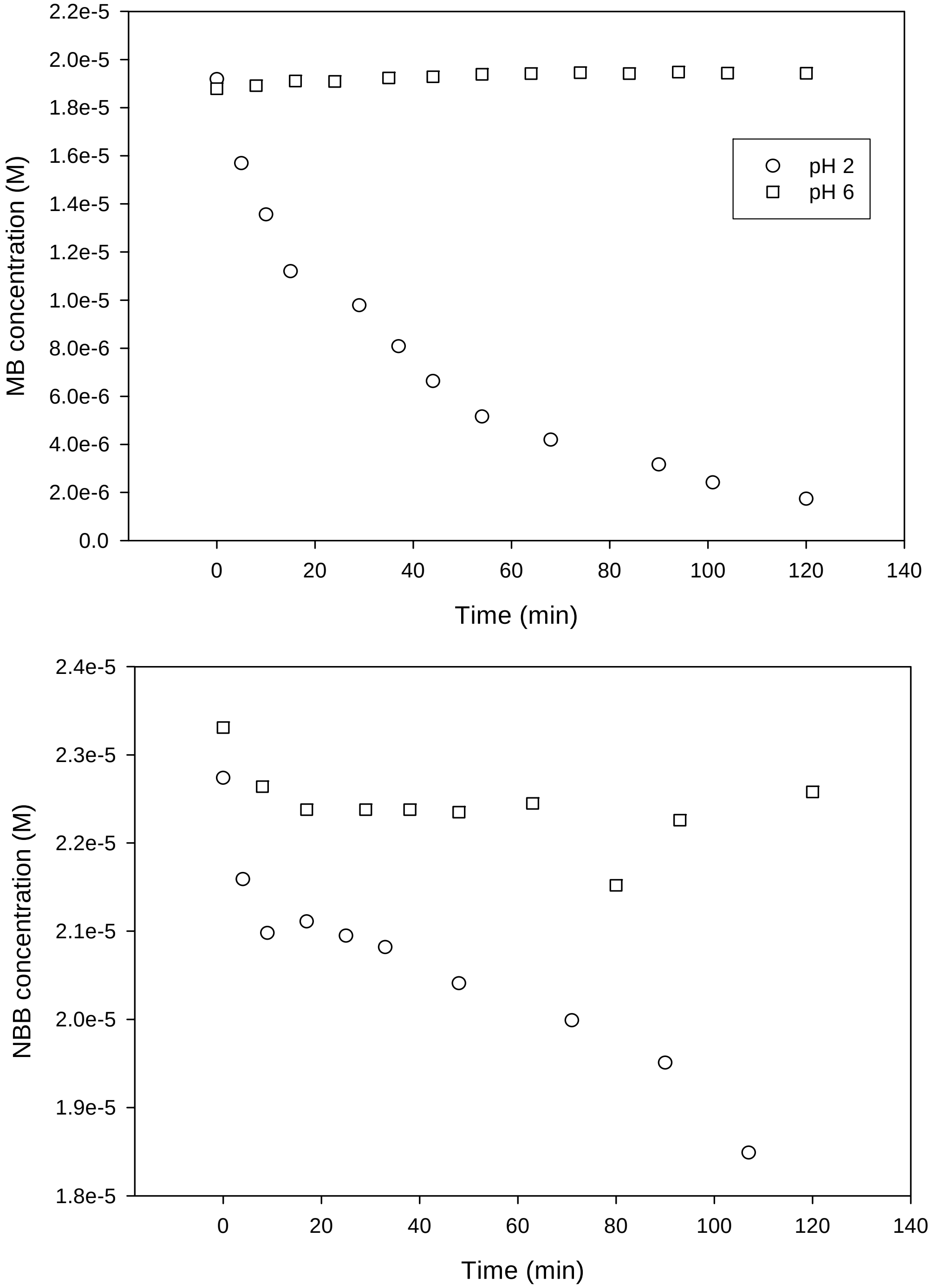


Figure 19. Effect of solution pH on dye degradation.

4. CONCLUSION

Fenton and sono-Fenton oxidations for decolourisation of dye-containing wastewater at very low Fenton reagent concentration (Fe^{2+} and H_2O_2) have been investigated and their efficiencies and kinetics are compared. Fenton oxidation produces high decolourisation efficiency depending on the types of dyes, Fenton reagent concentrations, and reaction conditions, pH and temperature. In general, decolourisation of MB will show higher efficiency than NBB. High H_2O_2 concentration and temperature will promote decolourisation. While maximum efficiency (80%) will be achieved at optimum pH and Fe^{2+} concentration. Sonolysis will promote decolourisation and sono-Fenton oxidation exhibits the highest removal efficiency. Decolourisation efficiency for two types of dyes (> 90% at 2 h) can be realised even at low dosage of Fe and H_2O_2. Both Fenton and sono-Fenton oxidations show the first-order kinetics.

Fenton-like and sono-Fenton-like oxidations at very low Fenton reagent concentrations for decolourisation of dye-containing wastewater have demonstrated higher efficiencies. Fenton-like oxidation produces high decolourisation efficiency depending on the types of dyes, Fenton reagent concentrations, and reaction conditions, pH and temperature. In general, decolourisation of MB will show higher efficiency than NBB. High H_2O_2 concentration and temperature will promote decolourisation. While maximum efficiency will be achieved at optimum pH and Fe^{3+} concentration. Fenton and Fenton-like oxidation will have much similar decolourisation efficiency. Sonolysis will promote decolourisation and sono-Fenton or sono-Fenton-like oxidation exhibits the highest removal efficiency. Both Fenton, Fenton-like, and sono-Fenton type oxidation show the first-order kinetics.

Activated carbon exhibits some adsorption for NBB but no adsorption of MB. Fenton oxidation is quite effective for dye decolourisation and the efficiency depends on the type of dye. Fenton oxidation presents strong decolourisation of MB but low efficiency for NBB. The presence of activated carbon in Fenton oxidation can promote the decolourisation at low dosage but exhibits inhibiting effect at high loading. H_2O_2 and pH will also affect the decolourisation rate and efficiency. The kinetic studies indicate that decolourisation rate of MB and NBB is different and follows the different kinetics. The decolourisation of MB can be described by simple first-order kinetics while the kinetics of NBB decolourisation is the combined first-order kinetics.

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Chapter 6

DECOLORATION OF TEXTILE WASTEWATERS

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ABSTRACT

Water is an important natural resource for sustainable ecosystems, human life and economical development. The control of water pollution has become of increasing importance in recent years. Dyes make the world more beautiful through colored products, but cause a lot of problems in the environment. For decoloration and degradation of textile wastewater many applicable methods have been developed, but because of the composition complexity of the textile wastewater the use of universal procedures seems to be impossible. So, there is a need to find an efficient and cost-effective wastewater treatment for the decoloration of textile wastewaters. In this chapter a survey of the most widely used and, according to many researches, the most promising textile wastewater decoloration methods are presented.

INTRODUCTION

Industry and agriculture are the two largest water users in Europe. The largest water industry consumer is the textile finishing industry. Processes, where most water is consumed are printing and dyeing, which consume on average 100-150 m^3 of water per ton of finished product with peaks above 500 m^3/t in multi-stage processes.[1] The annual consumption of fresh water at the European level is 600 million m^3. Besides being one of the greatest consumers of water, the textile industry is also one of the highest pollutants because of the large use of numerous organic compounds and different auxiliary substances (1 kg of chemicals and auxiliaries is processed per kg of textile product). On average, 90% of the

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water input in textile finishing operations needs to be treated end-of-pipe. In Europe, 108 million tons of wastewater is produced on a yearly basis and 36 million tons of chemicals and auxiliaries have to be removed from the textile wastewater. Textile wastewater typically contains a complex mixture of organic and inorganic chemicals, and this is the reason why the processes of cleaning and recycling of wastewater are difficult to perform. Organic contaminants in wastewater present a specific problem due to their toxicity, bioaccumulation and poor biodegrability. The price for waste water treatment varies on average from 0.5-2.5 €/m^3 and it is expected that the price in the future will increase (estimation value is from 3-5 €/m^3).

There are more than 100 000 commercially available dyes with the production of over 7×10^5 tons.[2] The exact data on the quantity of dyes discharged in the environment are also not available. It is assumed that 2 % of the dyes produced are discharged directly in aqueous effluent, and 10 % are subsequently lost during the textile coloration process.[3] On the other hand, most of the wastewater produced by the textile industry is coloured. Many dyes are difficult to decolourise due to their complex structure and synthetic origin.

Dyes cause a lot of problems in the environment:

1. Depending on exposure time and dye concentration, dyes can have acute and/or chronic effects on exposed organisms.
2. The presence of very small quantities of dyes in water (less then 1 ppm) is highly visible due to their brilliance.
3. The greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water. Light absorption diminishes photosynthetic activity of algae and seriously influence on the food chain.
4. Dyes can remain in the environment for an extended period of time, because of high thermal and photo stability. For instance, the half-life of hydrolysed Reactive Blue 19 is about 46 years at pH 7 and 25 °C.[4]
5. Many dyes and their breakdown products are carcinogenic, mutagenicand/or toxic to life. Dyes are mostly introduced into the environment through industrial effluents. There is ample evidenc of their harmful effects. Triple primary cancers involving kidney, urinary bladder and liver of dye workers have been reported. Most of the dyes, used in the textile industry are known only by their trade name, while their chemical nature and biological hazards are not known. Mathur[5] *et. al*. studied the mutagenicity of textile dyes (known only by their trade name, used in Pali, identified as one of the most polluted cities in India) and the effluents containing these dyes, and the influence on the health of textile dyeing workers and the environment. The dyes were used in their crude form and no following purification was attempted, because they wanted to test the potential danger that dyes represent in actual use. The results clearly indicated that most of the used dyes are highly mutagenic. Brown[6] *et. al*, published an article, to show it is possible to predict the toxicity of new azo dyes. The systematic backtracking of the flows of wastewater from textile-finishing companies led to the identification of textile dyes as a cause of strongly mutagenic effects. The textile dyes used in the textile-finishing companies in the European Union were examined for mutagenicity. According to the obtained results the dyes that proved to be mutagenic have been replaced with less harmful substances.[7],[8]. The degradation product of dyes could be carcinogenic. The formation of

carcinogenic aromatic amine *o*-tolidine from the dye Direct Blue 14 by skin bacteria has been established.[9]

6. Textile dyes can cause allergies such as contact dermatitis[10] and respiratory diseases[11],[12],[13], allergic reaction in eyes, skin irritation, and irritation to mucous membrane and the upper respiratory tract. Reactive dyes form covalent bonds with cellulose, woollen and PA fibres. It is assumed that in the same way reactive dyes can bond with $–NH_2$ and –SH group of proteins in living organisms. A lot of investigations of respiratory diseases in workers dealing with reactive dyes have been made. Certain reactive dyes have caused respiratory sensitisation of workers occupationally exposed to them.[14]

Public perception of water quality is greatly influenced by the colour. So, the removal of colour from wastewater is often more important than the removal of the soluble colourless organic substances. Removal of the dyes from the textile wastewater is often very costly, but a stringent environmental legislation has stimulated the textile sector in developing wastewater treatment plants.

TEXTILE DYES

Organic dyes contain substituted aromatic and heteroaromatic groups. The color of dyes results from conjugated chains or rings that can absorb different regions of wavelength. The chromophores of organic dyes are usually composed of double carbon-carbon bonds, double nitrogen-nitrogen bonds, double carbon-nitrogen bonds, aromatic and heterocyclic rings containing oxygen, nitrogen or sulphur. Reactive dyes are termed chemically as colored compounds with a functional group capable of forming a covalent bond with a suitable substrate. Azo dyes, which contain one or more azo bonds, are the most widely used synthetic dyes. Azo dyes are mostly used for yellow, orange and red colours. Anthraquinone dyes constitute the second most important class of textile dyes. They have a wide range of colours in almost the whole visible spectrum, but they are most commonly used for violet, blue and green colours.

With regard to method and domain of usage the dyes are classified into acid, reactive, direct, basic, disperse, metal complex, vat, mordant and sulphur dyes. Most commonly in use today are reactive and direct dyes for cotton and viscose-rayon dyeing and disperse dyes for polyester dyeing.

Generally, dyes can be classified with regard to their chemical structure, with regard to the method and domain of usage, and with regard to chromogen (Table 1).

Examples of the chemical structure of the azo dye with C.I. Direct Red 254 and reactive dichlorotriazine dye with C.I. Reactive Yellow 4 are presented in Figure 1 and Figure 2.

Table 1. Classification of the dyes

	Classification	
	Subclass	Characteristic
With regard to chemical structure (C.I.)	E.g. azo, anthraquinone, triphenylmethane, indigo,…	The classification of a dye by chemical structure into a specific group is determined by the chromophore.
With regard to method and domain of usage (C.I.)	E. g. direct, acid, basic, reactive, reductive, sulphuric, cromic, metal-complex, disperse, pigments,…	Dyes used in the same technological process of dyeing and with similar fastness are classified into the same group.
With regard to chromogen $n \rightarrow \pi^*$	E. g. absorptive, fluorescent and dyes with energy transfer,…	This classification is based on the type of excitation of electrons, which takes place during light adsorption.
With regard to the nature of donor – acceptor couple	E. g. 1-aminoanthraquinone, p-nitroaniline,…	These chromogenes contain a donor of electrons (unbound electron couple), which directly bonds to the system of conjugated π electrons.
With regard to the nature of polyenes:		
a) Acyclic and cyclic	E. g. polyolefins, annulenes, carotenoids, rhodopsin,…	Polyene chromogen contains sp^2 (or sp) hybridised atoms. The molecules enclose single and double bonds that form open chains, circles, or a combination of both.
b) Cyanine	E. g. cyanines, amino substituted di- and tri- arylmethane, oxonols, hydroxyarylmethanes,…	Cyanine chromogens have a system of conjugated π electrons, in which the number of electrons matches the number of p orbitals.

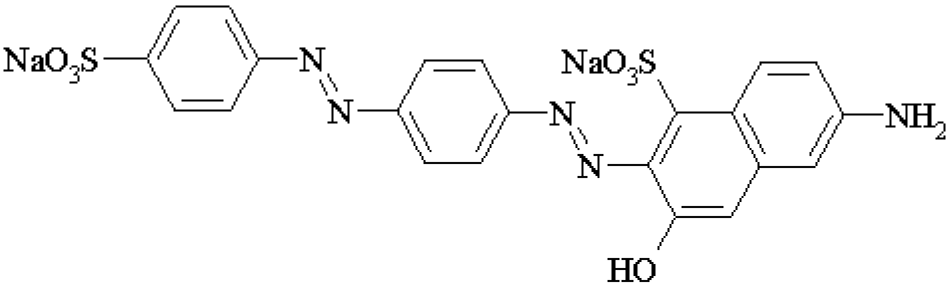

Figure 1. Chemical structure of the azo dye with C.I. Direct Red 254.

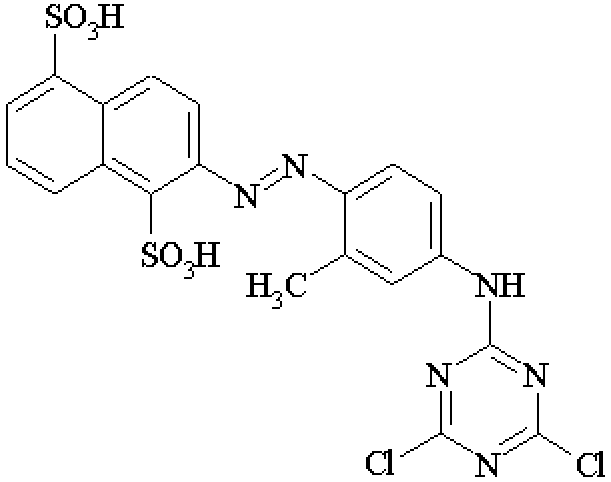

Figure 2. Chemical structure of the reactive dichlorotriazine dye with C.I. Reactive Yellow 4

DECOLORATION

The colour of water, polluted with organic colourants reduces, when the cleavage of the double carbon-carbon bond, double nitrogen-nitrogen bond and heterocyclic and aromatic rings occurs. The absorption of light by the associated molecules shifts from the visible to the ultraviolet or infrared region of the electro magnetic spectrum.

Dyes containing wastewater can be treated in two ways: (i) by chemical or physical methods of dye removal, which refers to the process called decoloration and by means of biodegradation, which tell us more about the fate of dyes in the environment.

In physical treatment methods the applications of physical forces predominate. Physical methods include different precipitation methods (coagulation, flocculation, sedimentation), adsorption (on a wide variety of inorganic and organic supports), filtration, reverse osmosis, ultrafiltration and nanofiltration. Biological treatments differ according to the presence or absence of oxygen to aerobic and anaerobic treatment. Since biological treatments simulate degradation processes that occur in the environment, it is also called biodegradation.

Chemical treatment methods are those, in which the removal or conversion of dyes and other contaminants is brought about by the addition of chemicals or by chemical reactions (reduction, oxidation, compleximetric methods, ion exchange and neutralisation).

The treatment of coloured wastewaters is therefore not restricted to the reduction of ecological parameters only (chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), adsorbable organic halide (AOX), temperature and pH), but also to reduction of dye concentrations in wastewaters.

PHYSICAL METHODS

Adsorption

Adsorption is the process of collecting soluble substances that are in solution on a suitable interface. Adsorption methods for decoloration are based on the high affinity of many dyes for adsorbent materials. Dye removal by adsorption is influenced by some physical and chemical factors like dye-adsorbent interactions, adsorbent surface area, particle size, temperature, pH and contact time. The main criteria for selection of an adsorbent should be based on characteristics such as high affinity and capacity for target compounds and the possibility of adsorbent regeneration.[15]

Activated carbon is the most commonly used method of dye removal by adsorption and it is very effective in adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent, disperse, direct, vat, pigment and reactive dyes.[16],[17] Performance depends on the type of carbon used and characteristic of the wastewater. It is, like many other dye-removal treatments, well suited for one particular waste system and ineffective for another. Activated carbon is relatively expensive and has to be regenerated offsite with losses of about 10 % in the thermal regeneration process.[18]

Adsorption on sludge is the main abiotic mechanism of removing dyes from the wastewater. The most important factors influencing the adsorption test are sludge quality, water hardness, duration of the test and test substance concentration. Static and dynamic removal studies involving water soluble dyes (acid, reactive) and poorly soluble dyes (disperse) have been described by Pagga[19] et al.

Biomass (dead plant and animal matter) is also a suitable adsorbent for wastewater treatment. The adsorption of organic material onto various types of waste biomass has been studied in detail. This has included sawdust[20], peat[21], chitin[22], bagasse pith[23], carbonised wool waste[24], wood chips[25], maize cob[26], banana pith[27], rice husk, hair, cotton waste and bark[28]. The capacities of these materials have been examined through their adsorption of synthetic dyes. Biomass decoloration is a result of two mechanisms: adsorption and ion exchange, and is influenced by many factors, such as, dye-sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time. Biomass of different origin has been used for decoloration of acid, direct and reactive dyes. Of all the described adsorbents only a few have characteristics necessary for commercial use. Considering the price and binding capacity, quarternized lignocellulose based adsorbents are the most appropriate for treating wastewater containing acid dyes. The disadvantage of adsorption processes is that the adsorbent needs to be regenerated, which adds to the cost of the process, and is sometimes a very time-consuming procedure.

Decoloration with alternative materials such as zeolites, polymeric resins, ion exchangers and granulated ferric hydroxide has also been studied in order to decrease adsorbent losses during regeneration.

Filtration Methods

In the textile industry the filtration methods such as ultrafiltration, nanofiltration and reverse osmosis can be used for both filtering and recycling not only pigment-rich streams, but also mercerising and bleaching wastewaters. The specific temperature and chemical composition of the wastewater determine the type and porosity of the filter to be applied. The main drawbacks of the membrane technology are high investment costs, the potential membrane fouling, and the production of a concentrated dyebath which needs to be treated.[29],[30]

Coagulation-flocculation

Coagulation-flocculation processes are widely used in several wastewater treatments in Germany and France. Coagulation-flocculation methods were successfully applied for colour removal of sulphur and disperse dyes, whereas acid, direct, reactive and vat dyes presented very low coagulation-flocculation capacity. Coagulant agents like aluminium sulphate, ferrous and ferric sulphate, ferric chloride, calcium chloride, copper sulphate, as well as several co-polymers like pentaethylene, hexamine and ethylediene dichloride are used to form flocs with the dye, which are then separated by filtration or sedimentation. Polyelectrolyte can also be dosed during the flocculation phase to improve the flocs settleability. [31],[32]

The main advantage of these processes is decoloration of the waste steam due to the removal of dye molecules from the dyebath effluents, and not due to a partial decomposition of dyes, which can lead to an even more potentially harmful and toxic aromatic compound. The major disadvantage of coagulation-flocculation processes is the production of sludge.

CHEMICAL METHODS

Oxidative Processes

Oxidation is the most commonly used chemical decoloration process. This is mainly due to its simplicity of application. Modern dyes are resistant to mild oxidation conditions such as those, which exist in biological treatment systems. Conventional oxidation treatments have found it difficult to oxidize dyes (mainly for removing colour) and toxic organic compounds in textile effluents. The chemical limitations of conventional chemical oxidation techniques can be overcome by the development of so-called advanced oxidation processes (AOPs). The goal of AOPs is to generate free hydroxyl radicals ($OH^{\bullet}$), which may represent a rate increase of one to several orders of magnitude compared with normal oxidants in the absence of catalysts. Table 2 shows the oxidation potential of common species. Hydroxyl radicals oxidize the dyes and toxic organic compounds that cannot be oxidized by conventional oxidants. In AOPs, oxidizing agents such as ozone and hydrogen peroxide are used with catalysts (Fe, Mn, TiO_2) either in the presence or absence of an irradiation source.

Table 2. Oxidation potential of common oxidizing agents

Oxidizing agents	*Oxidation potential/V*
Fluorine (F_2)	3.06
Hydroxyl radical ($OH^\bullet$)	2.80
Atomic oxygen	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.78
Potassium permanganate($KMnO_4$)	1.67
Hypochlorous acid (HClO)	1.49
Chlorine (Cl_2)	1.36
Bromine (Br_2)	1.09
Molecular oxygen (O_2)	1.23

Fenton's Reagent

Degradation of hydrogen peroxide into hydrogen radicals is activated by Fe^{2+} (ferrous ions) in an acid solution (pH = 3-4) (Table 3).

In this process it is important to find the optimal concentration of hydrogen peroxide because excess of H_2O_2 acts as a scavenger of radicals, disturbs the COD measurements and is toxic for microorganisms.

Fenton's reagent is very suitable for the oxidation of wastewaters which inhibit biological treatment or are poisonous. This system offers a cost effective source of hydroxyl radicals and it is easy to operate and maintain. Besides offering advantages in COD, colour and toxicity reduction, this process also has disadvantages. The major disadvantage of this method is sludge generation, through the flocculation; impurities are transferred from the wastewater to the sludge, which contains the concentrated impurities and is still ecologically questionable. Conventionally it has been incinerated to produce power, but such disposal is seen by some to be far from being environmentally friendly. To avoid this problem, Gnann[33] et al. suggest the regeneration of Fe^{2+} from iron sludge at pH < 1, with so called the Fenton Sludge Recycling System (FSRS), in which Fe(III)-sludge deposition is eliminated.

A lot of work has been carried out using Fenton's reagent as a decoloration agent. This method is suitable for different dye classes; acid, reactive, direct, metal-complex, disperse and vat dyes as well as pigments. Low decoloration rates were observed when C.I. Vat red (50 %) and C.I. Disperse Blue (0.5 %) were treated. [34]

Studies on the decoloration and mineralization of commercial reactive dyes using solar Fenton and photo-Fenton reaction indicated good colour removal. The use of solar light was proved to be clearly beneficial for the removal of colour, aromatic compounds and TOC.[35],[36]

Table 3. Degradation of hydrogen peroxide into hydrogen radicals activated by Fe^{2+}

$$\boxed{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + HO^-}$$

Ozone

Ozone is a powerful oxidant agent for water and wastewater. Once dissolved in water, ozone reacts with a great number of organic compounds in two different ways, namely direct molecular and indirect free radical-type reactions. The direct reactions are often highly solute selective, slow, and are dominant in acidic solutions. The indirect hydroxyl radical reactions are non-selective, fast, proceed more rapidly with increasing pH and constitute a significant portion of ozonation at basic pH. The direct reactions are very suitable for opening aromatic rings by means of ozone cycloaddition, while indirect attacks are very suitable for mineralization of total organic carbon (TOC).[37]

Although the original purpose of the oxidation with ozone is disinfection of potable water, it can also be used for removing many toxic chemicals from wastewater to facilitate the decomposition of detergents, chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons.[38]

The advantages of ozonation are: (i) decoloration and degradation occur in one step, (ii) danger to humans is minimal, (iii) no sludge remains, (iv) all residual ozone can be decomposed easily into oxygen and water, (v) little space is required and (vi) ozonation is easily performed.[39]

A disadvantage of ozonation is its very short half-life in water – it decomposes in about 20 minutes. The time can be significantly shortened if compounds like dyes are present.[40] Ozone stability is affected by the presence of salts, pH and temperature. If alkaline salts are present, the solubility of ozone is reduced, while neutral salts may increase its solubility.[41] Under alkaline conditions ozone decomposes more rapidly than under acidic conditions. With increasing temperature, ozone solubility decreases.[42]

Results presented by several authors revealed that ozone decolorizes all dyes, except nonsoluble disperse and vat dyes which react slowly and take longer time. [43],[44],[45] . Colour removal strongly depends on dye concentration.

Ozonation alone still has low total organic carbon (TOC) and chemical oxygen demand (COD) removal. Species like oxalic, glyoxalic and acetic acids cannot be completely mineralized by ozone alone at least at neutral or acidic pH.[46] To enhance the efficiency of ozonation various advanced oxidation processes have been developed, such as ozon-H_2O_2, ozon-UV, catalytic ozonation.

Ozone-H_2O_2

The addition of hydrogen peroxide to ozone enhances the production of hydroxyl radicals. The aqueous reaction between ozone and hydrogen peroxide are rather complex. The mechanisms and the kinetics of the production of hydroxyl radicals from ozone and hydrogen peroxide are known. The reactions and reaction rate constants are shown in Table 4. In the initiation sequence, reactive $OH^{\bullet}$ radicals are generated. During the promotion reactions, the hydroxyl radicals are converted into the peroxy radical.

At acidic pH, H_2O_2 reacts only very slowly with ozone whereas at pH values above 5 a strong acceleration of ozone decomposition by hydrogen peroxide has been observed.

The ozone decomposition rate will increase with increasing pH.

Table 4. Reactions between O_3-H_2O_2

Initiation:	
$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^{\bullet-}$	$k_r = 2{,}2 \cdot 10^6$ L/(mol s)
$H^+ + O_3^{\bullet-} \leftrightarrows HO_3^\bullet \rightarrow OH^\bullet + O_2$	$k_r = 1{,}1 \cdot 10^5$ L/(mol s)
$H_2O_2 + O_3 \rightarrow H_2O + 2\ O_2$	$k_r < 10^{-2}$ L/(mol s)
Promotion:	
$OH^\bullet + O_3 \rightarrow O_2 + HO_2^\bullet$	$k_r = 1{,}1 \cdot 10^8$ L/(mol s)
$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$	$k_r = 2{,}7 \cdot 10^7$ L/(mol s)
$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2^{\bullet-}$	$k_r = 7{,}5 \cdot 10^9$ L/(mol s)

Decoloration with O_3-H_2O_2 combination is applicable for direct, metal-complex or blue disperse dyes. There are some problems with the decoloration of acid and red disperse dyes, though, as well as with mixtures of direct, metal-complex, disperse and reactive dye decoloration. Decoloration of some dyes with O_3-H_2O_2 is presented in Table 5.

Table 5. Decoloration of dyes with O_3-H_2O_2 (adapted from Slokar [34] et.al)

Textile dye	*Decoloration/%*	*Time/min.*
Red 219	100	5
Blue 186	85	1
Direct Yellow 44	100	0.5
Direct Yellow 50	100	0.5
Red 23	100	0.5
Red 26	100	0.5
Direct Red 5B	99	45
Direct Blue 1	100	0.5
Direct Blue 25	100	0.5
Direct Blue 71	90	7
Disperse Yellow 3	95	1
Disperse Yellow 64	100	4.5
Red 13	100	0.7
Red 60	100	1
Red 279	99	98
Blue 60	100	0.7
Palanil Blue 3RT	90	31
Sulpho/disperse dye	98	30
Reactive Yellow 37	93	4
Reactive Yellow 125	98	2.5
Reactive Yellow 125	100	7
Remazol Yellov RNL	93	4
Reactive Red 35	99	4.5
Reactive Red 195	100	6
Blue 27	94	0.9
Blue 221	100	9
Green 13	98	4
Reactive dyes	100	1
Vat dyes	80	30
Azoic dyes	87	30

Ozone-UV

UV radiation decomposes ozone in water and generates highly reactive hydroxyl radicals. Hydroxyl radicals oxidize organics more rapidly than ozone itself. Combination of ozone with UV results in a net enhancement of organic matter degradation due to direct and indirect production of hydroxyl radicals upon ozone decomposition and H_2O_2 formation Table 6.

Table 6. Direct and indirect production of hydroxyl radicals in O_3-UV process

Direct:
$O_3 + h\nu \rightarrow O_2 + O$
$O + H_2O \rightarrow OH^{\bullet} + OH^{\bullet}$
$O + H_2O \rightarrow H_2O_2$
$H_2O_2 + h\nu \rightarrow OH^{\bullet} + OH^{\bullet}$
Indirect:
$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2$
$H_2O_2 + h\nu \rightarrow OH^{\bullet} + OH^{\bullet}$

The efficiency of ozone-UV treatment depends on pH (degradation favours neutral or slightly alkaline medium), operating temperature (at higher temperature the ozone solubility is lower) and ozone flow rate.

Degradation of eight commercial azo dyes in water[47] and a model dyehous wastewater[48] has been studied by using ozonation and ozone-UV process. In both studies the ozone-UV process did not significantly enhance the degradation rates, the dye competed with ozone for UV absorbance. But ozone-UV treatment is more effective compared to ozone alone, in terms of COD removal.[49]

H_2O_2-UV

In H_2O_2-UV processes hydroxyl radicals are formed when water-containing H_2O_2 is exposed to UV wavelengths of 200-280 nm. The most commonly used UV source is low-pressure mercury vapor lamps with a 254-nm peak emission.

Problems like sludge formation and regeneration, increased pollution of wastewater caused by ozone can be avoided by oxidation with hydrogen peroxide activated with UV light. The only chemical used in the treatment is H_2O_2, which, due to its final decomposition into oxygen is not problematic.

The most direct method for generation of hydroxyl radicals is through the cleavage of H_2O_2. Photolysis of H_2O_2 yields hydroxyl radicals by direct process with a yield of two radicals formed per photon absorbed at 254 nm. Hydroxyl radicals can oxidize organic compounds (RH) producing organic radicals ($R^{\bullet}$), which are highly reactive and can be further oxidized (Table 7). [50]

Table 7. The main reactions that occur during the H_2O_2-UV process

$H_2O_2 + h\nu \rightarrow OH^{\bullet} + OH^{\bullet}$
$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} \rightarrow$ further-oxidation

Table 8. Reactions of H_2O_2 as a radical scavenger:

$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$
$HO_2^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O + O_2$
$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$

The maximum absorbance of H_2O_2 is needed to generate sufficient hydroxyl radicals because of low-absorption coefficient. However, high concentration of H_2O_2 scavenges the radicals, making the process less effective, while low concentration of hydrogen peroxide doesn't generate enough hydroxyl radicals that are consumed by dye and this leads to a slow rate of oxidation. So, an optimum hydrogen peroxide dose needs to be verified experimentally (Table 8).

The rate of dye removal is influenced by the intensity of UV radiation, pH, dye structure and dyebath composition. In general, decoloration is most effective at neutral pH medium, at higher UV radiation intensity (1600 W rather than 800 W), with an optimal H_2O_2 concentration which is different for different dye classes, and with a dyebath that does not contain oxidising agents having an oxidising potential higher than that of peroxide.

Table 9. Decoloration of dyes with H_2O_2-UV

Textile dye	*Decoloration/%*	*Time/min.*	*k_d/min^{-1}*
Acid Yellow 17 [51]	98.2	40	
Orange 10 [51]	100	60	
Red 1 [51]	99.9	30	
Red 14 [51]	100	60	
Red 18 [51]	99.1	40	
Blue 186 [51]	80	10	
Black 1 [51]	89.9	60	
Direct Yellow 4 [51]	83.2	60	
Direct Blue 71 [59]	98.5	3	
Palanil Blue 3RT [59]	96	10	
Reactive Yellow 37 [59]	85	8	
Reactive Yellow 125 [59]	96	8	
Remazol Yellov RNL [59]	85	8	
Reactive Red 35 [59]	100	8	
Reactive Red 195 [58]	100	60	
Blue 21 [58]	95	150	
Blue 27 [59]	100	5	
Green 13 [59]	93	8	
Vat Blue [59]	15.5	10	
Reactive Black 5 [52]	100	4	0.88
Acid Red 1 [55]			0.063
Acid Red 1 [47]			0.717
Acid Yellow 23 [47]			0.183

According to Shu[53] et.al acid dyes are the easiest to decompose, and with an increasing number of azo groups, the decoloration effectiveness decreases. Yellow and green reactive dyes need longer decoloration times, while other reactive dyes as well as direct, metal-complex and disperse dyes are decolourised quickly. In the group of blue dyes examined, only blue vat dyes were not decolourised. For pigments, H_2O_2-UV treatment is not suitable, because they form a film-like coating on the UV lamp which is difficult to remove.

Several authors[54],[55],[56],[57] reported complete decoloration of reactive and azo dyes in 30-90 minutes. The results indicated that H_2O_2-UV processes could be successfully used for the decoloration of acid, direct, basic and reactive dyes but it proved to be inadequate for vat and disperse dyes.[58] Decoloration of some dyes with H_2O_2-UV are presented in Table 9.

A comparative study between ozone and H_2O_2-UV was carried out on simulated reactive dyebath effluent containing a mixture of monochlorotriazine type reactive dyes and various auxiliary chemicals. The H_2O_2-UV process presented the decoloration rates close to those rates obtained with ozone but at a lower cost. [59]

H_2O_2-UV systems may be set-up in a batch or continuous column unit.[60]

Ultrasound

Sonolysis is a relatively innovative advanced oxidation process and was found to be a very suitable method for the destruction of textile dyes.

The ultrasonic irradiation of liquids generates cavitation (typically in the range 20-1000 kHz). Cavitation is a phenomenon of micro-bubbles formation. Micro-bubbles grow during the compression/rarefaction cycles until they reach a critical size, and implode generating heat and highly reactive radical species. Inside the cavitation bubbles, the temperature and pressure rise to the order of 5000 K and 100 MPa, respectively. Under such conditions, water molecules degrade releasing hydroxyl radicals ($OH^\bullet$) and hydrogen radicals ($H^\bullet$) in Table 10.

These radical species can either recombine or react with other gaseous molecules within the cavity or in the surrounding liquid, after their migration. Pyrolitic and radical reactions inside or near the bubble and radical reactions in the solution are two major pathways for sonochemical degradation. Hydrophilic and non-volatile compounds mainly degrade through hydroxyl radical mediated reactions in the solution, while hydrophobic and volatile species degrade thermally inside or in the vicinity of the bubble.

Reactive azo dyes are non-volatile, water soluble compounds and their passage into the gas cavity is unlikely. Hence, oxidative radical reactions in the bulk solution are expected to be the major route for their destruction.

Table 10. Radical formation and depletion during water sonolysis

$H_2O \rightarrow))) OH^\bullet + H^\bullet$
$OH^\bullet + H^\bullet \rightarrow H_2O$
$2OH^\bullet \rightarrow H_2O + O^\bullet$
$2OH^\bullet \rightarrow H_2O_2$

Table 11. Technical Comparison of Oxidative Decoloration

Oxidation process	*Advantages*	*Disadvantages*
Fenton	Effective decoloration of both soluble and insoluble dyes. Simple equipment and easy implementation. Reduction of COD (except with reactive dyes). No alternation in volume.	Sludge formation. Long reaction times. Salt formation Hazardous waste. Prohibitively expensive.
FSR (Fenton Sludge Recycling System)	Simple equipment and implementation. Reduction of COD (except with reactive dyes).	Salt formation. Formation of gasses (H_2, O_2 during electrolysis).
Ozone	Applied in gaseous state. no alteration of volume. No sludge production. Effective for azo dye removal.	Short half-life (20 min). Not suitable for disperse dyes. Releases of aromatic amines.
Ozone-H_2O_2	No sludge formation. No salt formation. Short reaction times. Very short reaction times for reactive dyes	Not applicable for all types. Toxicity, hazard, problematic handling. No COD reduction. Additional load of water with ozone.
H_2O_2-UV	No sludge formation. No salt formation. Short reaction times. Reduction of COD.	Not applicable to all types of dyes. Requires separation of suspended solid particles
Ultrasound	Simplicity in use. Very effective in integrated system.	Relatively new method and awaiting full scale application.

According to several studies, it is difficult to obtain the total mineralization (degradation to carbon dioxide, short-chain organic acid, oxalate, formate and inorganic ions like, sulphate and nitrate) of the complex textile dyes with ultrasound alone. For this reason the combination of ultrasound with other advanced oxidation processes is a more convenient approach in the remediation of such pollutants.

Sonochemical degradation of textile dyes has become quite an interesting research area confirmed by several reports over the last few years.[61]

In Table 11 a comparison of individual AOP is given.

BIOLOGICAL DEGRADATION

Biological degradation or breakdown by living organisms is the most important removal process of organics which are transferred from industry processes into solid and aquatic ecosystems.

The application of microorganisms for the biodegradation of synthetic dyes is an attractive method and offers considerable advantages. The process is relatively inexpensive, the running costs are low and the end products of complete mineralization are not toxic. An extensive review of large numbers of different species of microorganisms tested for decoloration and mineralization of different dyes has been published by Forgacs[62] et. al.

The efficiency of biological treatment systems is greatly influenced by the operational parameters. To produce the maximum rate of dye reduction the level of aeration, temperature, pH and redox potential of the system must be optimised. The concentration of the electro donor and the redox mediator must be balanced with the amount of biomass in the system and the quantity of the dye present in the wastewater. The compounds present (sulphur compounds, salts) in the wastewater may have an inhibitory effect on the dye reduction process. For these reasons it is important to study the effect of these factors on decoloration before the biological system can be used to treat industrial wastewater.[63]

Biodegradation processes may be anaerobic, aerobic or involve a combination of both.

Aerobic Biodegradation

Aerobic biodegradation is a process that often takes place in the environment, e.g. in natural ecosystems like soil or surface waters, and it is often associated with technical systems such as wastewater treatment plants.

Although for a long time it was thought that azo dyes cannot readily metabolise under aerobic conditions some specific aerobic bacterial cultures were found to be able to reduce the azo linkage via an enzymatic reaction. The aerobic conversions of sulfonated azo dyes were studied by Heiss[64] et. al and Shaul[65] et. al., and sometimes even a complete mineralization of sulfonated azo dyes was found.

In some studies, aerobic color removal of certain azo dyes was achieved, but all these stains required an additional energy and carbon source for growth. Since the supply of this additional substrate could have easily led to the formation of anaerobic michroniches, the occurrence of anaerobic azo dye reduction certainly cannot be excluded.[66],[67],[68],[69]

The aerobic biodegradation of different aromatic amines (aniline[70, carboxylated aromatic amines[71], chlorinated aromatic amines[72], benzidines[73], sulfonated aromatic amines) has been extensively studied and many of these compounds were found to be degraded. Sulfonated aromatic amines are difficult to degrade.

Anaerobic Biodegradation

Under anaerobic conditions a low redox potential (<-50 mV) can be achieved, which is necessary for the effective decoloration of dyes. Colour removal under anaerobic conditions is also referred as dye reduction. Many bacteria under anaerobic conditions reduce the highly electroplhilic azo bond in the dye molecules and produce colourless aromatic amines. The anaerobic decoloratization of azo dyes was first investigated using intestinal anaerobic bacteria.[74],[75],[76] Later it was found that azo dyes can also be decolorised with various other anaerobical cultures.[77],[78],[79] The efficacy of various anaerobic treatment applications for the degradation of a wide variety of synthetic dyes has been many times demonstrated. The exact mechanism of azo dye reduction is not clearly understood yet. The different mechanisms may be involved like enzymatic[80],[81], non-enzymatic[82], mediated[83], intracellular[84],[85], extracellular[86] and various combinations of these mechanisms. A complete anaerobic mineralization of the azo dye azodisalicylate was observed under methanogenic conditions.[87]

The reduction of azo dye under anaerobic condition strongly depends on the presence and disponibility of the cosubstrate. It acts as an electron donor for the azo dye reduction. The decoloration of reactive water soluble azo dyes was achieved under anaerobic conditions using glucose as a cosubstrate.[88] Anaerobic decoloration of reactive dyebath effluents with tapioca as a cosubstrate also enhances the color removal efficiency.[89] The suitable cosubstrates were also hydrolyzed starch, yeast extract, a mixture of acetate, butyrate and propionate.

Much effort has been devoted to the study of the influence of various modern technologies on the decomposition rate of the dyes and the effect of the presence of the other compounds in the media. It has been recently established that the development of high rate systems, in which hydraulic retention times are uncoupled from the solid retention times, facilitate the removal of dyes from textile processing wastewater. [62]

The effect of nitrate and sulfate salts used in textile dyeing on the microbial decoloration of a reactive azo dye has been studied. The results indicated that nitrate delays the onset of decoloration while sulphate did not influence the biodegradation process.[90]

The reduction of azo dyes proceeds better under anaerobic thermophilic conditions than under mesophilic conditions, although the termophilic process seems to be less stable compared to the mesophilic process.[91]

Carliell [92] et. al. studied the biodegradation of reactive dyes and they decolorised 80 % of a range of tested dyes. From a detailed study of a selected dye, it was proposed that this occurred via a reduction mechanism. The results were supported by tentative chemical identification of the dye degradation products.

Hu[93] isolated *Pseudomonas luteola* bacteria, after 6 month adaptation in a coloured wastewater he obtained micro-organisms capable of reductive cleavage of the azo group in the dye. Decoloration with these microorganisms was complete within 4 days.

Zee van der [94] et. al. studied the decoloration of 20 selected azo dyes by granular sludge from an upward-flow anaerobic sludge bed reactor and for all azo dyes tested the complete reduction was achieved.

Aromatic amines, as a result of azo dyes reduction, are not commonly degraded under anaerobic conditions. Many of different aromatic amines were tested, but only a few were degraded. Some aromatic amines, substituted with hydroxyl or carboxyl group were degraded under methanogenic and sulfate reducing conditions.[95],[96],[97]

Combination of Anaerobic/aerobic Biodegradation

Although the anaerobic reduction of azo dyes is generally more satisfactory than aerobic degradation, carcinogenic aromatic amins, as products of anaerobic degradation, have to be degraded by an aerobic process. Diverse technologies for the successive anaerobic/aerobic treatment of textile wastewater have been developed. Anaerobic/aerobic conditions can be implemented by spatial separation of the two sludges using a sequential anaerobic/aerobic reactor system.[98] These conditions can also be imposed in one reactor in the so-called integrated anaerobic/aerobic reactor system.[99]

EXAMPLES OF DECOLORATION STUDIES WITH AOP

Decoloration of Chlorotriazine Reactive Azo Dye with H_2O_2-UV and Optimization of the Process

The decoloration of chlorotriazine reactive azo dye C.I. Reactive Red 120 (Figure 3) with the H_2O_2-UV has been studied. The decoloration with H_2O_2-UV was performed on a pilot plant manufactured by Solvay Interox. The efficiency of decoloration was examined by time-dependent color intensity reduction, as well as by ecological parameters such as COD, BOD_5 and TC. Decoloration has been performed on a dyebaths containing chlorotriazine reactive azo dye C.I. Reactive Red 120 and chemicals (NaCl, NaOH and oxidizing agent) usually added when dyeing with such dyes. Chemicals used in the dyeing process reduced the efficiency of the decoloration process, especially the oxidizing agent and NaOH. Concerning the reaction conditions, it was further observed that the rate of decoloration was proportional to the output of the UV irradiator. The results show that the decoloration process using UV activated H_2O_2 is very suitable for decoloration of reactive azo dyes of the triazinyl type, since a decrease was noted both in the intensity of the color and in the values of the ecological parameters.[100]

The H_2O_2-UV decoloration process may depend on many different factors. So, the optimization of the decoloration process cannot be solved by simple linear multivariate correlation. Artificial neural networks (ANNs) represent a set of methods that may be useful for optimization of the H_2O_2-UV decoloration process. The decoloration of chlorotriazine reactive azo dye C.I. Reactive Red 120 with the H_2O_2-UV process depends on seven variables, (i) the intensity of UV lamp radiation; (ii) the addition of hydrogen peroxide; (iii) decoloration time; (iv)the concentration of dye; (v)the concentration of salt; (vi)the concentration of an alkali; (vii)the concentration of an oxidizing agent. The experiments needed for determining the significance of the variables' influences were determined by Plackett-Burman's factorial design. In general, the more variables, the more complicated is the model; therefore, the number of variables is tried to be reduced. The purpose of the modelling was, therefore, to optimize the procedure in such a way that it would be possible to "prescribe" the appropriate intensity of UV-light and the addition of peroxide according to the dyebath composition that is actually used in the textile industry. With appropriate decoloration conditions one has in mind the optimum conditions in which the decoloration time would be as short as possible, and also the pertinent ecological parameters. As responses, absorbance and ecological parameters (TIC, TOC and COD) were chosen. For all experiments the reduction of absorbance is larger with more hydrogen peroxide, less alkali and less oxidizing agent present in the bath. TOC values are greater in baths with more dye and more oxidizing agents. The greatest influence on COD is salt. Influence of the variables are greater than the experimental bias, which means that all of them are significant, and need to be taken into consideration for optimization.[101]

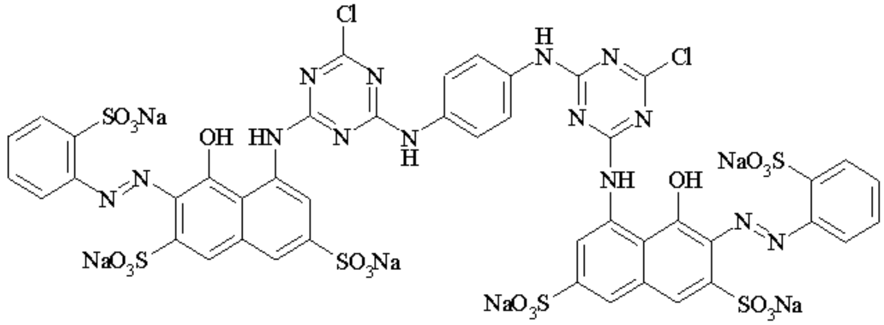

Figure 3. Chemical structure of the chlorotriazine reactive azo dye C.I. Reactive Red 120.

Decoloration of Rective Vinylsulphone Dyes with H_2O_2-UV, H_2O_2-O_3, H_2O_2-Fe^{2+} and Ultrasound

The influence of chemicals added (concentration of reactive dyes, NaOH, NaCl, urea) and influence of reaction conditions (intensivity of UV irradiation, amount of H_2O_2 added, decoloration time) on H_2O_2-UV decoloration of rective vinylsulphone dye C.I. Reactive Blue 19 (Figure 4) have also been studied.[102]

It was established that with the decoloration of reactive vinylsulphone dye C.I. Reactive Black 5 (Figure 5) treated by H_2O_2/UV the most important variables are: intensity of UV irradiation, decoloration time, concentration of H_2O_2, and the dye, NaCl, NaOH and urea concentrations. The values of the ecological parameters are higher than values permitted by the law, since the decolorations were not carried out to complete decoloration, but were stopped at times, specified by Plackett-Burman's experimental design. Experimental design is used to establish which variables influence in the positive or negative sense the efficiency of the decoloration process. The intensity of UV irradiation has mainly a significant influence on measuring the ecological parameters (COD, TOC and absorbance) at maximum level. Decoloration time affects positively absorbance, COD and TOC values. H_2O_2 has positive effect on minimum level. So, better results can be obtained by using lower concentrations of H_2O_2. The influence of sodium chloride and sodium hydroxide is variable on measuring ecological parameters. In some cases positive and in others negative effects have been observed. Urea has positive effects on absorbance at maximum level, but it has negative influence at minimum level.[103]

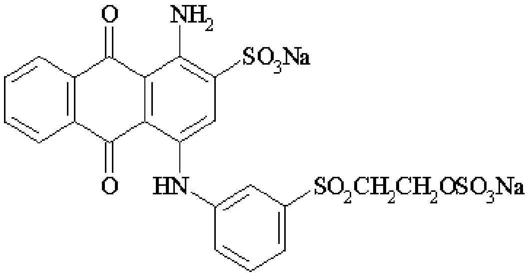

Figure 4. Chemical structure of the reactive vinylsulphone dye with C.I. Reactive Blue 19.

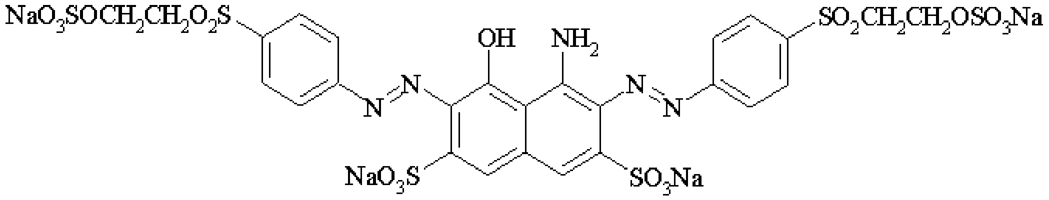

Figure 5. Chemical structure of the reactive vinylsulphone dye with C.I. Reactive Black 5.

The decoloration effectiveness of different advanced oxidation processes like (H_2O_2-UV, H_2O_2-O_3, H_2O_2-Fe^{2+}) in the case of dyebaths of six vinylsulphone reactive dyes (C.I. Reactive Blue 220, C.I. Reactive Black 5 (Figure 5), Remazol Dark Black N, C.I. Reactive Blau 28, C.I. Reactive Red 22 (Figure 6) , C.I. Reactive Yellow 15 (Figure 7)) have been studied. The concentration of dyes and chemicals were similar to the concentration in the dyebath after dyeing. The efficiency of decoloration was measured by decoloration time, absorbance, COD and TOC. The decoloration process was stopped at the moment when the solution became visually colorless. The results are on Table 12.

Table 12. Results of comparison studies of H_2O_2-UV, H_2O_2-O_3, H_2O_2-Fe^{2+}

Textile dye	*AOP type*	*COD/ (mg/L)*	*TOC/ (mg/L)*	*Time/ min*	*Decoloration/ %*
C.I. Reactive Blue 220	H_2O_2-UV	170	1800	120	99.6
C.I. Reactive Black 5	H_2O_2-UV	200	1900	50	100
Remazol Dark Black N	H_2O_2-UV	200	1900	60	99.5
C.I. Reactive Blau 28	H_2O_2-UV	190	2000	40	100
C.I. Reactive Red 22	H_2O_2-UV	200	1950	50	100
C.I. Reactive Yellow 15	H_2O_2-UV	200	1950	30	100
C.I. Reactive Blue 220	H_2O_2-O_3	170	1750	120	99
C.I. Reactive Black 5	H_2O_2-O_3	300	1990	80	100
Remazol Dark Black N	H_2O_2-O_3	350	2000	90	99.5
C.I. Reactive Blau 28	H_2O_2-O_3	190	2000	85	100
C.I. Reactive Red 22	H_2O_2-O_3	400	2000	95	100
C.I. Reactive Yellow 15	H_2O_2-O_3	300	2000	60	99
C.I. Reactive Blue 220	H_2O_2-Fe^{2+}	570	2000	40	100
C.I. Reactive Red 5	H_2O_2-Fe^{2+}	620	1900	30	100
Remazol Dark Black N	H_2O_2-Fe^{2+}	720	1900	30	99.6
C.I. Reactive Blau 28	H_2O_2-Fe^{2+}	605	2000	30	100
C.I. Reactive Red 22	H_2O_2-Fe^{2+}	590	1950	30	100
C.I. Reactive Yellow 15	H_2O_2-Fe^{2+}	900	2000	20	98

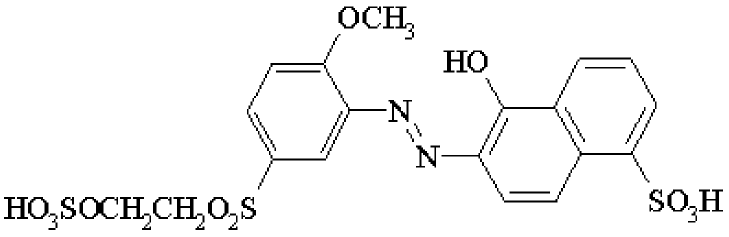

Figure 6. Chemical structure of the reactive vinylsulphone dye with C.I. Reactive Red 22.

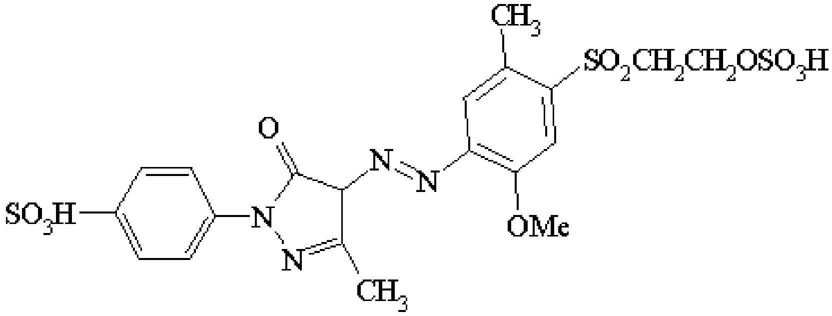

Figure 7. Chemical structure of the reactive vinylsulphone dye with C.I. Reactive Yellow 15.

The decoloration with H_2O_2/Fe^{2+} was the fastest, and the costs of such process are low, but it is not really suitable for environmental reasons (sludge removal).

The decoloration with H_2O_2/O_3 yields lower COD values, it causes additional water pollution because of ozone; the disadvantages of this procedure are high investment and operating costs. Decoloration with H_2O_2/UV is an environmentally friendly procedure. It produces no sludge and no additional water pollution, while COD values were low, but investment and operating costs are high.[104

The decoloration of the same vinylsulphone reactive dyes has also been performed using ultrasound and ultrasaound/H_2O_2 treatment. Decoloration has been performed on an Ultrasound Processor Sonics&Materials VibraCell VCX 600 with a constant frequency of 20 kHz and power of 80 W/cm^2 and 1 cm^2 titanium horn. It was found that the efficiency of the ultrasound treatment was significantly enhanced when H_2O_2 was added. The rate of color degradation was twice as fast as that accomplished by sonolysis alone (Table 13).[105]

The reactive dye C.I. Reactive Black 5 was also treated by low (20 kHz) and high (279 and 817 kHz) ultrasonic irradiation, without the addition of any oxidant. Experiments were carried out with low frequency probe type, and high frequency plate type transducer at 50, 100 and 150 W of acoustic power. Sonochemical decoloration was increased with rising frequency, acoustic power and irradiation time. The addition of a radical's scavenger (2-methyl-2-propanol) significantly inhibited the sonochemical decoloration, which confirmed radical-induced reactions of decoloration. Acute toxicity to marine bacteria *Vibrio fischeri* have been tested before and after ultrasound irradiation. Under the conditions employed in this study, no toxic compounds were detected. Mineralization of the dye was followed by TOC measurements. Relatively low degradation efficiency (50 % after 6 h of irradiation) indicates that ultrasound is rather inefficient in overall degradation, when used alone. [106]

Table 13. Decoloration of reactive dyes with ultrasound and ultrasound/H_2O_2

Textile dye	*AOP type*	*Time/h*	*Decoloration/%*
C.I. Reactive Blue 220	Ultrasound	7	70.4
C.I. Reactive Black 5	Ultrasound	7	96.2
Remazol Dark Black N	Ultrasound	7	74.9
C.I. Reactive Blau 28	Ultrasound	7	57.4
C.I. Reactive Red 22	Ultrasound	7	81.5
C.I. Reactive Yellow 15	Ultrasound	7	91.0
C.I. Reactive Blue 220	Ultrasound/H_2O_2	4	93.4
C.I. Reactive Black 5	Ultrasound/H_2O_2	4	98.6
Remazol Dark Black N	Ultrasound/H_2O_2	4	92.2
C.I. Reactive Blau 28	Ultrasound/H_2O_2	4	91.0
C.I. Reactive Red 22	Ultrasound/H_2O_2	4	96.7
C.I. Reactive Yellow 15	Ultrasound/H_2O_2	4	96.1

SHORT CONCLUSION

For decoloration and degradation of textile wastewaters many physical, chemical and biological methods have been developed. Every existing technology presents limits; advantages and disadvantages. The composition of textile wastewater is very complex, so the use of a universal wastewater treatment seems to be impossible. Which decoloration process will be used depend on the wastewater characteristic (type, dye concentration and auxiliaries, pH). A single wastewater treatment system is unable to overcome all problems by itself to provide an efficient treatment of effluents and be also cost effective.

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