Chapter III

Fenton Oxidation Of Dyes
3.1. Introduction

Recently there has been a renewed interest in the use of Advanced Oxidation Process (AOP) as a viable treatment option for the removal of refractory organics, color and substantial COD and TOC from industrial effluents. A common feature that all of them share is the generation of highly reactive Hydroxyl radicals (OH') which in turn degrade organic pollutants, usually to carbon dioxide and water. Hydroxyl radicals are ubiquitous in the environment and are present in low concentrations under normal conditions in surface water (Hoigne, 1990) and in the atmosphere (Atkinson (1989). They are among the most reactive oxidants known and are responsible for the degradation of many environmental contaminants such as NO₂, PAHs (Atkinson, 1989) and for formation of organic polymers (Larson et al., 1991). In the natural waters hydroxyl radicals are generated by photolysis of nitrate, which could in turn cause the degradation of trace organic pollutants (Mabury and Crosby, 1994). However, the natural generation of hydroxyl radical is slow and much of it is scavenged through competitive reactions with different kinds of Dissolved Natural Organic Matter (DNOM), bicarbonate or carbonate, bromide and even hydrogen peroxide (Hoigne, 1997). Therefore, if these hydroxyl radicals could be generated synthetically and at will, its immense oxidation potential could be directed towards oxidizing many toxic and refractory organics. The Advanced Oxidation Processes (AOP) achieves this objective. Hydroxyl radicals can be generated through chemical and photochemical processes.
In the chemical process, reaction between ferrous or ferric salt with hydrogen peroxide produces hydroxyl radicals, while in photochemical reaction, OH\(^{-}\) is produced via photolysis of hydrogen peroxide, or through a combination of TiO\(_2\) and UV or a combination of Ozone and UV or Ozone-hydrogen peroxide and UV combinations. In addition surface adsorbed hydroxyl radicals are the oxidants that possibly occur on passivated anodes and on illuminated semi-conductors. The most commonly used AOP's include hydrogen peroxide, ozone or oxygen as the bulk oxidant (Legrini et al., 1998). The common feature that all the Advanced Oxidation Processes (AOP's) such as TiO\(_2\)/UV, O\(_3\)/UV, O\(_3\)/H\(_2\)O\(_2\) and O\(_3\)/H\(_2\)O\(_2\)/UV share is the generation of a principal active species, the hydroxyl radical (OH\(^{•}\)). These hydroxyl radicals being non-specific in its reactions, is useful for degrading a variety of environmental pollutants (Spadaro et al., 1994). One method of producing the hydroxyl radical from hydrogen peroxide is through the Fenton reaction (Fe\(^{2+}\)/ Fe\(^{3+}\)- H\(_2\)O\(_2\)) (Barb et al., 1951; Walling, 1975). This method is effective in removing organic pollutants (Sedlak and Andren, 1991 and Arnold et al., 1995) but requires stoichiometric amounts of ferrous ions. The method of ferrous-hydrogen peroxide oxidation is also known as Fenton’s reagent method.

Fenton reaction can also be made catalytic, by photo reducing the ferric ions in the near UV region in the presence of hydrogen peroxide. The combined process is known as the photo-assisted Fenton or photo-
Fenton reaction and yields a more effective system for oxidative degradation (Pignatello, 1992).

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \underset{hv}{\rightarrow} \text{Fe(OH)}^{2+} + \text{OH}^- \]

\[ \text{Fe(OH)}^{2+} \rightarrow \text{Fe}^{2+} + \text{OH}^- \]

The photo-Fenton reaction is optimum at pH 2.8 (Pignatello, 1992) where approximately half of the ferric is present as ferrous ion and half as Fe(OH)\(^{2+}\) ion, the photoactive species. Below this pH the concentration of Fe(OH)\(^{2+}\) declines and at higher pH the ferric ions precipitates as oxyhydroxide. The Fe(OH)\(^{2+}\) ions absorb light at wavelengths up to about 410 nm. Hence, the reaction can be carried out efficiently with longer wavelength light than other AOP's such as O\(_3\)/UV or H\(_2\)O\(_2\)/UV, which require wavelengths below 300 nm. The ferric ions catalyst can be removed by raising the pH of the solution.

The hydroxyl radical formation in the Advanced Oxidation processes, involving UV light, H\(_2\)O\(_2\) and Fe(II) or Fe(III) salts can be represented by the following simplified reaction scheme (Prousek, 1995).

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2(\text{OH}^+) \quad (1) \]

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^+ + \text{HO}^- \quad (2) \]

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 + \text{hv} \rightarrow \text{HO}_2^- + \text{H}^+ (\lambda > 300 \text{ nm}) \quad (3) \]

Reaction (2) takes place both in the presence and absence of light, and the concentration of ferrous ions is low as long as there is sufficient H\(_2\)O\(_2\) in the reactor. The drawback of the dark reaction is that when all the
ferrous ions are converted to ferric ions, generation of hydroxyl radicals considerably slows down, due to the slow rate of reduction of ferric to ferrous in the dark (Oliveros et al., 1997). On the other hand, although reaction (3) can be facilitated by UV/Visible light, the depletion or scarcity of hydrogen peroxide may result in an undesired accumulation of ferrous ions in the reactor. The initial rate of mineralization is reported to be faster with Fe(II)/H₂O₂ (Fenton reagent), than Fe(III)/H₂O₂ (Fenton-like reagent), due to the immediate formation of hydroxyl radicals with Fenton reagent. Further, the presence of Fenton-like reagents is reported to increase the chain length by the formation of Fe(III)-hydroxy complexes, resulting in a more complete destruction of the organic compounds (Ruppert et al., 1993) and as in this case dyestuffs.

Several researchers have explored the photo-Fenton reaction as a possible wastewater treatment method. Rate enhancement of Fe(II)/H₂O₂ degradation of 4-nitrophenol by UV irradiation has been reported (Lipezynska-Kochany, 1991). Sun and Pignatello (1993a) showed that the photo-Fenton reaction completely mineralizes 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Sun and Pignatello (1993b) studied the oxidation of pesticides like metolachlor and methyl parathion under mild conditions. Pignatello and Sun (1995) and Muszkat et al., (1992) used sunlight to the Fe(III)/H₂O₂ system in a survey of the destruction of various herbicides, several aliphatic and aromatic halogenated compounds. Detailed mechanistic studies have also been carried out with compounds such as phenol (Chen and Pignatello, 1997).
and 4-chlorophenol (Bauer, 1994; Ruppert et al., 1993), 2-and 4-nitrophenols (kiwi et al., 1994), di-n-butyl-ortho-phthalate (Halmann, 1992), polychlorinated biphenyls (PCBs) (Pignatello and Chapa, 1994) and perhalogenated alkanes (Huston and Pignatello, 1996). High concentrations of suspended solids limits the efficiency of photocatalytic oxidation processes due to the limited depth of photon penetration (Venkatadri and Peters 1993).

The advantage of Fenton's reagent over conventional chemical oxidation processes and other Hydroxyl radical (OH*) generating systems is its simplicity and being environmentally benign are easy to handle. As the chemicals are commonly available and inexpensive there is no need for special equipments like UV lamps, complex reaction vessels, TiO₂ particles or ozone generators (Scott et al., 1995). In addition these processes are characterized by the absence of kinetic limitations and generation of highly reactive free radicals, which are 10⁶ to 10⁹ times faster than the strongest chemical oxidants known, such as ozone and hydrogen peroxide (Bicher et al., 1997) Ozonation can also be used as a wastewater treatment option, but the major disadvantages are its low reactivity (Neta et al., 1988) and selective degradation (Dowideit et al., 1995). Therefore, when a more general oxidant is required, the OH radical is the chosen one. A comparison of redox potentials show that hydroxyl radicals having a redox potential of 2.8 V is much higher than that of ozone which is 2.07 V (Carey, 1992) Sequentially these hydroxyl radicals come next only to Fluorine,
which has a redox potential of 2.87 V (Johannes, 1985). There are two mechanisms by which the OH* reacts with organic matter (Von Sonntag, 1987):

(i) By addition to the C=C bond.

$$\text{OH}^* + R_2C=CR_2 \rightarrow R_2(\text{HO})C-CR_2^*$$

(ii) By abstracting a carbon-bound H-atom.

$$\text{OH}^* + RH \rightarrow \text{H}_2\text{O} + R^*$$

The addition to double bonds is generally faster than the hydrogen abstraction.

The second order rate constants of the hydroxyl radicals with compounds containing C-H or unsaturated C-C typically are of the order of $10^7$ to $10^{10}$ L mol$^{-1}$s$^{-1}$ (Buxton et al., 1988). According to Jurg Hoigne (1997) a typical second-order rate constant for medium sized or large organic molecules is $5 \times 10^{-9}$ M$^{-1}$ s$^{-1}$ or $2.5 \times 10^{-9}$ M$^{-1}$ s$^{-1}$ (typical for small sized organic molecules). Reaction of hydroxyl radicals with aromatic compounds occurs almost at the diffusion-controlled rate. Continued reaction of the hydroxylated compounds with the hydroxyl radicals leads to aromatic ring cleavage. Products arising from ring cleavage are subsequently oxidized. This means that many compounds are potentially mineralized to carbon dioxide, water and inorganic ions. All these features make the Advanced Oxidation Processes (AOP) one of the most sought after and potentially important as a viable treatment option.
Two components go into the making of Fenton's reagent; namely ferrous ions ($\text{Fe}^{2+}$) and hydrogen peroxide. The use of both iron and hydrogen peroxide in the field of wastewater treatment is not new. The most important environmental application of iron to date involves wastewater treatment via coagulation, which culminates in the association of solute particles to form flocculated agglomerates (Shaw, 1968). Iron salts such as $\text{FeCl}_3$, $\text{Fe}_2(\text{SO}_4)_3$ and $\text{FeSO}_4$ are used alone or in combination with other coagulated inorganic salts such as calcium hydroxide (lime), calcium sulfate, magnesium hydroxide, magnesium sulfate and aluminium sulfate (alum). Iron salts are added to wastewater containing toxic heavy metals (e.g. Chromium (III), lead and arsenic) to form ferric hydroxide precipitates. The toxic metals are trapped within and adsorbed onto the precipitate leaving a purified effluent Eilbeck (1987).

Another approach to removing toxic metals from wastewater involves adsorptive filtration. First, soluble heavy metals are removed from aqueous media by adsorption onto a thin layer of ferrihydrite that has been immobilized on the surface of sand particles. Then, the sand is filtered. Because the resulting ferrihydrite remains trapped on the sand particles, the adsorbent is later regenerated in a back washing step (USEPA, 1987) and Benjamin and Slettin (1993). Toxic metals have been removed from industrial wastewater electrolytically. Wastewater is recirculated between two iron electrodes and an electric current is passed between the electrodes when it begins to slowly remove iron from the anode in the form
of Fe$^{2+}$. The ferrous ions generated combine with hydroxide ions produced at the cathode to give Fe(OH)$_2$. The iron hydroxide and adsorbed substances are then removed by flocculation and filtration (Reife, 1993; and Wilcock et al., 1996).

Iron salts are effective coagulants for removing phosphates, providing a potential solution to the problem of phosphate-induced eutrophication of lakes, streams and rivers. Taking advantage of this property, iron salts have also been used to remove phosphate ions from organic dye filtrates following the synthesis of azo dyes in a medium containing phosphoric acid (USEPA, 1987).

The second component of the Fenton's reagent is hydrogen peroxide. Hydrogen peroxide is a potent source of free radicals, has a redox potential of 1.78V and being a powerful oxidant its use in the environmental systems is not new. Hydrogen peroxide is considered to be a "clean" reagent since any of it that is not consumed in oxidation of the pollutant quickly decomposes to form only water and oxygen as products. Hydrogen peroxide is used to oxidize of sulphides with respect to odour control, notably in pulp and paper manufacture and textile plant wastes. Sulphide corrosion of waste pipes may be controlled by the addition of hydrogen peroxide to wastewater (Cadena and Peters, 1988) Hydrogen peroxide can also be used as an additional oxygen source for overloaded activated sludge plants (Houtmeyers et al., 1977) and controlling filamentous bulking (Saayman et al., 1996 and Saayman et al., 1998).
Peroxide is used in paper manufacture (Prat et al., 1988) and during deinking in waste paper recycling (Grayson and Eckroth, 1981) Peroxide is used in the removal of colour and it is applied extensively as a bleaching agent in the textile industry. Ince (1999) showed the cost-effectiveness in using peroxide for the photochemical degradation of dyes. Lin and Peng (1995) reported that the efficiency of the Fenton oxidation to remove COD was dependent on the hydrogen peroxide concentrations used. Hydrogen peroxide also finds wide application in the form a pretreatment option for refractory organics. The partial oxidation of recalcitrant compounds may also be advantageous in combined chemical/biological wastewater treatment processes. Two chlorinated aromatics tested by Carberry and Bensing (1991) showed enhanced biodegradability after pre-oxidation at molar ratios of peroxide to pollutant between 2:1 and 6:1, with an optimum at 4:1. The reactions related to hydrogen peroxide can be summarized into five main reactions (Snell and Ettre, 1971):

Decomposition: \[ 2H_2O_2 \rightarrow 2H_2O + O_2 \]
Molecular addition: \[ H_2O_2 + X \rightarrow X.H_2O_2 \]
Substitution: \[ H_2O_2 + RX \rightarrow ROOH + HX \]
Or
\[ H_2O_2 + 2RX \rightarrow ROOR + 2HX \]
Oxidation: \[ H_2O_2 + X \rightarrow XO + H_2O \]
Reduction: \[ H_2O_2 + X \rightarrow XH_2 + O_2 \]

Hydrogen peroxide may react either directly or after it has first ionized or dissociated into free radical. In spite of the powerful oxidizing
ability of hydrogen peroxide, it acts as a reductant when reacting with stronger oxidizing agents such as chlorine, potassium permanganate and potassium dichromate. The reaction mechanism is very complex and may be affected by the reaction conditions and the type of the catalyst. Some of the factors influencing stability of hydrogen peroxide are concentration, temperature, pH, concentration of the stabilizer and presence of contaminants such as chromium, copper, iron and zinc (Grayson, 1981).

These apart, a major application of hydrogen peroxide and the ferrous salts combined is however, in the Advanced Oxidation Process, after it was observed that the high oxidative power of hydrogen peroxide could be further increased through a combination with UV radiation or metal salts. Several metals like titanium, vanadium, manganese, cobalt or nickel catalyze the decomposition of hydrogen peroxide. However, iron is the cheapest and least questionable of these metals making it the most preferred.

3.1.1. Mechanism of Fenton Oxidation

Historically, Fe/H₂O₂ oxidations have been of interest mostly from a synthetic or mechanistic perspective, their relevance to enzyme reactions and free-radical damage to cells. Recently, their potential for waste water treatment have been realized and reactions that generate hydroxyl radical (OH⁻) in solution at low temperature have attracted interest for destruction of toxic organic compounds in wastewaters (Joseph J. Pignatello., 1992).
In 1894, H.J.H. Fenton reported that ferrous ion strongly promoted the oxidation of malic acid by hydrogen peroxide. The Fe^{2+}/H_{2}O_{2} system is often referred to as Fenton’s reagent (Fenton, 1894). In the Fenton’s mechanism reactions with H_{2}O_{2}, cycle iron between the +II and +III oxidation states, yielding hydroxyl (OH\(^{+}\)) radicals and other byproducts. OH\(^{+}\) is a powerful indiscriminate oxidant that reacts with many compounds at near diffusion controlled rates (Walling, 1975; Haag and Yao 1992). The basis of all Fenton based Advanced Oxidation Processes is that, when hydrogen peroxide is added to an aqueous system containing an organic substrate and excess Fe^{2+} at pH 0-2, the hydroxyl radicals generated attack the substrate and the subsequent course of the reaction and stoichiometry (moles of Fe^{2+} oxidized pre mole of H_{2}O_{2} added, \Delta[Fe^{2+}] / \Delta[H_{2}O_{2}] depend upon the fate of the organic radicals so produced. For a system containing a variety of C-H bonds, the postulated reaction steps are (Walling, 1975):

\[
\begin{align*}
Fe^{2+} + H_{2}O_{2} & \rightarrow Fe^{3+} + HO^{-} + HO^{-} \\
HO^{-} + Fe^{2+} & \rightarrow Fe^{3+} + HO^{-} \\
HO^{-} + R_{i}H & \rightarrow H_{2}O + R_{i}^{-} \\
HO^{-} + R_{i}H & \rightarrow H_{2}O + R_{i}^{-} \\
HO^{-} + R_{k}H & \rightarrow H_{2}O + R_{k}^{-} \\
R_{i}^{-} + Fe^{3+} & \rightarrow Products + Fe^{2+} \\
2R_{i} & \rightarrow Product (dimmer) \\
R_{k}^{-} + Fe^{2+} & \rightarrow Fe^{3+} + R_{k} \rightarrow R_{k}H
\end{align*}
\]
Unsaturated molecules (3) may also represent stoichiometrically equivalent addition reactions, but in either case it is assumed that the resulting radicals belong to three distinct classes:

Those oxidized by Fe$^{3+}$, R$_{i}^{•}$
Those which are inert and dimerize, R$_{i}^{•}$, and
Those which undergo reduction by Fe$^{2+}$, R$_{k}^{•}$

Thus, in the above reaction that follows between ferrous iron and hydrogen peroxide in the presence of organic compounds but in the absence of complexing ligands other than water, decomposition of hydrogen peroxide in homogeneous aqueous solution involves the formation of organic radicals which react with molecular oxygen forming oxyl radicals namely the hydroxyl (OH$^{•}$) radicals and the hydroperoxyl (HO$_{2}^{•}$radicals). Compared to the hydroxyl radical, the hydroperoxyl radical is much less reactive and its conjugate base O$_{2}^{•-}$($pK_a$ 4.8) is practically unreactive as a free radical (Frimer, 1988). These can in turn react with molecules of the organic compounds present, leading to a chain auto-oxidation of the compound with the formation of considerable quantities of peroxides and peroxide radicals which can react with ferrous ions or with hydrogen peroxide or they may decompose spontaneously. The carbon centered radicals generated by the oxyl radical attack may react with oxygen if present to form organoperoxy radicals (ROO$^{•}$) which can decompose to form hydroperoxyl radical (HO$_{2}^{•}$) or ultimately non-radical oxygenated products (Von Sonntag et al., 1997). Organo radicals may in
some cases be reduced by ferrous iron or be oxidized by ferric iron. The formation of hydroxyl radical (OH\(^{\cdot}\)) is considered to be the primary step in peroxide-iron reaction (Walling, 1975).

The Fenton's reaction has been the subject of a plethora of studies and many mechanisms derived from spectrophotometric and kinetic studies have been proposed. Haber and Weiss (1934) proposed a mechanism, with hydroxyl radicals as the actual oxidant species. Their initial hypothesis was subsequently proved by many techniques including ESR spectroscopy. The hypothesis states that under acidic conditions the reaction is

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^{\cdot} + \text{HO}^{-} \quad (k = 51 \text{ M}^{-1}\text{s}^{-1}) \quad (1)
\]

resulting in the formation of hydroxyl radicals, which are highly unstable but have a very high oxidation potential. They react with organic substances either by hydrogen abstraction or electrophilic addition to double bonds. Reacting with molecular oxygen, they initiate a non-selective sequence of oxidative reactions (dehydrogenation and or hydroxylation), resulting in destruction of the organic pollutants and conversion to CO\(_2\) and simple inorganic compounds with very high rate constants that approach diffusion controlled limits. Hydroxyl radicals (OH\(^{\cdot}\)) are consumed with a rate constant of about 10\(^5\) s\(^{-1}\) i.e., they have a mean lifetime of only about ten microseconds (Hoigne, 1997).

The hydroxyl radical so formed may be scavenged by reaction with another Fe\(^{2+}\) according to the reaction
\[ \text{OH}^- + \text{Fe}^{2+} \rightarrow \text{HO}^- + \text{Fe}^{3+} \quad (2) \]

or the presence of excess hydrogen peroxide, the reaction that takes place is given by

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \leftrightarrow \text{Fe}-\text{OOH}^{2+} + \text{H}^+ \quad (3) \]

\[ \text{Fe}-\text{OOH}^{2+} \rightarrow \text{HO}_2^- + \text{Fe}^{2+} \quad (4) \]

Since reaction (4) is generally much slower than reaction (1) \([\text{Fe}^{2+}]\) is small relative to \([\text{Fe}^{3+}]\)

\[ \text{Fe}^{2+} + \text{HO}_2^- \rightarrow \text{Fe}^{3+} + \text{HO}_2^- \quad (5) \]

\[ \text{Fe}^{3+} + \text{HO}_2^- \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (6) \]

\[ \text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (7) \]

Reaction (7) is an additional mechanism for hydroxyl (OH\(^{-}\)) radical scavenging.

It should be noted that the concentration of peroxide employed in the oxidation process should be carefully controlled, as excess peroxide is involved in non-productive internal reactions and efficiency of oxidation can actually decrease with increased peroxide levels. Peyton and Glaze (1986) reported that if excess hydrogen peroxide is used the hydroxyl radicals will produce hydroperoxyl radicals which are much less reactive than hydroxyl radicals and therefore reduce the efficiency of the Advanced Oxidation Process.

Organic radicals formed by any of these reactions may quickly add a dissolved oxygen molecule to form reactive peroxyl type intermediates.
These react further to form hydroperoxyl (HO$_2^*$) radicals, hydrogen peroxide and a series of different peroxides, aldehydes, acids etc. The primary requirement for the generation of hydroxyl radicals is that the concentration of ferrous ions must be sufficient enough so as to ensure that there is sufficient hydrogen peroxide in the reactor. On the other hand, the depletion or scarcity of hydrogen peroxide may result in an undesired accumulation of Fe(II) in the reactor. The initial rate of mineralization is reported to be faster with Fe(II)/H$_2$O$_2$ (Fenton reagent), than Fe(III)/H$_2$O$_2$ (Fenton-like reagent), due to the immediate formation of hydroxyl radicals with Fenton reagent (Ruppert et al., 1993). Further, in the presence of Fenton-Like reagents the chain length is increased by the formation of Fe(III)-hydroxy complexes, resulting in a more complete destruction of the organic compound (Ruppert et al., 1993) in this case the dye molecule.

The reaction between hydrogen peroxide and ferrous iron in dilute solution in the presence of oxygen and organic compounds leads to induced oxygen oxidation of ferrous iron. The extent of the induced oxidation may be quite large, particularly in oxygen-saturated solutions of the order of 10$^3$ M in peroxide and iron, in which the concentration of oxygen is relatively high. The amount of ferrous iron oxidized by the induced reaction may be two to three times as great as the amount oxidized by the stoichiometric reaction under certain circumstances. When the reaction between ferrous iron and hydrogen peroxide is carried out in the presence of various organic compounds, organic radicals are formed
which can react with oxygen forming oxyl radicals namely the hydroxyl 
(OH*) radicals and the hydroperoxyl (HO2*) radicals. These can in turn react with molecules of the organic compound present, leading to a chain auto-oxidation of the compound, with the formation of considerable quantities of peroxides or the peroxide radicals may react with three ferrous ions or with hydrogen peroxide or they may decompose spontaneously.

In the presence of oxygen it is stated that all the organic compounds show qualitatively similar behavior, without distinction between “Promoting” and “Suppressing” compounds. On the other hand, in the Fenton reaction chloride ion is a suppressing agent in the presence or absence of oxygen.

In aqueous solutions [Fe(II)]^3+ is the predominant species at pH less than 2. At pH greater than 2, Fe(III)-hydroxy complexes [Fe(III)(OH)2]^+ and [Fe2(III)(OH)2]^4+ may also catalyze the decomposition of H2O2. The Fenton’s process employs ferrous ions and hydrogen peroxide. Under acidic pH the strong oxidative hydroxyl radical is produced and the ferrous ions are oxidized to ferric ions (Fenton, 1894; Walling and Kato, 1971). The ferric ions that is generated may form ferric hydroxo complexes with hydroxide ions as in the following two equations

$$[\text{Fe(H}_2\text{O)}_6]^3^+ + \text{H}_2\text{O} \rightarrow [\text{Fe(H}_2\text{C)}_5\text{OH}]^{2+} + \text{H}_3\text{O}^+ \quad (1)$$

$$[\text{Fe(H}_2\text{O)}_5\text{OH}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Fe(H}_2\text{O)}_4\text{OH}_2]^{+} + \text{H}_3\text{O}^+ \quad (2)$$

These complexes have a pronounced tendency to polymerize at pH 6.5 to 7, according to the following equations (3) – (5). (Stumm et al., 1962)
\[ 2[\text{Fe(H}_2\text{O})_5\text{OH}]^{2+} \rightarrow [\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2]^{4+} + 2\text{H}_2\text{O} \] (3)

\[ [\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_2]^{4+} + \text{H}_2\text{O} \rightarrow [\text{Fe}(\text{H}_2\text{O})_7(\text{OH})_3]^{3+} + \text{H}_3\text{O}^+ \] (4)

\[ [\text{Fe}(\text{H}_2\text{O})_7(\text{OH})_3]^{3+} + [\text{Fe}(\text{H}_2\text{O})_5(\text{OH})_2]^{2+} \rightarrow [\text{Fe}_3(\text{H}_2\text{O})_6(\text{OH})_4]^{5+} + 2\text{H}_2\text{O} \] (5)

Fenton’s oxidation possesses the dual advantageous of both oxidation and coagulation in addition to increasing the amount of oxygen in water (Chin and Hicks, 1970; Kang and Chang, 1997).
3.2. Review on Fenton Oxidation:

Lin and Chen (1997), studied a combination of electrochemical and chemical coagulation along with ion exchange for treating textile wastewater for reuse. The primary objective was to lower colour, turbidity and COD through electrochemical method and coagulation while ion exchange was primarily to further lower the COD concentration and reduce iron conductivity and total hardness of the wastewater. They observed that pH (optimum pH observed around 3) of the wastewater was an important operating factor that influenced the performance characteristics of electrochemical process. Addition of hydrogen peroxide was highly beneficial in enhancing the efficiency of electrochemical method. The efficiency enhancement was attributed to the presence of dissolved iron from the electrodes, which in the presence of hydrogen peroxide initiated a Fenton like reaction.

Kuo (1992), studied decolorization using the Fenton's reagent for five types of simulated dye wastewater prepared with disperse, reactive, direct, acid and basic dyes. The optimum pH was found below 3.5 and temperature enhanced the rate of decolorization. While the Fenton's reagent resulted in 97% decolorization for all the dye types studied the percentage decolorization was found to be structure dependent and on an average resulted in 90% COD removal.

Prat et al., (1988), examined the use of hydrogen peroxide in combination with ultraviolet radiation for the treatment of wastewaters from chlorination and alkaline extraction stages of paper-pulp bleaching. They
found that for a similar reaction time color reduction in the effluent was maximum at basic pH and that residual hydrogen peroxide would not be detrimental to the posterior biological processes. A combination of hydrogen peroxide and ultraviolet radiation, although achieved a greater reduction of color in the effluent it did not turn out to be economically competitive.

Pitroff et al., (1992), studied the decolorization of textile wastewaters by UV-radiation and hydrogen peroxide. They observed the degradation rate of the dye to be heavily dependent on the UV radiator output. The efficiency of the process although increased with higher dye concentrations, had a limit as increased dye concentration resulted in decreased permeability of the UV radiation. Reactive dyes were found to be easily decolorized with exceptions of yellow and green dyes. The green dyes required relatively longer treating time. The study also reported that UV/H$_2$O$_2$ treatment reduced toxicity (bacterial inhibition). Similar study was conducted by Shu et al., (1995), for the decolorization of eight azo dyes. The system was found to be a very efficient treatment method for colour removal. Chang et al., (1996), used a modified Nemst equation to described the decolorizing reaction using the oxidation-reduction potential (ORP) as an on-line monitoring and control parameter of the chemical reaction. The study utilized sodium hypochlorite to reduce the colour of wastewater spiked with five dyes, namely methyl red(MR), methyl violet (MV), methyl blue (MB), malachite green (MG) and methyl orange (MO). The ascending order of decolorization was MG>MV>MO>MT>MB.
Yang et al., (1998), explored the potential of ultraviolet light/hydrogen peroxide photochemical oxidation technology for treating textile-dyeing effluent. The effects of dye class and structure, dyebath concentration, radiation intensity and hydrogen peroxide level on a UV/H$_2$O$_2$ system's ability to decompose and decolorize dyes were studied. Results indicated that acid, direct, basic and reactive dyes appeared to be viable candidates for photochemical oxidation, however, the limited solubility seemed to hinder the UV/H$_2$O$_2$ degradation of disperse and vat dyes.

Bekbolet et al., (1998), studied the photocatalytic color removal of humic acid in the presence of some inorganic anions. The results showed that the removal rates could be explained in terms of Langmuir-Hinshelwood kinetics and the presence of common inorganic anions such as chloride, nitrate, sulfate and phosphate ions retarded the photocatalytic removal rate. Chloride, nitrate and sulphate although reduced the color removal rate of humic acid in water, the photocatalytic oxidation rates were found to be fast enough. However, phosphate ions retarded the rate significantly. First order equation was not found to satisfactorily explain the removal kinetics. Freundlich adsorption isotherm was found helpful in explaining the adsorption effect of anions on the photocatalytic removal rate. The authors observed that both Color$_{436}$ and Color$_{400}$ could be used as parameters to follow the decolorization of humic acids in natural waters.

Namboodri and Walsh, (1996), investigated the optimization and decolorization of spent reactive dyebath water with ultraviolet radiation in
the presence of hydrogen peroxide using both batch and continuous circulation processes. For a given concentration of the dye, under similar radiation intensity and peroxide concentration the continuous operation was found more efficient, due to the improved circulation and radiation exposure in the column.

Rodriguez et al., (1999) studied the treatment of pulp mill effluent using Fenton-type reactions assisted by 2,3-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid and 1,2-dihydroxybenzene. Efficiency of the treatment process was evaluated by the removal of absorbable organochloride compounds and toxicity reduction. Dihydroxybenzenes were found to increase the oxidative efficiency while 3,4-dihydroxybenzoic acid and 1,2-dihydroxybenzene inhibited Fenton reaction.

Solozhenko et al., (1995), studied the optimization and intensification of monoazo dye decolorization by Fenton's reagent. They observed that a hydrogen peroxide concentration of 17 mg/L resulted in 95 – 97% decolorization. The decolorization system was greatly affected by pH and occurred only in an acidic medium. The efficiency of decolorization increased under the influence of solar radiation or by an increase in the reaction temperature. The effectiveness of hydrogen peroxide was found dependent on the initial dye concentration with the consumption of hydrogen peroxide increasing with an increase in the initial dye concentration.

Wanpeng et al., (1996), studied the application of ferrous ion-peroxide oxidation combined with coagulation as a pretreatment option for
treating wastewater from H-acid manufacturing process rich in various substituted derivatives of naphthalene. The optimum pH value was below 4 and at suitable ferrous ion and peroxide dosage the overall COD removal reached 90% or more. The groups on naphthalene ring, such as nitrite and sulphide were substituted by hydroxyl free radical, and resulted in ring cleavage during oxidation process. The oxidation of H-acid by Fenton’s reagent was a three-step process. First, hydroxyl radical substituted passive groups on naphthalene ring. It made the naphthalene ring activable. Secondly, naphthalene ring was oxidized and broken down, producing elementary unsaturated fatty acid. Thirdly, unsaturated fatty acid decomposed into inorganic substances. The authors reported that [Fe²⁺], [H₂O₂] and [OH⁻] were all the rate determining factors that directly influenced the concentration of hydroxyl free radical generated in aqueous system.

Spadaro et al., (1994), studied the degradation of azo dyes by hydroxyl radicals. The study demonstrated that Fe³⁺ - H₂O₂ treatment degraded a substantial portion of azo dyes to water-soluble products and carbon dioxide. The study indicated a definitive evidence for the generation of benzene when azo dyes with a phenyl azo substitution were degraded with Fe³⁺ - H₂O₂.

Ince and Tezcanli (1999), investigated the effect of process parameters such as temperature, pH and alkalinity to optimize the treatability of textile dye-bath effluents by advanced oxidation. Fenton (Fe(II)/H₂O₂) and Fenton-like (Fe(III)/H₂O₂) reagent in the presence and
absence of UV light, was used to oxidize a reactive azo dye (Procion Red HE7B), and typical dye bath constituents. They reported that when the system was operated at pH 3 and with a $\text{H}_2\text{O}_2$/Fe(II) molar ratio of 20:1, with in 20 minutes of irradiation complete color removal accompanied by a 79% reduction in total organic carbon and a 50% reduction in TDS was obtained. The color removal was found unaffected by variations in the molar ratios under dark conditions, whereas degradation was found 0.75 time faster at higher molar ratios, when the solution was irradiated. Under UV irradiation, complete color removal was possible in 20 min, as opposed to 90 minutes in dark. The authors report that the reaction occurred in two stages, a fast step followed by a slow step during which the reaction was found to follow first order kinetics. An increase in the molar ratio was found more effective for TOC degradation. It is reported that pH 6 to 4 did not show any effect on decolorization, but a significant increase in the decolorization was observed as the pH was lowered to 3 and more so as it was further lowered to 2. This observation was attributed to the reduction in the solubility of ferrous sulphate at increased pH, resulting in inhibition of the Fenton reactions. However, the authors suggest the use of an appropriate membrane system to remove the dissolved solids to make the treated effluent reusable.

Sewekow and Leverkusen., (1993), studied Fenton oxidation of reactive dye effluent. The authors observed that wastewater treatment with Fenton’s reagent destroyed residual colour and AOX in the effluent. Heavy metals introduced by metal-complex dyes precipitated out together with
iron hydroxide in the neutralization stage. Apart from a reduction in the COD, Fenton oxidation was found to enhance the degradability of the residues.

Tang and Chen., (1996), Investigated the oxidation kinetics and mechanism of three dyes in a well-mixed batch reactor. The optimal pH ranged from 2.0 to 3.0. The optimal ratio of $H_2O_2$ to iron metal was 0.001M to 1g L$^{-1}$. The initial oxidation rates were obtained according to pseudo-first-order kinetics and dye structure was found to influence oxidation kinetics. Dimerization occurred at high dye concentrations. The $H_2O_2$/ iron powder system was found to be better than the Fenton's reagent system due to the continuous dissolution of iron powder.

Kang et al., (2002), evaluated Fenton process, involving oxidation and coagulation, for the removal of color and chemical oxygen demand from synthetic textile wastewater containing polyvinyl alcohol and a reactive dye. The variables studied included dosages of iron salts and hydrogen peroxide, oxidation time, mixing speed and organic content. Fenton oxidation primarily removed color (95% with in 5 minutes) while COD was removed by Fenton coagulation.

Bandara et al., (1997), studied the effectiveness of Fenton's reagent to degrade orange II under light and dark conditions. They observed the degradation to be strongly dependent on initial pH of the solution. Significant mineralization rates were observed only at pH below 5. Degradation of the dye was found to depend on the speciation of iron in solution, dissociation of hydrogen peroxide and the photolytic equilibria of
the dye each of which was a function of pH. Under irradiation the dye was completely mineralized in 40 minutes as indicated by the formation of carbon dioxide, water, nitrates, ammonia and sulfate. The $\text{Fe}^{3+}/\text{H}_2\text{O}_2/hv$ system was found to be catalytic instead of stoichiometric in iron.

Bandara et al., (1996) investigated the degradation of Orange II by Fenton type reagent aided by sunlight. They observed that concentrated solutions (2.9 mM) of the azo dye Orange II could be mineralized to 95% in less than 8 hours by the Fenton’s reagent in the presence of sun light. This indicated that light and thermal processes associated with UV component of natural sunlight was sufficient to promote degradation of the dye. The author’s reported that the thermodynamic potential for the redox couple in Fenton like process is not the only process involved. The highly stable iron complexes in combination with hydrogen peroxide and the near surface radical formation are also processes actively responsible for the abatement of the dye. Since no activation energy was detected during the mineralization the authors suggest the involvement of a radical mechanism in the reaction.

Balanosky et al., (2000), reported the treatment of textile wastewaters from nano-filteration of biologically treated secondary textile effluents by Fenton and photo-assisted Fenton treatment. The influence of hydrodynamic and chemical parameters affecting the degradation of non-biodegradable residues of the textile waters were studied in both batch and flow reactors. Copper and ferric or ferrous ions mediated the oxidation process under irradiation analogous to the Haber-Weiss cycle and were
found to be suitable to degrade the recalcitrant part in the textile waters after the initial biological treatment. Hydrogen peroxide was effective only in the presence of ferrous or ferric ions. At lower hydrogen peroxide concentrations the reaction proceeded slowly since the oxidant concentration was not sufficient. The effect observed on the degradation kinetics upon variation of light intensity showed that ferric ion is the active chromophore absorbing the light for the solutions. The optical absorption of the iron-chromophore and the spectral emission of the light source used were identified as the most important factor determining the kinetics and efficiency of the treatment and not the intensity of the applied light. The TOC curves against time followed a near exponential decay law and a single polynomial exponential expression was constructed for TOC that could integrate the numerical values found during the degradation.

Fung et al., (1999), studied the treatability of cuprophenyl yellow RL in wastewater by UV/H₂O₂/Ultrasonication process. The effects of pH, hydrogen peroxide dosage and ultrasonication on the oxidation process was investigated on a bench-scale reactor and their performance on colour removal were evaluated. Improved generation of hydroxyl radicals was observed at higher pH. The oxidation efficiency could be enhanced by increasing the amount of hydrogen peroxide, however high concentrations had little positive effects on dye removal due to the competitive reaction of hydrogen peroxide with the hydroxyl radicals. Dye degradation was found to be an oxygen consuming process and ultrasonication was found to dramatically increase the oxidation efficiency. The dye was found to follow
pseudo-first order kinetics at different pH and hydrogen peroxide concentrations. The rate constants were linearly correlated with the pH but fitted better into a second order polynomial expression.

Fung et al., (2001), studied the effect of flow rate, and feeding rate of H$_2$O$_2$ on a dyeing wastewater containing reactive dye under the influence of UV and Ultrasound light. The decoloration process was found to follow first order kinetics. UV light was the most significant factor in comparison to Ultrasound light. The degradation rates increased at low flow rates and high feeding rate of the oxidant.

Fernandez et al., (1999), the study for the first time showed the use of immobilized iron clusters on membrane supports as being catalytically active in the decomposition of H$_2$O$_2$ during the photo assisted degradation of the dye i.e., the highly dispersed Fe ions supported onto dissolved Nafion membranes were found to have similar effect as Fe ions on the decomposition of H$_2$O$_2$ in homogeneous solution. The treatment was found to proceed via Fenton-like process with out sludge production due to the selective decomposition of H$_2$O$_2$ on the iron ions exchanged on the membrane. The variables studied include, H$_2$O$_2$ concentration, solution pH, azo dye concentration and light intensity.

Kang et al., (1997), evaluated the use of hydrogen peroxide to improve Fenton's coagulation for COD and color removal from textile effluents. It was found that hydrogen peroxide could enhance ferrous coagulation. The study indicated that the optimum pH for ferrous coagulation and Fenton's pre-oxidation ranged between 8.0-10.0 and 3.0-
5.0 respectively. The rate of colour removal was faster than COD removal. For the same ferrous dosage, the ratio of COD removal for Fenton's coagulation versus ferrous coagulation, range from 1.4 to 2.3 and for color removal ranges from 1.1 to 1.9.

Lin and Chen., (1997) studied the treatment of waste water from secondary treatment plant of dyeing and finishing mill using a combination of Fenton process, chemical coagulation and ion exchange. Results indicated that the combined system was very effective in elevating the water quality thereby suggesting the possibility for reuse.

Nadtochenko and Kiwi., (1997) using steady state and pulsed laser photolysis studied the effect of added oxalate on the activity of Fenton's reagent (Fe\textsuperscript{2+}/Fe\textsuperscript{3+}-H\textsubscript{2}O\textsubscript{2}). The authors reported dark and light reactions during the decolorization of Orange II. The study indicated that the excited states of Fe(OX)\textsubscript{3} \textsuperscript{3-} or the (Fe(II)-Orange II) complexes were the active species during decolorization of the dye. Based on a radical theory of Fenton catalysis and direct evidence obtained from laser spectroscopy, the authors demonstrated the formation of OH\textsuperscript{*} adducts for Orange II as the initial degradation step leading to oxidation of the dye.

Lin and Lo., (1997) studied the influence of pH, temperature, treatment time and COD removal efficiency of a simulated desizing wastewater using Fenton oxidation along with chemical coagulation. Chemical coagulation using polyaluminium chloride and polymers were found to complement the Fenton treatment process by reducing the floc
settling time, enhancing color removal and reducing the ferrous ion concentration.

Pulgarin et al., (1996) studied the photocatalytic degradation of Tinopal CBS-X (1 disodium 4,4'-bis (2-Sulfostyryl) 1 biphenyl) via the Fenton reaction. 90% degradation was observed in 2 hours and complete degradation took about 4 hours. The variables studied included substrate concentration, Fe\(^{3+}\) ions, the contribution of the dark reaction and the presence of hydrogen peroxide. In all cases the fluorescence intensity decreased as the Fenton reaction proceeded, but the shape of the spectra did not change indicating that the degradation products were not fluorescent. The Photo-Fenton process enhanced the adsorption of Tinopal CBS-X on activated sludge.

Kaique et al., (1998) studied the oxidation of malachite green using Fe\(^{3+}\) and H\(_2\)O\(_2\) in the presence of visible light and compared it to the reaction in dark. The results indicated that visible irradiation could significantly accelerate the Fenton degradation of dyes. Similar observations were reported by Wu et al., (1999) on Malachite green.

Ince and Stefan, (1997) studied the oxidation and toxicity reduction of an azo dye - Remazol black by a UV/H\(_2\)O\(_2\) oxidation system. Although the dye was completely mineralized in 30 minutes only 44% of the organic carbon was mineralized. The toxicity reduction was 68%. The authors observed that beyond an effective concentration, the influence of hydrogen peroxide was found inhibitory.
Anat and Deshpande., (1996) studied the influence of pH, concentrations of ferrous sulphate and hydrogen peroxide as well as different ratios of ferrous sulphate to hydrogen peroxide during the Fenton oxidation of reactive dyes. The authors report that the initial reaction period for cleaving the dye molecule was almost instantaneous accompanied by reduction in toxicity.

Lin et al., (1998) used Fenton oxidation aided with sulphur oxidizing bacteria and granular activated carbon. During the process sulfur compounds were completely oxidized to sulfate and the biodegradable organics were simultaneously degraded at a removal of 55%. The combination of sulfur oxidizing bacteria and granular activated carbon treatment transformed any refractory toxic compounds present into biodegradable organics with a 95% removal of dissolved organic carbon.

Liao et al., (1999) studied the effects of light intensity, concentrations of ferrous and hydrogen peroxide and pH on the oxidation of effluents from a dye manufacturing unit. The oxidation process was enhanced for a higher intensity of radiation and increased concentration of ferrous ions during the initial reaction periods. However as the reaction progressed with an increase in the ferrous ions the removal profiles leveled off due to the lack of hydrogen peroxide residue. The authors also observed that an increased concentration of hydrogen peroxide did not necessarily mean increased removal rates of COD and color. The optimum pH was 3 and 4 for the removal of COD and color respectively.
Park et al., (1999) achieved 91.2%, 18.1% and 45.7% decolorization efficiencies for red and yellow wastewater and final effluent respectively during the Fenton oxidation of pigment wastewater. The BOD/COD ratio was increased from 0.04 to 0.36 indicating that Fenton oxidation enhanced biodegradability.

Herrera et al., (1999) studied the Photo-Fenton oxidation of Remazol brilliant blue and Uniblue - A through Laser flash photolysis and report that electron transfer between the excited dye and Fe$^{3+}$ was found to be the initiating step, either as a bimolecular process ($D^* + Fe^{3+} = D^{0+} + Fe^{2+}$) or through a dye - iron complex ($D^* + Fe^{3+} = D...Fe^{3+}$) which again forms ($D^{0+} + Fe^{2+}$). A radical chain reaction was observed between Fe$^{3+}$/ H$_2$O$_2$ during the initiation step. Photo dissociation reaction of the $D...Fe^{3+}$complex was found to be more important in the initiation of the chain reaction rather than bimolecular quenching between $D^*$ and Fe$^{3+}$.

Balcioglu et al., (2001) compared the treatment efficiency of TiO$_2$/UV, dark and UV-light assisted Fenton and Fenton like processes of an azo dye and copper phthalocyanine dye in acidic medium. All the oxidation processes completely detoxified the azo dye, which had initially showed 70% inhibition to a marine alga Dunaliella Tertiolecta. The copper phthalocyanine dye underwent only limited oxidative degradation and abatement was primarily through adsorption on the photocatalyst surface or coagulative effect of ferric or ferrous ions.

Sevimil and Kinaci., (2002) investigated the effect of some operational parameters on the efficiency of Ozonation and Fenton’s
process for the decolorization and COD removal of Acid Red 337 and Reactive Orange 16. Ozonation resulted in 60 to 91% color removal, while COD removal was 9-17%. The influence of pH, temperature, dosage of ferrous and hydrogen peroxide and the ratio of ferrous to hydrogen peroxide were the variables studied on the Fenton’s process. pH had a profound influence while temperature was not found to influence either the color or COD removal. Increased concentration of hydrogen peroxide and ferrous sulphate resulted in increased color and COD removal. The optimum ratio of Fe(II)/H₂O₂ was between 0.5 and 0.83.

Kang et al., (2002) studied the influence of dosages of iron salts and hydrogen peroxide, oxidation time, mixing speed and organic content on Fenton’s process involving oxidation and coagulation for the removal of color and COD from synthetic textile wastewater containing polyvinyl alcohol and a reactive dye. When color removal was attributed to Fenton oxidation, COD removal was low and attributed to Fenton coagulation. The Fenton process was found to be more efficient for color removal rather than COD and the ratio of removal efficiency between Fenton process and ferric coagulation was 5.6 for color removal and 1.2 for COD removal.

Kang et al., (2000) observed that color removal was strongly related to generation of hydroxyl radical. The optimum pH for both hydroxyl radical generation and color removal was observed at 3.5. Up to 96% decolorization was achieved with in 30 minutes.

Bogatu et al., (2000) studied Fenton oxidation of four azo dyes and proposed that the reaction took place in three steps: first, breakage of the
azo bond leading to color removal; second, oxidation and partial cleavage of benzene and triazine rings; third, advanced oxidation and mineralization of organic nitrogen (approx. 80%).

Yang et al., (2001) observed 95.8% color removal and 72.7% COD after 60 min. reaction. The optimum Fe$^{2+}$:H$_2$O$_2$ ratio was 1:20.

Salem and Maazawi, (2000) observed that Fenton oxidation was first order with respect to Methylene blue and with respect to hydrogen peroxide and ferrous sulphate the order was found to be dependent on the concentration range. At low hydrogen peroxide concentrations, the reaction was found to be first order, which becomes zero order with increase in hydrogen peroxide concentration before becoming negative. Formation of colored intermediate on the surface of the catalyst was observed, which had an inhibiting effect on the rate of color removal. The rate of the reaction was strongly influenced by pH and ionic strength of the solution.

Swaminathan et al., (2003) observed that the initial oxidation reaction was found to fit into first order kinetics and the rate of oxidation of H-acid was found to be higher than the dyes. The authors observed the release of chloride and sulfate from H-acid indicating that the Fenton oxidation of dyes proceeded through cleavage of the substituent group.

Pignatello and Sun., (1995) suggests that non-selectivity of the reaction and ability to achieve complete mineralization within a reasonable time period make photo-assisted Fenton oxidation a mild and effective remedy for treating dilute pesticide wastes.
Huston and Pignatello., (1999) studied the destruction of pesticide active ingredients like alachlor, aldicarb, atrazine, azinphos-methyl, captan, carbofuran, dicamba, disulfoton, glyphosate, malathion, methoxychlor, metolachlor, picloram and simazine. In most cases complete loss of the active ingredients occurred in less than 30 min. and took over 120 min. for mineralization. This was evidenced by the appearance of inorganic ions and the decline in total organic carbon of the solution. The results suggest that many pesticides and their commercial formulations in dilute aqueous solution are amenable to photo-Fenton treatment. Longer reaction time, higher initial peroxide concentration, or additional amendments of peroxide could enhance mineralization. As mineralization proceeds carbon acquired higher oxidation states, while the organic compounds remaining in solution become less reactive with the hydroxyl radicals. This results in decay of the hydroxyl radical due to scavenging by hydrogen peroxide or self-reaction or scavenging by the ferrous ion.

Scott et al., (1995) studied the degradation of Atrazine by Fenton's reagent as a function of reagent concentration, ratios and pH in batch treatments. The optimal ratio of FeSO₄:H₂O₂ was found to be 1:1 at which Atrazine was completely degraded in ≤ 30s. Increase in pH from 3 to 9 resulted in a decrease from 99% degradation to 37% degradation.

Joseph J. Pignatello, (1992) studied the degradation of two herbicides 2,4-D and 2,4,5-T in acidic aerated solutions of H₂O₂ and Fe²⁺ or Fe³⁺. Complete mineralization was achieved using Fe³⁺/H₂O₂ and the transformation was found to be pH sensitive. The optimum pH was
between 2.7-2.8. Methanol and chloride ions were found to inhibit the reaction due to scavenging of the active oxidant and by sulfate due to complexation with Fe$^{3+}$. Visible light above 300 nm accelerated degradation with complete mineralization in < 2h.

Sun and Pignatello., (1993) presented a detailed investigation on the mineralization of 2,4-dichlophenoxy acetic acid (2,4-D) by Fe$^{3+}$/H$_2$O$_2$/UV system, focusing on photochemical reactions that contribute to enhancement. The authors report that one contributing reaction to photo enhancement is photolysis of aquated ferric ions. The photo reduced iron then becomes a precursor to a second hydroxyl radical when peroxide is present via the Fenton reaction. Several species of Fe$^{3+}$ are known to be photoactive, and their importance depends on pH and wavelength of the emitted light. It is reported that the oxidation process occurred in two stages. The first stage, where there is dechlorination and conversion of approx. 40% of ring and carboxy carbon of 2,4-D is mostly due to hydroxyl radical reactions generated under irradiation. The remaining 60% of carbon mineralization where hydroxyl radical play no significant role occurs almost exclusively by photolysis or decarboxylation of Fe$^{3+}$ complexes of degradation intermediates probably ring-opened products coordinated via carboxyl and hydroxyl groups. The study reveal that hydroxyl radical is ineffective in oxidizing the organic intermediates remaining after the completion of the first stage, most likely due to the lower reactivity of the highly oxygenated intermediates toward the hydroxyl radical and competition for the hydroxyl radical by other solutes. The hydroperoxyl
The radical produced by the reaction between hydrogen peroxide and the ferrous ion was found incapable of producing any CO₂ from the ring, indicating the poor reactivity of the hydroperoxyl radical (HO₂⁺) compared to the Hydroxyl radical (OH⁺). Oxygen played an important role in these reactions.

Kalpana and Ann, (1998) studied the degradation of pesticides by hydroxyl radicals generated from reaction between hydrogen peroxide and electrochemically generated ferrous iron. Multiple addition of hydrogen peroxide in smaller doses was found to enhance the degradation compared to a single dose. Small molar excess of hydrogen peroxide to iron increased the degradation of atrazine. The optimum ratio of hydrogen peroxide to iron was 5:1.

Herve et al., (1998) studied the oxidation of Atrazine by Fenton’s reagent over pH ranging from 1-8. Oxidation was found to follow the mechanism proposed by Barb et al., (1951) only when the pH was less than 3. Results suggested that the reaction of hydrogen peroxide with ferrous ion involves an intermediate which leads to the formation of another intermediate that in turn reacts with Fe(II) to give Fe(III) without the formation of OH⁺.

Lu et al., (1997) report that Fenton’s reaction is extremely sensitive to anions and phosphate ions in particular suppress the oxidation reaction. This was attributed to complex formation by phosphate ions either with ferrous or ferric iron. The reported sequence of anions suppressing the reaction is given as H₂PO₄⁻ >> Cl⁻ > NO₃⁻ = ClO₄⁻. The rate of oxidation after
the addition of ferrous ions was found greater than that of ferric ions. An increased concentration of ferrous ions resulted in an increase in the oxidation rate of Dichlorvos.

Lu et al., (1997) studied the Fenton oxidation of Dichlorvos. The authors observed that oxidation of Dichlorvos were a two-stage reaction with the first stage where the decomposition was high being over with in 30s. This stage was attributed to a Fe$^{2+}$/H$_2$O$_2$ reaction. The second stage was slow and attributed to Fe$^{3+}$/H$_2$O$_2$ reaction. The optimum pH range was 3-4. The decomposition rate of Dichlorvos was found to increase with an increase in the concentration of ferrous ions or hydrogen peroxide.

Balmer and Sulzberger., (1999) observed that both oxalate concentration and pH greatly influenced the rate of Atrazine transformation. At all pH values, the rates were considerably higher at higher oxalate concentrations and no degradation occurred at pH > 7.

Takemura et al., (1994) studied the decomposition of tetrachloroethylene used in dry cleaning in both static and circulating experiments. Reticulated iron was chosen as the test material after comparison of several kinds of iron as an iron source. Although the organic chlorine compounds added in pure water were easily decomposed by Fenton’s reaction on the reticulated iron in aqueous phase, the system could not achieve high efficiency in the case of wastewater from the actual laundry process. The reason given was the coexistence of high COD residuals, such as dirt and organic acids. A combination of circulation and air bubble agitation was found to enhance the removal of trichloroethylene.
Sedlak and Andren, (1991) investigated the degradation of chlorobenzene and its oxidation products by Fenton's reagent. The primary step associated with degradation was hydroxylation followed by ring cleavage and mineralization. Another possible reaction pathway involved the formation of dimers and colored aromatic polymers, which were oxidized subsequently by hydroxyl attack. Depending on the presence or absence of oxygen marked differences in the reaction products have been reported during Fenton's oxidation. In the absence of oxygen, chlorophenols, dichlorobiphenyls and phenolic polymers were the predominant initial products. In the presence of oxygen, there was marked decrease in the yields of dichlorobiphenyls, which was further oxidized to chlorinated and non-chlorinated diols. The highest yield of product formed per mole of hydrogen peroxide consumed was observed in the pH range of 2-3. pH dependence and product distributions led the authors to suggest that complexes of aromatic intermediate compounds with iron and oxygen played a key role in regulating the reaction pathways.

Huston and Pignatello, (1996) carried out kinetic and product studies to elucidate the mechanism and role of oxygen during the degradation of carbon tetrachloride and hexachloroethane in UV-illuminated (300-400 nm) acidic oxic or anoxic solutions containing Fe(III) and oxalate. The authors found the addition of ferrioxalate as a photo-Fenton precursor to be advantageous because it strongly absorbed visible light up to 550 nm and had a high quantum yield for the generation of
Fe(II). This addition, apart from generating hydroxyl radical had an added advantage of requiring lower energy of irradiation.

Sedlak and Andren., (1991) observed that hydroxyl radical generated by Fenton's reagent could rapidly oxidize polychlorinated biphenyls in aqueous solutions via addition of a hydroxyl group to one of the non-halogenated sites.

Walter and Huang, (1996) evaluated the effect of chlorine content on the oxidation kinetics of chlorinated phenol by Fenton's reagent. The reactivity of chlorophenols decreased with increasing chlorine substitution on the aromatic ring. Under conditions of excess hydrogen peroxide and ferrous ions the pseudo first order rate coefficients were found to be proportional to the number of unsubstituted positions, whereas no correlation was observed between dechlorination constants and the number of unoccupied sites on the aromatic ring. At constant hydrogen peroxide and ferrous concentrations, initial dechlorination rates were not found to change significantly suggesting that the generation of hydroxyl radical was the rate-limiting step in Fenton chemistry.

Tang and Huang. , (1997) studied the stoichiometry of Fenton's reagent in the oxidation of dichloroethylene, trichloroethylene, tetrachloroethylene and dichloroethane. The optimal ratio between Hydrogen peroxide and ferrous was 5-11 and the optimum pH was observed at 3.5. The amount of hydrogen peroxide required to oxidize an organic compound and the accumulation of chloride ions released was found to be dependent on the initial concentration, and followed the order
of TCE, Tetra-CE<DCE<<DCEA. The amount of chloride ions detected at a constant concentration of hydrogen peroxide followed the order DCEA<<DCE<TCE<Tetra-CE.

Tang and Huang, (1996) studied the effect of pH and concentrations of hydrogen peroxide, ferrous sulphate and substrate concentration on both oxidation and dechlorination kinetics of 2,4-DCP. The study used a mathematical model to describe the oxidation kinetics and chloride ion production at constant concentration of hydrogen peroxide and ferrous sulphate.

Tang and Huang, (1996) developed an oxidation kinetic model of TCE by Fenton's reagent based upon transition state theory. According to which hydroxylated active complexes was assumed to be the transition state after the hydroxyl radicals had attached to the organic compound. The complex either disproportionate or return to their original reactants. Both OH* and the active complexes were highly reactive. The model indicated that Fenton oxidation was first order with respect to the concentration of organic substrate. The degree of oxidation was found dependent on the dosage of H2O2 and Fe2+. The authors also stated that because both Fe2+ and H2O2 can react with OH*, neither of them should be overdosed if the maximum reaction rate was to be achieved. Another observation made is that during the Fenton Oxidation of chlorinated compounds an increase in the chlorine content would bring about a decrease in the reactivity of the Fenton’s reagent.
Tang and Huang., (1996) based on the rate constants derived the authors reported that chlorine positions of mono, di and trichlorophenol had a significant effect on the dechlorination kinetics during Fenton oxidation. They observed that closer the location of chlorine atoms on the aromatic ring, the more difficult is the dechlorination process. Dechlorination kinetics during the Fenton's oxidation was found to be affected both by directory effects of OH and Cl' groups, as well as by steric hindrance of the chlorine atoms.

Wang et al., (1998) report that compared to other organic chelators pyrophosphate was found to be more stable and could significantly increase the concentration of iron in aqueous solutions. This enhanced the dechlorination of tetra chloroethene (PCE) by Fenton reaction. A decrease in the dechlorination rate was observed with time, which was attributed to both the conversion of Fe(II) to Fe(III) and the decrease of aqueous iron.

Prouslek and Duriskova., (1998) studied the oxidation of PEG and 6-Caprolactam by Fenton and Photo-Fenton reactions. They observed a COD reduction ranging from 72-84% and found the photo-Fenton reaction more efficient than the Fenton reaction.

Li et al., (1996) used furnace slag along with hydrogen peroxide to degrade 2,4-dichlorophenol. Under acidic conditions the slag dissociated to produce ferrous ions that react with hydrogen peroxide to produce hydroxyl radical which in turn degraded 2,4-dichlorophenol by Fenton-like mechanism. The results show that 100 mg L\(^{-1}\) of 2,4-dichlorophenol and its
oxidation intermediates could be totally decomposed within 2 hours. The observed optimum pH was 2.8.

Kuo and Lo., (1999) reported that the optimum pH for degradation and mineralization of chlorobiphenyl was 3. The reaction was found to be first order with respect to hydrogen peroxide and with respect to Fe(II) concentration it was a saturation type reaction.

Margaret et al., (1999) reported that saturated aqueous solutions of Creoste and PCP could be effectively treated by Photo-assisted Fenton reaction. Acute toxicity of the treated solution to Fathead minnows was nearly eliminated and reduced the acute toxicity to Daphnia.

Brain et al., (1998) observed that in aqueous solution TNT rapidly degraded after three sequential additions of hydrogen peroxide and ferrous sulphate in a molar ratio of 25:15:1 \((\text{H}_2\text{O}_2: \text{Fe}^{2+}: \text{TNT})\) at pH between 2.5 and 3.

Chen and Pignatello., (1997) examined the oxidation of phenol by Fenton systems in dark and under UV/Visible light. Reactions were conducted at an initial pH of 2.8, with the hydrogen peroxide concentration in excess and iron in catalytic concentrations. In all cases, the reactions displayed autocatalysis. An important finding of the study was that quinones served as electron-transfer catalysts between dihydroxycyclohexadienyl radical – the \(\text{OH}^+\) adduct of phenol – and \(\text{Fe}^{3+}\) by way of a semiquinone radical thus, playing an important catalytic role in Fenton oxidation of aromatic compounds.
Esther et al. (1995) the study was carried out to find if OH* are formed in the reactions of divalent iron complexes Fe (II) L; L= EDTA, HEDTA and TCMA in neutral and slightly acidic solutions using the β-elimination reaction as an assay for the formation of OH*. The results showed the formation of an Iron (II) peroxide intermediate complex which at pH < 5.5 decomposes to yield free hydroxyl radical indicating that the non-participating ligand-L has an appreciable effect on the mechanism of reaction of the metal center with hydrogen peroxide.

Sychev and Isak, (1995) report that high peroxide concentrations could also be detrimental to the degradation kinetics since after the initiation step the propagation step would be hindered by an excess hydrogen peroxide acting as a scavenger of the hydroxyl radical.

Jurg Hoigne, (1997) experimentally quantified and compared the efficiencies of various hydroxyl radical sources following the oxidation of inter-calibrated probe compounds that react during the process only with the OH radicals. However, water quality parameters control the lifetime of the OH radicals via scavenging reactions by pollutants and other solutes, must be quantified before the results can be applied.

Sonntag et al., (1997) report that with a few exceptions, such as phenoxy radicals; radicals formed as a result of the hydroxyl radical attack on organic matter react with oxygen yielding peroxyl radicals whose formation and decay contributes decisively to the oxidative degradation of Dissolved Organic Carbon. The authors claim that in the application of Advanced Oxidation Processes it must be ensured that oxygen should not
be depleted because the HO$_2^*$ or O$_2^*$ radical liberated in the various peroxyl radical reactions would rapidly react with oxygen to generate the OH$^*$.

Isak et al., (1996) studied the oxidation of formaldehyde, isobutyaldehyde, benzaldehyde and anisaldehyde in the presence of Fe$^{2+}$/H$_2$O$_2$/H$^+$ and observed that the oxidation was first order with respect to hydrogen peroxide for aliphatic aldehydes and 0.5 order for aromatic aldehydes. Fe$^{2+}$ played the role of a catalyst dissociating H$_2$O$_2$ to OH$^+$ and OH$^-$. An increase in the rate of the reaction was observed when ascorbic acid capable of reducing Fe$^{3+}$ to Fe$^{2+}$ was added.

Ansari et al., (1996) studied the oxidation of hydrogen sulphite to sulfate through three different routes. Fenton and photo-Fenton reactions were used to carry out the oxidation process while; γ-FeOOH was used in order to promote the photocatalytic oxidation. According to them intermediate species like HSO$_5^-$ and or SO$_5^{2-}$ generated during the oxidation was involved in the autocatalytic mechanism.

Zakharov and Kumpan., (1996) found benzoic acid and acetyl salicylic acid to function as inhibitors of the radical chain decomposition of hydrogen peroxide catalyzed with iron ions in aqueous solution leading to the formation of a singlet oxygen dimmer which in turn resulted in chemiluminescence that become intense in the presence of oxygen. The inhibition was accounted for by the decay of OH$^*$ and HO$_2^*$.

Aldershof et al., (1997) showed that there was no difference in the decomposition rates of different types of commercially available hydrogen
peroxide solutions in spite of the differences in the types and amounts of the added proprietary stabilizers.

Lloyd et al., (1997) used both H$_2$O$_2$ and water labeled with $^{17}$O, together with ESR spin trapping, to detect the formation of hydroxyl radical. The authors report that the hydroxyl radical was derived exclusively from H$_2$O$_2$ and there was no exchange of O$_2$ atoms between H$_2$O$_2$ and the solvent water. The reaction with ordinary H$_2$O$_2$ and $^{17}$O labeled water also showed that none of the OH$^*$ was derived from water.

Scott et al., (1998) Used the spin trap compound α-(4-Pyridyl-1-Oxide) − N-tert-butylnitroxide (4-POBN), as a probe to establish the activity of Fenton derived hydroxyl radical. The rate of disappearance of the probe was used to analyze the system kinetics and oxidation efficiency. The authors observed that the reaction of hydrogen peroxide with hydroxyl radical was an appreciable sink for the hydroxyl radical, but the reaction did not contribute significantly to the depletion of hydrogen peroxide. Non-productive reactions involving hydrogen peroxide (those that did not contribute to the production of hydroxyl radicals) represented a significant source of overall reaction inefficiency.

Leonard et al., (1998) report that chelation of Co(II) by biological chelators such as glutathione altered its oxidation-reduction potential and makes Co(II) capable of generating OH$^*$ via a Co(II) − mediated Fenton like reaction.

Nadtochenko and Kiwi., (1998) examined primary photochemical reactions in water solutions of ferric chloride complexes in the presence
and absence of hydrogen peroxide by laser photolysis using Xyldine as the pulse molecule. The Xyldine radical formed by the oxidation of Xyldine by Cl* or Cl2* was found to decay within 2 minutes in a second order reaction. An increase in the oxidant concentration resulted in an increase in the concentration of XYL*, indicating that hydrogen peroxide competes with Cl* and XYL for the available Cl* in solution.

Nadtochenko and Kiwi, (1998) observed a decrease in the photodegradation of Xyldine in the presence of Cl⁻ anion in comparison to sulfate or perchlorate ions. The photoactive iron complex intermediates that formed in the dark and not the organic intermediates were found responsible for XYL degradation after the initial induction period.

Kiwi et al., (2000) studied photo-assisted Fenton oxidation of Orange II, in the presence of chloride anion. The authors observed that the hydroxyl radical originated from photolysis of Fe(OH)₂ complexes while Cl₂ radical was the product of photolysis of FeCl₂ complexes. The rate of decolorization decreased with increase in Cl⁻ concentration.

William et al., (1996) reported that Fenton's reagent removed chlorinated organics more effectively than hydrogen peroxide alone. The optimum range was 2.5-4. Reaction rates appeared to be highest at the lowest peroxide to iron ratio.

Herera et al., (1998) observed that p-coumaric acid undergoes accelerated degradation via photo-assisted Fenton reactions. The authors report that the Fenton's reagent form precursor intermediates that are susceptible to degradation under light. Degradation experiments
performed via alternate light and dark cycles showed the importance of the dark precursor species.

Anthony and Emily, (1998) report that hydroxyl radical can be generated independently of Fe or other transition metal in reactions involving hydrogen peroxide and nitric oxide.

Ali et al., (1997) identified lactic acid as an ingredient in Chlorella T-1 which was found to enhance the formation of DMPO-OH which did not serve as a source for OH* but accelerated the Fenton reaction.

Sawyer, (1997) established that the Fenton chemistry involves the formation of hydroperoxide (ROOH) adducts of reduced transition metals \([\text{Fe}^{2+}, \text{Cu}^{1+} \text{ and Co}^{2+}]\) via nucleophilic addition. These reactive intermediates react with excess catalyst to form \(L_x\text{Fe}^{3+}\text{OH} (R)\) or with excess ROOH to form \(\text{O}_2, \text{H}_2\text{O}\) and \(\text{ROH}\) or with excess hydrocarbon \((\text{RH})\) to form \(\text{ROH}\) (Fenton chemistry) or with ambient dioxygen to form adducts \([L_x[\text{Fe}^{3+}\text{OOR, BH}^+]\]

Alexei and Kiwi, (1997) reports the transient kinetics for the species observed on application of pulsed laser to Quinoline, Quinoline and \(\text{Fe}^{3+}\) and quinoline solutions in the presence of Fenton's reagent. The authors report the formation of intermediates having a transient lifetime of less than 4\(\mu\)s. The intermediates were affected by reagent concentration, concentration of the oxidant, pH and energy of the laser pulse.

Alexei and Kiwi, (1997) studied and compared the degradation of Quinoline solutions in homogeneous Fenton like reactions and heterogeneous photocatalytic \(\text{TiO}_2\)-mediated degradation and found that
the heterogeneous photocatalytic degradation proceeds at a slower rate than the homogenous reactions. Quinoline degradation was possible both under light and dark conditions. Complex formation occurred during photodegradation with Fenton like reagents, such as \( \text{Cr}^{6+} \) or \( \text{Cu}^{2+} \) ions and combinations of \( \text{Cu}^{2+} \) and \( \text{Fe}^{3+} \) ions, in the presence of hydrogen peroxide.

Sara and Dan., (1999) report that radicals may be formed via reactions that do not involve the formation of either \( \text{OH}^* \) or \( \text{OR}^* \) radicals.

Yoon et al., (2001) investigated characteristics of the Fenton system using high concentrations of iron (1-10 mM). The authors found that high ferrous enhanced the production of hydroxyl radicals that led to faster consumption of hydrogen peroxide. The possible draw backs associated with the system is the scavenging of hydroxyl radical by ferrous ions, changes in the oxidation products due to oxygen depletion and precipitation of ferric ions.

Huling et al., (2001) studied the influence of peat on Fenton systems. Increased concentration of peat was found to enhance the production of hydroxyl radical. This was attributed to the ability of organic matter to reduce ferric to ferrous ions.

Tachiev et al., (2000) proposed a kinetic model for free iron catalyst assuming the formation of a reversible complex (\( \text{Fe} - \text{H}_2\text{O}_2 \)) followed by irreversible decomposition using the pseudo-steady-state hypothesis. The reaction was found first order at low hydrogen peroxide concentrations, while at high hydrogen peroxide concentrations the reaction was found to be zero order. The rate constants were determined by the initial rate
method. pH had a significant influence on the reaction. At low pH the ferrous iron was mostly uncomplexed and in the free form, while high pH ranges (6 - 9) resulted the formation of Fe(III) complexes. Fenton's reagent (free iron catalyst) had a significant level of activity only in pH range from 2 – 4, while the complexed iron catalysts were found to be effective in the pH range from 2 – 10.

Perez and Arias., (1999) observed that both chromium(VI) and copper(II) were efficient catalysts for the decomposition of hydrogen peroxide. However, when present jointly the two catalysts exert mutual inhibition effect on the catalytic activity of the other. The inhibition effect produced by chromium (VI) on the catalytic activity of Cu(II) was found to be more pronounced than that of Cu(II) on Cr(VI).

Kremer., (1999) observed the formation of a new intermediate, which was identified as [FeOFe]$_5^{5+}$. The existence of free radicals in the system was not found to be compatible with the data and proposed a new mechanism for the reaction involving FeO$_2^{2+}$ as the key intermediate.

Pignatello et al., (1999) suggested the involvement of a high-valent oxo iron complex (ferryl) in addition to the hydroxyl radical in the oxidation of organic compounds. The authors observed that hydrogen peroxide formed a complex with iron, Fe(O$_2$H)$_2^{2+}$, that absorbs in the visible region, which could be the precursor of the ferryl complex.

Lindsey and Tarr., (2000) observed that the hydroxyl radical formation increased linearly with hydrogen peroxide concentration.
Brillas et al., (1996) studied the mineralization of aniline in acidic solution using the electro-Fenton method. OH\textsuperscript{+} was produced at the anode by the oxidation of water and the bulk solution via Fenton reaction between Fe\textsuperscript{2+} and the electro generated H\textsubscript{2}O\textsubscript{2}. The process was found to be highly efficient and the efficiency could be enhanced when irradiated with UV light (\(\lambda_{\text{max}} = 360\) nm).

Sanchez et al., (1996) investigated the oxidation of 2,4-D using ZnO as photo-catalyst in the presence of in-situ photogenerated Fenton reagent. The photo-degradation process was dependent on the mass of the semi-conductor and light intensity. The reaction was found independent of pH except at the point of zero charge of the semi-conductor. Results showed that the photo-degradation followed Langmuir-Hinshelwood kinetics and addition of small amounts of Fe(II) increased the rate of photo-degradation.


Specht et al., (1996) report that a combination of biological and chemical oxidation by the Fenton's reagent could be used to oxidize PAH in
water to yield biodegradable products. Zambrowski et al (1997) and Evelyn et al., (1997) have also reported similar observations.

Miller et al., (1996) studied the chemical and microbiological response of pendimethalin contaminated soils after treatment with Fenton’s reagent. The authors observed that the efficiency of oxidation was highest for soils with low organic matter and neutralizing capacity, in accordance with the role of organic matter as a free radical scavenger and the optimum formation of the free radical at low pH. Before treatment with the Fenton’s reagent, the Heterotrophic activity as measured by glucose mineralization decreased with increasing pendimethalin concentration indicating its inhibitory effect, however, this effect was removed after the Fenton’s treatment. The oxidation products were found to be biologically amenable serving as substrates for subsequent microbial growth.

Lei et al., (1998) observed that effective degradation of polyvinyl alcohol was achieved by the application of photochemically enhanced Fenton Oxidation. Oxidation was effective when low iron(II) concentrations of approximately 1 equivalent of iron(II) per 20 PVA units was employed.

Fernando et al., (1998) studied the Fenton oxidation of three polynuclear aromatic hydrocarbons, fluorine, phenanthrene and acenaphthene. The variables studied were reactant concentration, pH and the presence of humic bicarbonate ions and substances. The results indicated that the hydroxyl radical generation was higher than those from other advanced oxidation systems involving O₃, UV radiation and H₂O₂.
The decreasing order of reactivity was reported as phenanthrene > fluorine > acenaphthene.

Ralf et al., (1999) studied the kinetics of light induced degradation of TNT and 16 other nitro aromatic compounds in aqueous TiO$_2$ slurries and in homogeneous solutions containing Fenton reagent. Reaction rates of photo-Fenton reaction were found higher than that of TiO$_2$-mediated photocatalytic reactions. The rate of the reaction was found to be enhanced by the addition of potassium oxalate and depended on the kind and number of substituents attached to the aromatic ring. The nitro groups were found electron withdrawing with the reaction rate decreasing with an increase in the number of nitro groups attached to the aromatic ring.

Bin et al., (2001) investigated the degradation of nitroaromatics using four different AOP’s. Of these Ozonation and Fenton oxidation was found to be the most effective.

Lee and Hosomi., (2001) compared the biodegradability between Benz(a)anthracene contaminated soil and Benz(a)anthracene contaminated soil after Fenton oxidation. When 98% of Benz(a)anthracene was degraded after 63 days following Fenton oxidation only 12% was found to be degraded in soil without Fenton oxidation indicating that Fenton oxidation enhanced biodegradability. Similar observations were made by the same authors on Benzo(a)pyrene.

Turan and Gurol., (2002) studied the oxidation of diethylene glycol by ozone and modified Fenton process in aqueous solution. They observed that both the oxidation processes could effectively oxidize high
concentrations of diethylene glycol (DEG). The stepwise addition of hydrogen peroxide and ferric salt resulted in a much higher removal than the one-time pulse addition of chemicals. Increased concentrations of hydrogen peroxide and ferrous sulphate enhanced the oxidation of diethylene glycol. Oxygen consumption per mole of DEG was found higher for Fenton oxidation than for ozone.

Lu et al., (1994) compared experiments using ferric ions instead of ferrous ion for catalytically oxidizing phenol-containing wastewater. The variables tried were concentration of hydrogen peroxide, ferric and initial pH. The results indicated that under acidic conditions the reduction of phenol, COD and TOC were excellent when using both Fe$^{3+}$ and Fe$^{2+}$ as catalysts, but at pH 7.0 the catalytic activity of both the ferric and ferrous ions was distinctly lower.

Lin et al., (2000) used Fenton oxidation in combination with Ultra sonic to remove 2-chlorophenol from wastewater. The combination was found to enhance the decomposition efficiency by decreasing the reaction time. More than 99% of 2-chlorophenol was decomposed and 86% was mineralized. The oxidation kinetics of 2-chlorophenol was found to be pseudo first order and the rate constants were found to increase with an increase in the concentration of the Fenton's reagent.

Kuo et al., (1998) studied the oxidation of 2,4-chlorophenol and 2,4,6-trichlorophenol in aqueous solution using the Photo-Fenton process. The oxidation was found to be first order. The study was conducted in two parts. The first part explored the treatment efficiency and reaction rate
expression. The second part identified the products intermediates and observed that some of the intermediates were more toxic than the primary compound.

Enric et al., (1998) studied the degradation of 4-Chlorophenol in acidic solution by different electrochemical methods involving H₂O₂ electro-generation from an oxygen diffusion cathode. The authors found electro-Fenton and photoelectro-Fenton to be more efficient than peroxycroagulation.

Basu and Wei., (1998) studied the effect oxidant and catalyst in the Fenton's oxidation of 2,4,6-trichlorphenol. Progress of the reaction was monitored in terms of TCP removal, release of chloride ions from the organic structure, changes in pH and reductions in COD and TOC. The authors also studied the effects of various reaction parameters such as temperature, pH, oxidation state of the catalyst, mode of addition of oxidant to the reactor and the presence of dissolved oxygen. The optimum molar ratio of the oxidant to the substrate was found to be 5.5:1 and for that of the catalyst to the oxidant was 0.10:1. Rate of the reaction was found to increase with an increase in temperature from 15-35°C and the utilization of hydrogen peroxide could be enhanced by the addition in smaller increments. The optimum pH range was 2-3.5 and dissolved oxygen was found to accelerate the reaction rate.

Wang et al., (1999) compared several Fenton-related oxidative processes to isolate one that could effectively remove 2,4-dinitrophenol from industrial wastewater. The authors found that initially the Photo-
Fenton process gives the same oxidation ability as the Fenton process, however gradually the Photo-Fenton process begin to out-rank the other treatment options as irradiation stimulates the regeneration of ferrous ion, resulting in enhanced generation of hydroxyl radicals.

Gun et al., (1999) studied the effect of hydrogen peroxide concentration, p-chlorophenol and chloride level on the Fenton oxidation of p-chlorophenol. The authors observed that the optimum pH range was between 2 - 4. The process was a two-step process. A fast initial stage, which was found to be first order with the rate constants proportional to the initial levels of Fe$^{2+}$ and H$_2$O$_2$. The slow step was primarily attributed to the depletion of Fe$^{2+}$ caused by Fe-organic complex formation. The effect of chloride on oxidation was found to be pH dependent and increased with an increase in concentration.

Bier et al., (1999) reported that RDX could be oxidized using Fenton's reagent. The extent of transformation and mineralization was enhanced in the presence of UV irradiation.


Kang et al., (1999) applied Fenton's reagent to decolorize and degrade 2,4-dinitrophenol. The variables studied were concentration of ferrous ion, hydrogen peroxide and dissolved oxygen. At low dosages of ferrous ions and hydrogen peroxide, a linear increase in the initial removal rates of DNP and color is observed. High dosages of ferrous ions (>1mm) led to insignificant response of the initial removal rate of DNP, while that of
color was not affected and kept increasing constantly. Because of the non-selective feature of the hydroxyl radical, leveling off in the initial removal rates was observed at high hydrogen peroxide concentrations.

Lu., (2000) observed that the oxidation rate of 2-chlorophenol in a reaction where the decomposition of hydrogen peroxide was catalyzed by goethite increased with decreasing goethite particle size. The mechanism of oxidation was attributed to catalysis of ferrous ions and goethite surface.

Kwon et al., (1999) studied Fenton oxidation of p-chlorophenol and observed that the oxidation was a two-step process. An initial fast step that resulted in a significant oxidation within a few minutes followed by a slow step. The initial fast rate was found first order with respect of p-chlorophenol and its rate constant was proportional to the initial level of Fe$^{2+}$ and hydrogen peroxide. The occurrence of the slow phase was attributed to the depletion of ferrous ions caused by the formation of Fe–organic complex. The extent of oxidation was limited by hydrogen peroxide.

Banerjee et al., (1995) showed that landfill leachate with an initial COD concentration of 390 mg L$^{-1}$ could be reduced to below the discharge limit (35 mg L$^{-1}$) by using the Fenton’s reagent or a combination of UV/H$_2$O$_2$/catalyst.

Kim et al., (1997) investigated the treatment of landfill leachate by a combination of the classical Fenton reaction with UV light (Photo-assisted Fenton reaction). The degradation rate was found to be influenced by the amount of hydrogen peroxide, Fe(II) added, pH value and radiation
intensity. The optimum conditions observed were $1 \times 10^{-3}$ mole L$^{-1}$ Fe(II), pH 3 and a molar ratio of COD:H$_2$O$_2$ of 1:1.

Gau and Chang., (1996) instead of using the traditional Fenton method and ferric chloride coagulation, a 2-stage Fenton process accompanied by Fenton method with powdered activated carbon was studied. Molecular weight chromatography was used to evaluate the fraction of organic removal. The study indicated that a proper combination of the two stage Fenton process with activated carbon was found advantageous as Fenton coagulation could remove low molecular weight better than FeCl$_3$ with activated carbon efficiently adsorbing oxidation resistant organics.

Kim and Vogel, (1998) studied the degradation of landfill leachate by utilizing combinations of Fe(II)/H$_2$O$_2$/UVA and Fe(III) oxalate/H$_2$O$_2$/UVA. Degradation rates were found to be dependent on the concentrations of hydrogen peroxide, iron catalyst, pH and the concentration of dissolved oxygen. The Photo-Fenton process gave a higher COD reduction.

Choi et al., (1998) Showed that the Fenton's reagent could effectively treat landfill leachate and removed all humic material and over 99% of fulvic material.

Yoon et al., (1998) compared Fenton reaction with coagulation in removing landfill leachate organics. When both the processes were found effective in removing the organics a relation was observed with respect to the molecular weight of organic compounds. Coagulation removed 59-73% of organics with molecular weight greater than 500 and less than 18% for
compounds with molecular weight less than 500. Fenton process removed 72-89% of organics with molecular weight greater than 500 and less than 43% of organics with molecular weight less than 500. The efficiency of removal was higher for Fenton reaction.

Li et al., (1997) observed that Fenton's reagent effectively oxidized TNT in a soil slurry (1.5 wt/vol. Soil: H2O) containing 4300 mg TNT kg⁻¹. The process was influenced by factors such as temperature, dissolved organic matter and clay mineralogy and was more efficient with the sequential addition of hydrogen peroxide rather than a single batch addition. In spite of both fulvic acid and humic acid capable of effectively reducing ferric to ferrous ions, the TNT mineralization rate was not greatly affected by either of them.

Peterson et al., (1997) combined Fenton oxidation and soil washing to remediate TNT contaminated soil to test whether it was possible to grow plants on the washed soil. Complete destruction of TNT in the wash solutions with 40% mineralization was achieved by Fenton oxidation. No significant reduction in germination or early seeding development was observed in Festuca arundinacea schreb. The study reported that an integrated treatment combining soil washing, Fenton oxidation and phytoremediation could be used for treating TNT contaminated sites.

Li et al., (1997) determined the potential of Fenton's reagent to remediate TNT contaminated in water, aqueous extracts of contaminated soil and soil-water slurries. The transformation and mineralization rates were evaluated in terms of the variables such as concentrations of Fe²⁺.
and H2O2, solution pH, temperature and initial TNT concentration. The authors reported a marked influence of irradiation on mineralization with 40% mineralization occurring in the dark and subsequent exposure to light resulting in 90% mineralization. The primary mechanism of TNT oxidation was reported to be oxidation of the methyl group followed by decarboxylation (indicated by the formation of 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene). Subsequent transformation involved the removal of nitro moiety with ring hydroxylation and cleavage (indicated by the formation of oxalic acid).

Rose and Peter., (1995) developed an efficient solar photocatalytic reactor to degrade chemical warfare agents and toxic byproducts in aqueous solutions and then compared its efficiency with that of the conventional TiO2 slurry photocatalysis. The study reported that the Photo-Fenton reaction (80% mineralization within 2 hours) was more efficient than the TiO2 mediated photocatalysis (No mineralization).

Li et al., (1998) studied UV - catalyzed Fenton oxidation of mono, di and tri Nitrotoluene in aqueous solution. The number and position of nitro substitutions was found to influence the oxidation rate. The UV – catalyzed Fenton oxidation mineralized more than 95% of TNT in aqueous extracts of contaminated soils.

Arienzo, (1999) used solid pyrite in place of ferrous sulphate to clean water contaminated with 2,4,6-trinitrotoluene. The study showed that unlike the classical Fenton reaction, an increased addition of hydrogen peroxide did not show an increase in the pseudo first order rate constant.
Compared to the classical Fenton reaction the modified Fenton was a slower process.

Kaiqun et al., (1999) compared Photo-Fenton oxidation (aided by visible light) of Malachite Green with the dark reaction. The authors report that visible light enhanced the generation of hydroxyl radical and Electron transfer from the excited dye by visible light into Fe$^{3+}$ was a probable mechanism for the oxidation of Malachite Green.

Poulios and Aetopoulou., (1999) observed the disappearance of the dye to follow pseudo first order kinetics according to Langmuir-Hinshelwood model.

Barburinski and Helena., (1997) studied Fenton oxidation of an industrial wastewater producing maleic acid anhydride and observed that an increase in the concentration of both hydrogen peroxide and ferrous ions resulted in increased COD removal and caused no inhibition of microbial activity or disadvantageous changes in the structure of activated sludge flocs.

Oliveros et al., (1997) studied the oxidation of industrial wastewater containing toxic aromatic amines and observed that Fenton's reagent in the presence of UV/Vis irradiation was found to significantly enhance the degradation rates of xylidine.

Horng et al., (1996) assessed the treatability of high strength wastewater from a Brewery plant using anaerobic and aerobic process accompanied by Fenton oxidation. The operating parameters were
COD/H₂O₂ = 1, Fe²⁺/H₂O₂ = 2 pH = 2-3 and reaction time 1h. The COD and suspended solids removal efficiency was 90 and 75% respectively.

Bowers et al., (1989) evaluated the possibility of using hydrogen peroxide as a pretreatment option prior to biological oxidation of refractory organic compounds viz., 2,4-dichlorophenol, dinitro-ortho-cresol and two unknown phenolic wastewaters of industrial origin. The treatment efficiency was evaluated by subjecting the residual by-products to toxicity (Microtox) tests. In all cases the by-products were an order of magnitude less toxic than the initial compounds. The hydrogen peroxide pretreatment process, coupled with biological treatment, resulted in substantial savings in the required oxidant dosage for further chemical oxidation.

Bauer and Fallman., (1997) compared the treatment efficiency of the various Advanced Oxidation Processes and observed that the Photo-Fenton system driven by sunlight was the most cost effective treatment process.

Kittis et al., (1999) studied the effectiveness of the Fenton's reagent as a pretreatment option for recalcitrant non-ionic surfactants. The authors found that Fenton's oxidation was an effective pretreatment option as it enhanced the biodegradability of both ethylene oxide and propylene glycol.

Yoo et al., (2001) evaluated the use of coagulation combined with Fenton oxidation to treat refractory organics in leachate. The authors observed a 9% increase in COD removal and a 50% reduction in the sludge to be disposed by recirculating the sludge generated from the Fenton oxidation to a coagulation process. Stepwise addition of the
reagents in Fenton oxidation increased the COD removal by 5% and a 25% reduction in chemical consumption.

Clarke et al., (1997) proposed a method that included providing a potential difference across the medium to cause the peroxide and the ferrous ions to migrate towards and react with the contaminants to form non-toxic byproducts of the organic contaminants.

Chien et al., (1998) observed that Fenton’s reagent could completely mineralize soils contaminated with 2-methyl naphthalene, n-hexadecane and diesel fuel, provided enough hydrogen peroxide is added. The process was found effective at neutral pH.

Richard et al., (1999) studied the ability of iron containing minerals like hematite and magnetite to oxidize PCP in soil through a Fenton like oxidation. Magnetite catalyzed reactions provided the most efficient oxidation, however a decrease in oxidation efficiency was reported with time, attributed to the formation of an amorphous layer of iron oxide on the surface.
Abstract

Fenton’s reagent is very efficient in degrading almost any refractory organic substance. The list includes compounds like phenol (Smis, 1981), chlorophenols (Sedlak and Andren, 1991), municipal wastewater (Bishop et al., 1968) and printing and dyeing wastewater (Smis, 1983). Hydrogen peroxide and iron have been used to generate OH* and oxidize undesirable contaminants in soils and aquifers (Watts et al., 1993; Ravi Kumar and Gural 1994; Yeh and Ñovak, 1995). Several investigators have reported that Fenton’s oxidation can reduce effectively refractory organics, such as color and COD in synthetic textile wastewaters (Kuo, 1992; Gregor, 1994 and Solozhenko et al., 1995) and real textile wastewaters (Lin and Peng, 1995 a, b). Organic substances in the dye intermediate wastewater are often aromatic compounds substituted by some groups, such as -NH2, -NO2, -SO3 etc. They have strong toxicity to organisms. The biological processes cannot effectively degrade these substances and decolorize the wastewater (An Huren, Qian Yi. (1994). The Fe2+-H2O2 treatment has been suggested as an alternative method for removing dyes from industrial effluent (Bigda et al., 1992; Moore et al., 1993 and Kuo, 1992). To compare their effects on specified target compounds it is therefore necessary to have data to predict the rates with which they react with such target compounds relative to the rate with which they are consumed or scavenged by the other compounds present.

The objective of this study was to investigate the oxidation kinetics of a few commercially available dyes by an Advanced Oxidation Process
(AOP) involving hydrogen peroxide and ferrous sulphate under ambient light and temperature conditions. The study involved preparation of a synthetic dye bath to simulate a conventional batch dyeing process. Monitoring the effluents for residual dye concentration tested the effectiveness of the Advanced Oxidation Process. Three operating variables namely concentration of hydrogen peroxide, ferrous sulphate and the dye concentration on the performance of Fenton Oxidation was investigated with an aim of determining their optimum conditions in the oxidation of the dyes. The study also involves kinetic aspects of the oxidation reaction and the kinetic rate coefficients based on the observed data derived from the batch experiments have been established.
3.3. **Fenton Oxidation of Dyes**

The objective of this study was to investigate the treatability of a strongly colored azo dye (C.I. Direct Brown 3B, Direct Catachine Brown), a reactive dye (C.I. Yellow-6, Reactive Yellow), a basic dye (C.I. Basic blue 9, Methylene Blue) and an Acid dye (C.I. Acid Orange AO – 9, Acid Orange) by an Advanced Oxidation Process (AOP) involving Fenton's reagent under ambient light and temperature conditions. Monitoring the effluents for residual dye concentration tested the effectiveness of Fenton's oxidation.

Azo dyes can also be significantly decolorized by the reduction of its azo linkages. However, such a process would lead to the formation of aromatic amines which are generally not considered as environmentally safe end products, as they are suspect carcinogens and mutagens. This study was conducted to show that the Fenton oxidation leads to the mineralization of the azo dyes without the formation of toxic amines.

Reactive dyes are used for dyeing cotton. The strong nitrogen bond and ring structure of these dyes makes biological oxidation difficult and at times incomplete.

Basic dyes have been used extensively for dyeing silk and cellulose acetate. However, these dyes have poor fastness leading to their gradual decline. Leather and paper still continue to be dyed with basic dyes. The first basic dye to be synthesized was Mauve, by Perkin in 1856. Since then many new dye structures have been synthesized. In addition to mauve
there is also a whole range of other synthetic basic dyes such as fuchsine, methyl violet, aniline blue etc. available to dye natural vegetable products as straw, raffia and jute. The use of Basic dyes gained advantage during the mid-1950 with the synthetic fiber material polyacrylonitrile hitting the market. The advantage of this fiber was that the positively charged colored ion of the basic dye i.e., the cation, was attracted strongly by the negatively charged ions in the acrylic fiber and this combination had unusually good light and wash fastness.

The name “Acid dye” is derived from the dyeing process. These dyes are applied to wool, silk and polyamides in the presence of an organic or inorganic acid and hence are called acid dyes. The term acid dye denotes a large group of anionic dyes with relatively low molecular weights that carry from one to three sulfonic acid groups. Chemically, acid dyes belong to such various subclasses as nitro, nitroso, monoazo, diazo, triphenyl methane, xanthene, azine, quinoline, ketone-imine and anthraquinone. When dissolved in water, they produce colored anions (RSO₃⁻) and colorless sodium cations (Na⁺). On the basis of their application and wet-fastness properties, acid dyes can be divided into three groups namely leveling dyes, milling dyes and super milling dyes. Leveling dyes are usually applied either to wool or to nylon. Leveling dyes for wool have low molecular weights and usually require highly acidic dyebath for good exhaustion. Leveling dyes for nylon are of high molecular weight and they are applied at a neutral or weakly acidic pH. Milling dyes on the other hand has a higher molecular weight than leveling dyes. These dyes are
applied from weakly acidic liquor in the pH range of 5.2 to 6.2; and they are usually applied with acetic acid. Super milling dyes are applied from neutral solutions. The application of such dyes requires utmost care as they have comparatively high molecular weights. They are often referred to as fast acid dyes or acid milling types because originally they were used in wool fabrics, which were to be subjected to severe wet treatments in processing (milling) to improve the fabric density.

The study is divided into two parts:

Part 1: Deals with determining the optimum concentration of ferrous sulphate and hydrogen peroxide required to decolorize the dye to over two half lives and to optimize the operating conditions for maximum color removal.

Part 2: Investigates the effect of process variables such as the concentration of ferrous sulphate, hydrogen peroxide and the dye, to elucidate the reaction mechanism behind the Fenton oxidation of the dye.

The results obtained have been interpreted using the initial rate method.
3.3.1. Materials and methods

(i) Reagents and supplies

The dyes whose structure and other related features are shown in figures 3.1 to 3.4 were obtained from M/s. Dhaval Dye Chem., Mumbai, India. This dye is chosen for the study as it happens to be the most widely used dye among the class of Direct dyes finding applications in the textile industry where it is used to dye cotton and also in the coir dyeing units of the Alappuzha district, in Kerala, India. The commercially available dye samples were used for the study with out any further purification.

Analytical grade Hydrogen peroxide used in the experiments obtained from Qualigens (India) was 30% (W/W).

Ferrous sulphate heptahydrate (99.5% purity) from Merck (India) was used for the study.

The strength of both hydrogen peroxide and ferrous sulphate was determined every day by permagnometry prior to starting the experiment.

Fenton’s reagent was prepared by the sequential addition of ferrous sulphate and hydrogen peroxide.

Reagent grade hydrochloric acid and sodium hydroxide was used for pH adjustments. Conventionally Fenton Oxidation is carried out in sulphuric acid medium, however, for our experiments hydrochloric acid is used as solar salts are in most cases widely used in the dye bath.

(ii) Instruments and experimental set up

Optical absorption spectra of the dye in dilute solutions were recorded using a Varian UV/Vis. Cary – 50 single beam spectrophotometer
and λ_{max} of the dye was determined. This was followed by determining the residual dye concentration in the reaction mixture using a 1 mm quartz cell against a calibration diagram.

All observations have been drawn from well-mixed batch experiments carried out in 1L glass beakers in a multiple spindle constant speed stirrer rotating at 75 rpm.

pH measurements have been made using a Systronics pH meter.

3.3.2. Experimental Procedure

UV-Vis spectrum of the dye in aqueous medium was recorded and absorption maximum of the dye in the visible region was identified. A calibration curve of the dye was prepared at this wavelength, thereby; the decrease in optical density could be directly related to the decrease in dye concentration. All experiments were carried out at dye concentrations where the absorbance values at the respective λ_{max} of the dye ranged between 0.2 and 3 absorbance units.

Stock solution of the dye was prepared by weighing out appropriate amounts of the dye in distilled water. The solution was then heated to near boiling, which was then cooled and filtered. Working standards and calibration curve for the dye was prepared from such solutions.

In typical experiment aliquots of the stock dye solution was mixed with appropriate concentration of ferrous sulphate. pH of the reaction mixture was adjusted to 2 ± 0.1. The reaction was initiated by the addition of hydrogen peroxide to the reaction mixture followed by stirring (75 rpm).
Test samples were withdrawn at regular time intervals and the residual dye concentration was determined through comparison with the calibration diagram.

Preliminary runs were carried out to arrive at a minimum workable concentration of ferrous sulphate and hydrogen peroxide. The concentrations were chosen in such a manner that the reaction proceed at a rate that could be monitored by spectrophotometry. A ferrous sulphate to hydrogen peroxide mole ratio of 1:15 was found ideal to monitor the reaction. Hence, in all preliminary tests the mole ratio has been maintained at 1:15. From these preliminary experiments the minimum concentration of ferrous sulphate and hydrogen peroxide to follow the reaction to at least three half-lives was determined. In subsequent experiments the influence of hydrogen peroxide was determined by fixing the concentration of ferrous sulphate found optimum through preliminary tests for varied concentrations of hydrogen peroxide and for a fixed concentration of the dye. The criterion behind fixing the dye concentration was half the maximum concentration of the dye at which the \( \lambda_{\text{max}} \) gave an absorbance value of less than 3 absorbance units. From this experiment the minimum concentration of hydrogen peroxide to take the reaction to over three half-lives was chosen as the optimum. Fixing the hydrogen peroxide concentration at this obtained optimum for varied concentrations of ferrous sulphate established the optimum concentration of ferrous sulphate which was again the minimum concentration required to take the reaction to over three half lives.
Fixing both hydrogen peroxide and ferrous sulphate concentrations at the obtained optimum for varying dye concentrations established the influence of dye on Fenton oxidation.

There are several reports, which suggests that the optimum pH for Fenton's oxidation is around 3 (Barbeni et al., 1987). In our experiments it is observed that even at pH 3, high ferrous sulphate concentrations could result in precipitation of ferric hydroxide. Since, the reaction loses its efficiency during the oxidation of ferrous to ferric ions and there is a shift from the classical Fenton mechanism (Fe$^{2+}$ - H$_2$O$_2$ system) to Fenton-like mechanism (Fe$^{3+}$ - H$_2$O$_2$ system) it was considered ideal to carry out all experiments at pH 2. At this pH no precipitate formation was observed even when moderately high ferrous sulphate concentrations was employed. Ince and Tezcanli (1999) report that the rate of colour degradation and total colour removed at pH 2 and 3 were found to be nearly the same ($k=0.16$ min$^{-1}$ and $k=0.15$ min$^{-1}$ estimated by regression analysis using the data of the first ten minutes of treatment; where degradation kinetics was linear, and the percentage decolorization was 99% and 98%). All the experiments have been conducted at pH 2.
3.4. Results and Discussion

3.4.1. Molecular structures and other related features of various dyes used in the study are shown in figures 3.1 to 3.4.

(i) Molecular structure of Catachine brown is shown in figure 3.1.

![Molecular structure of Catachine brown](image_url)

**Figure 3.1. Molecular structure of C.I.Direct Brown 3B**

C.I. General name: C.I.Direct Brown 3B  
C.I. Constitution number: 35520  
Commercial Name: Catachine Brown  
Application class: Direct  
Chemical class: Tetra azo

(ii) The molecular structure of Reactive Yellow is shown in figure 3.2.

![Molecular structure of Reactive Yellow](image_url)

**Figure 3.2. Molecular structure of Reactive Yellow**

C.I.Name: Yellow-6  
C.I.No: 15985  
Commercial Name: Reactive Yellow  
Application class: Reactive  
Chemical Class: Azo
(iii) The molecular structure of Methylene Blue is shown in figure 3.3.

Figure 3.3 Molecular structure of Methylene Blue

C.I. Generic name: Basic blue 9  
C.I. Constitution No.: 52015  
Commercial name: Methylene Blue  
Classification based on mode of application: Basic  
Classification based on chemical structure: Thiazine dye.

(iv) The molecular structure of Acid Orange is shown in figure 3.4

Figure 3.4 Molecular structure of Acid Orange

C.I. General name: Acid Orange AO - 9  
C.I. Constitution number: 17925  
Commercial Name: Acid Orange  
Application class: Acid  
Chemical class: Mono azo
Figure 3.5
UV-Vis absorption spectrum of Direct Catachine Brown (DCB) in water.
Concentration of the dye 100 mg/L, path length 10 mm.

Figure 3.6
UV-Vis absorption spectrum of Reactive Yellow (RY) in water.
Concentration of the dye 50 mg/L, path length 10 mm.
Fig. 3.7
UV-Vis absorption spectrum of Methylene Blue (MB) in water.
Concentration of the dye 10 mg/L, path length 10 mm.

Fig. 3.8
UV-Vis absorption spectrum of Acid Orange (AO) in water.
Concentration of the dye 50 mg/L, path length 10 mm.
3.4.2. UV-Vis spectrum of the different dyes studied is shown in figures 3.5 to 3.8.

(i) Two main peaks characterize the absorption spectrum of an acidified solution of Direct Catachine Brown, as shown in figure 3.5. One in the visible range ($\lambda_{\text{max}} = 411.5$ nm, Abs.$= 0.621$) and another in the UV region ($\lambda_{\text{max}} = 241$ nm, Abs.$= 0.526$). The visible band is due to the long conjugated $\pi$ system of aromatic rings connected by the two azo groups, whereas the UV band at 241 nm is characteristic of the two adjacent rings (Silverstein et al., 1991).

(ii) The absorption spectrum of the acidified solution of Reactive Yellow is characterized by a single peak in the visible region with wavelength of maximum absorption at 415 nm ($\lambda_{\text{max}} = 415$ nm, Abs.$= 0.974$) as shown in figure 3.6.

(iii) Absorption spectrum of an aqueous solution of Methylene Blue at pH 2 is shown in figure 3.7. The spectrum is characterized by a single peak in the visible region with the wavelength of maximum absorption at 665.5 nm ($\lambda_{\text{max}} = 665.5$ nm, Abs.$= 1.006$).

(iv) The absorption spectrum of an aqueous solution of Acid Orange at pH 2 is given in figure 3.8 indicates a single peak in the visible region ($\lambda_{\text{max}} = 483.9$ nm, and Abs.$= 1.784$).
3.4.3. Calibration curves for all the dyes used in the study is shown in figures 3.9 to 3.12.

Calibration curve for Direct Catachine Brown was prepared at 411.5 nm. The dye solution obeys Beer-Lambert's law in the concentration range from 0 to 400 mg L$^{-1}$ and the calibration curve is shown in figure 3.9. Concentration of the dye chosen for the experiments covered the entire range up to which the dye obeyed Beer-Lambert's law. The residual dye concentration in the samples drawn was determined by comparison with the calibration curve.

A calibration curve for Reactive Yellow was prepared at 415 nm. The dye solution obeyed Beer-Lambert's law over the concentration range from 0 to 150 mg L$^{-1}$ and the calibration curve is shown in figure 3.10. Residual dye concentration was determined by comparison with the calibration curve.

Calibration curve for Methylene Blue was prepared at a wavelength of 665.5 nm. The dye solution obeys Beer-Lambert's law in the concentration range from 0 to 20 mg L$^{-1}$. The calibration curve is shown in figure 3.11. The residual dye concentration in samples was determined by comparison with the calibration curve.

Calibration curve for Acid Orange was prepared at a wavelength of 483.9 nm and is shown in figure 3.12. The dye solution obeys Beer-Lambert's law in the concentration range from 0 to 100 mg L$^{-1}$. Concentrations of the dye chosen for the experiments covered the range up to which the dye obeyed Beer-Lambert's law.
Figure 3.9
Calibration curve according to Beer Lambert’s law for Direct Cattachine Brown (DCB) (Conc. range 0 to 400 mg L⁻¹), path length 10 mm, analytical wavelength 411.5 nm
Figure 3.10
Calibration curve according to Beer Lambert's law for Reactive Yellow (RY) (Conc. range 0 to 150 mg L$^{-1}$), path length 10 mm, analytical wavelength 415 nm.
Figure 3.11
Calibration curve according to Beer Lambert's law for Methylene Blue (MB)
(Conc. range 0 to 20 mg L⁻¹), path length 10 mm, analytical wavelength 665.5 nm ($r^2 = 0.99$)
Figure 3.12
Calibration curve according to Beer Lambert's law for Acid Orange (AO)
(Conc. range 0 to 100 mg L\(^{-1}\)), path length 10 mm, analytical wavelength 483.9 nm
3.5. Optimization studies

3.5.1. Optimization of hydrogen peroxide

To define the influence of hydrogen peroxide on the oxidation of Catachine Brown, a series of experiments were carried out in which the concentration of hydrogen peroxide exceeded the dye concentration (150 mg L$^{-1}$). The extent of oxidation was monitored by following the decrease in absorbance at 411.5 nm as a function of time. The concentration of hydrogen peroxide was varied according to its mole ratio with respect to ferrous sulphate. The mole ratios ranged from 1:15 to 1:90. Figure 3.13 shows the results of a typical experiment carried out to study the influence of hydrogen peroxide on the kinetics of Fenton oxidation of the dye.

As can be seen from figure 3.13, there is an increase in oxidation of the dye with an increase in hydrogen peroxide concentration. However, there is an optimum concentration (367 mg L$^{-1}$) beyond which a further increase in hydrogen peroxide concentration did not result in any significant increase in oxidation of the dye.

In the case of Reactive Yellow, the effect of hydrogen peroxide on Fenton's oxidation was studied by fixing concentration of the dye at 75 mg L$^{-1}$ and ferrous sulphate at 60 mg L$^{-1}$ over a range of hydrogen peroxide concentrations. The extent of oxidation was monitored by following decrease in absorbance at 415 nm as a function of time. The results are shown in figure 3.14.

The general inference drawn is that there is a definite increase in the rate of the reaction with an increase in concentration of hydrogen peroxide.
This increase continues only up to an optimum concentration above which a further increase in hydrogen peroxide concentration does not significantly enhance the oxidation. At low hydrogen peroxide concentrations (above a critical minimum) the reaction followed zero order kinetics (indicated by a linear decrease in dye concentration with time). This could be because the concentration of hydroxyl radicals produced is proportional to the concentration of both hydrogen peroxide and ferrous sulphate. At low concentrations of hydrogen peroxide the concentration of hydroxyl radicals produced is also low. The excess of ferrous ions present scavenges the hydroxyl radical leading to formation of hydroperoxyl radical. Being of lower reactivity than the hydroxyl radical the hydroperoxyl radical probably participates in the oxidation through an extremely slow step, which is represented by zero order kinetics.

The optimum concentration of hydrogen peroxide required to oxidize Reactive Yellow at a concentration of 75 mg L\(^{-1}\) is fixed at 110 mg L\(^{-1}\), as a further increase did not show any significant influence on oxidation of the dye.

The effect of hydrogen peroxide on Fenton oxidation of Methylene Blue has been studied by fixing the dye concentration at 10 mg L\(^{-1}\), ferrous sulphate at 35 mg L\(^{-1}\) and for varying concentrations of hydrogen peroxide. The extent of oxidation was monitored by following the decrease in absorbance at 665.5 nm as a function of time. Preliminary experiments indicated that the optimum concentration of hydrogen peroxide was observed at around 65 mg L\(^{-1}\), the concentration of hydrogen peroxide was
varied in such a manner that there were two concentrations below the optimum one concentration close to optimum and two concentrations above optimum. The results are depicted in figure 3.15. The figure indicates that up to an optimum hydrogen peroxide concentration there is an increase in the amount of dye oxidized with increase in concentration of hydrogen peroxide. However, for a further increase in the hydrogen peroxide concentration above optimum the amount of dye removed tends to level off, before recording a decrease. This behavior can be explained because an increase in the hydrogen peroxide concentration would result in the generation of hydroxyl radicals, which would in turn lead to oxidation of the dye. From figure 3.15, it is observed that this phenomenon continues up to a hydrogen peroxide concentration of 60 mg L\(^{-1}\); probably up to which the ratio of ferrous sulphate to hydrogen peroxide to generate hydroxyl radicals are in balance. For a further increase in hydrogen peroxide concentration, the ferrous ions tend to become limiting. This leads to an excessive build up of hydroxyl radicals, which associate between them and get scavenged to form hydroperoxyl radicals (HO\(_2^*\)), having lower reactivity. The possible reaction involved is shown in below

\[
\begin{align*}
H_2O_2 + OH^* & \rightarrow H_2O + HO_2^* \\
2 OH^- & \rightarrow H_2O_2
\end{align*}
\]

Liao et al. (1999) used photo-Fenton oxidation for the simultaneous removal of COD and color from dye wastewater. The authors observe that an increased concentration of hydrogen peroxide does not necessarily mean increased removal rates of COD and color. Fig. 3.15. shows that the
optimum concentration of hydrogen peroxide to oxidize Methylene Blue at a concentration of 10 mg L\(^{-1}\) is 60 mg L\(^{-1}\).

The effect of hydrogen peroxide on the Fenton oxidation of Acid Orange was studied by fixing both the dye (at 50 mg L\(^{-1}\)) as well as ferrous sulphate concentration (at 40 mg L\(^{-1}\)) for varying concentrations of hydrogen peroxide. The extent of oxidation was monitored by following the decrease in absorbance at 483.9 nm. as a function of time. The concentration of hydrogen peroxide was varied in such a manner that there were two concentrations below the optimum (obtained from preliminary experiments), one concentration at the optimum and two concentrations above optimum. Results of a typical experiment to highlight the influence of hydrogen peroxide are shown in figure 3.16.

Results of the study indicate that, oxidation of the dye could be enhanced by increasing the concentration of hydrogen peroxide. However, there exists an optimum beyond which a further increase does not significantly enhance the oxidation. Fig. 3.16 indicates that the optimum hydrogen peroxide concentration is 91.7 mg L\(^{-1}\).

The results indicate that by increasing the concentration of hydrogen peroxide an increase in oxidation of the dye could be achieved at a fixed concentration of ferrous sulphate. Experiments were carried out to find if oxidation of the dye could be enhanced even if one of the reagents were held at low concentrations with the other in excess. The results indicated that an increased oxidation of the dye occurred even for a lower concentration of ferrous sulphate provided the concentration of hydrogen
peroxide was raised. Similarly, a lower concentration of hydrogen peroxide could also produce the same effect provided the concentration of ferrous sulphate is increased. These results suggest the flexibility of Fenton oxidation. Thus, effect of these two reagents was found complementary. However, an increase in the hydrogen peroxide concentration above a particular optimum did not significantly enhance the oxidation of the dye. On the other hand elevated hydrogen peroxide concentration could decrease the amount of dye oxidized. This means that although the formation of hydroxyl radical propagates according to the reaction proposed by Haber and Weiss (1934)

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^- \]

The generation of the hydroxyl radical does not follow the stoichiometry suggested Haber and Weiss (1934). After initiation of the reaction the hydroxyl radical generation propagates through a free radical mechanism. An increase in hydrogen peroxide concentration initially increases the oxidation of the dye at lower hydrogen peroxide concentrations. Further increase in its concentration above an optimum adversely affected the reaction. This observation clearly indicates that at higher hydrogen peroxide concentrations a non-productive reaction that leads to scavenging of hydroxyl radical occurs. The results indicate a decrease in the amount of dye decolorized Similar observations of on decrease in decolorization of the dye at increased concentrations of
hydrogen peroxide were reported. (Kang et al., 2002 and Solozenko et al., 1995).

Sychev and Isak (1995), in studies on the mechanisms of the homogeneous catalysis of the activation of $\text{O}_2$ and $\text{H}_2\text{O}_2$ and the oxidation of organic substrates report that higher peroxide concentrations can also be detrimental to the degradation kinetics since after the initiation step the propagation step would be hindered by an excess hydrogen peroxide acting as a scavenger of the hydroxyl radical.

An explanation of this phenomenon has been attempted in the second part of this study that deals with the elucidation of the reaction mechanism.

The general inference drawn is that there is a definite increase in the rate of the reaction with an increase in concentration of hydrogen peroxide. This increase continues only up to an optimum concentration above which a further increase in hydrogen peroxide concentration does not significantly enhance the oxidation. At low hydrogen peroxide concentrations (above a critical minimum) the reaction followed zero order kinetics (indicated by a linear decrease in dye concentration with time). This could be because the concentration of hydroxyl radicals produced is proportional to the concentration of both hydrogen peroxide and ferrous sulphate. At low concentrations of hydrogen peroxide the concentration of hydroxyl radicals produced is also low. The excess of ferrous ions present scavenges the hydroxyl radical leading to formation of hydroperoxyl radical. Being of lower reactivity than the hydroxyl radical the hydroperoxyl radical probably
participates in the oxidation through an extremely slow step, which is represented by zero order kinetics.
Figure 3.13
Influence of mole ratio of Fe$^{2+}$ to H$_2$O$_2$ on the oxidation of Direct Catachine Brown (DCB)
[FeSO$_4$] = 100 mg L$^{-1}$, [DCB]= 150 mg L$^{-1}$, pH 2, vol. 1L, stirring rate 75 rpm,
[H$_2$O$_2$] varied 183.5, 367, 550, 735, 917.5 and 1101 mg L$^{-1}$. 
Figure 3.14
Influence of H$_2$O$_2$ on the oxidation of Reactive Yellow (RY)
[FeSO$_4$] = 60 mg L$^{-1}$, [RY] = 75 mg L$^{-1}$, pH 2, vol. 1L, stirring rate 75 rpm,
[H$_2$O$_2$] varied 90, 100, 110, 120 and 130 mg L$^{-1}$. 
Figure 3.15
Influence of H$_2$O$_2$ on the oxidation of Methylene Blue (MB)
[FeSO$_4$] = 35 mg L$^{-1}$, [MB] = 10 mg L$^{-1}$, pH 2, vol. 1 L, stirring rate 75 rpm,
[H$_2$O$_2$] varied 20, 40, 60, 80 and 100 mg L$^{-1}$. 
In Figure 3.16, the influence of H$_2$O$_2$ on the oxidation of Acid Orange (AO) is shown. The conditions were as follows: [FeSO$_4$] = 50 mg L$^{-1}$, [MB] = 40 mg L$^{-1}$, pH 2, vol. 1L, stirring rate 75 rpm, [H$_2$O$_2$] varied 30, 60, 91.7, 120 and 150 mg L$^{-1}$. The graph demonstrates the amount of dye oxidized (mg L$^{-1}$) as a function of hydrogen peroxide concentration (mg L$^{-1}$).
3.5.2. Optimization of Ferrous Sulphate

Experiments to determine the influence of ferrous sulphate on the oxidation of Direct Catachine Brown was carried out by fixing the concentration of both hydrogen peroxide (at optimum) and the dye but for varying concentrations of ferrous sulphate. The results are shown in figure 3.17.

The results indicate that for the range of concentration of ferrous sulphate concentrations studied (90-130 mg L⁻¹) there is an increase in the oxidation of the dye up to about 100 mg L⁻¹. Beyond this point addition of ferrous sulphate did not significantly enhance the oxidation of the dye. This behavior is similar to that of hydrogen peroxide, where an increased concentration above a certain limit does not significantly improve the oxidation of the dye.

The effect of ferrous sulphate on Fenton oxidation of Reactive Yellow was studied by fixing concentration of the dye at 75 mg L⁻¹, hydrogen peroxide at 110 mg L⁻¹ and for varying concentrations of ferrous sulphate. Figure 3.18 shows the results obtained and indicate that an increase in the ferrous sulphate concentration clearly enhances the amount of dye oxidized. At low ferrous sulphate concentrations the reaction was found to be zero order as a linear decrease in dye concentration with time was observed. Higher ferrous sulphate concentrations beyond an optimum, does not cause any significant improvement in oxidation of the dye. Zero order kinetics can be accounted for, as at low concentrations of ferrous sulphate, the small concentrations of hydroxyl radicals generated
are not sufficient to carry out the oxidation reaction. Excess hydrogen peroxide, leading to the formation of hydroperoxyl radicals, rapidly scavenges the hydroxyl radical. The hydroperoxyl radicals being of lower reactivity results in decreased oxidation of the dye. Fig. 3.18 indicates that the optimum concentration of ferrous sulphate is 60 mg L\(^{-1}\).

The influence of ferrous sulphate on the oxidation of Methylene Blue was studied for a fixed concentration of the dye at 10 mg L\(^{-1}\), hydrogen peroxide at 60 mg L\(^{-1}\) (obtained as the optimum concentration in step 3.3) and for varying concentrations of ferrous sulphate. Preliminary experiments showed that the optimum ferrous sulphate concentration was about 35 mg L\(^{-1}\). Therefore, the range of ferrous sulphate concentrations was chosen in such a manner that there were two concentrations below optimum, one concentration at optimum and two concentrations above it. The decrease in dye concentration with time was monitored at 665.5 nm. Figure 3.19 show results of the experiment carried out to determine the influence of ferrous sulphate for a fixed concentration of dye and hydrogen peroxide. Results show that increased ferrous sulphate concentrations enhance the oxidation of the dye and can significantly reduce the concentration of hydrogen peroxide required for reaction. In other words, the amount of dye oxidized can be increased even for a lower concentration of hydrogen peroxide provided concentration of ferrous sulphate is high. Increased addition of ferrous sulphate had a positive effect on oxidation kinetics of Methylene Blue as it not only resulted in
almost complete oxidation but also significantly reduced the concentration of hydrogen peroxide and the time required for oxidation.

Tang and Huang (1996) studied the oxidation kinetics of unsaturated chlorinated aliphatic compounds by Fenton's reagent. Based on the transition state theory, hydroxylated active complexes were assumed to be the transition state after hydroxyl radicals attached to the organic compound. The complex either disproportionate or returns to their original reactants. Both OH\(^{-}\) and the active complexes had extremely high reactivity. The model indicates that Fenton oxidation was first order with respect to the concentration of organic substrate. The degree of oxidation was found dependent on the dosage of H\(_2\)O\(_2\) and Fe\(^{2+}\). The authors also state that because both Fe\(^{2+}\) and H\(_2\)O\(_2\) can react with OH\(^{-}\) neither of them should be overdosed if the maximum reaction rate is to be achieved. Figure 3.19 indicates that the optimum concentration of ferrous sulphate is 40 mg L\(^{-1}\).

Influence of ferrous sulphate on the oxidation of Acid orange was studied for a fixed concentration of dye and hydrogen peroxide but for varying concentrations of ferrous sulphate. The dye concentration was fixed at 50 mg L\(^{-1}\) and concentration of hydrogen peroxide at 91.7 mg L\(^{-1}\) (as obtained in step 5.1). The decrease in dye concentration with time was monitored at the \(\lambda_{\text{max}}\). Results of the experiment for different concentrations of ferrous sulphate are shown in figure 3.20. From the figure it can be seen that the ferrous sulphate concentration has an influence on oxidation of the dye with the amount of dye oxidized
increasing with an increase in the ferrous sulphate concentration. However, similar to hydrogen peroxide there exists an optimum concentration beyond which no significant influence on oxidation of the dye was observed. A higher concentration of ferrous sulphate resulted in rapid oxidation of the dye at a rate that could not be effectively monitored by spectrophotometry. On the other hand at low ferrous sulphate concentrations amount of dye oxidized was negligible and the oxidation kinetics followed zero order (indicated by a linear decrease in the dye concentration with time). Figure 3.20 indicates that the optimum concentration of ferrous sulphate is 40 mg L$^{-1}$. 
Figure 3.17
Influence of ferrous sulphate concentration on the oxidation of Direct Catachine Brown in aqueous solution.

$[\text{H}_2\text{O}_2] = 367 \text{ mg L}^{-1}$, $[\text{DCB}] = 150 \text{ mg L}^{-1}$, pH 2, vol. 1L, stirring rate 75 rpm,

$[\text{FeSO}_4]$ = varied 90, 100, 110, 120 and 130 mg L$^{-1}$
Figure 3.18
\([\text{H}_2\text{O}_2]\) = 110 mg L\(^{-1}\), \([\text{RY}] = 75\) mg L\(^{-1}\), pH 2, vol. 1L, stirring rate 75 rpm,
\([\text{FeSO}_4]\) = varied 40, 50, 60, 70 and 80 mg L\(^{-1}\)
Figure 3.19

$[\text{H}_2\text{O}_2] = 60 \text{ mg L}^{-1}$, $[\text{MB}] = 10 \text{ mg L}^{-1}$, pH 2, vol. 1L, stirring rate 75 rpm,

$[\text{FeSO}_4] =$ varied 10, 20, 30, 40 and 50 mg L$^{-1}$
Figure 3.20
Effect of ferrous sulphate concentration on the oxidation of Acid Orange [AO] in aqueous solution.
\([H_2O_2] = 91.7 \text{ mg L}^{-1}, [AO] = 50 \text{ mg L}^{-1}, \text{pH} 2, \text{vol. 1L, stirring rate 75 rpm,}
\[\text{FeSO}_4] = \text{varied 30, 40, 50, 60 and 70 mg L}^{-1}\)
3.5.3. Influence of dye concentration

The Influence of dye concentration on Fenton oxidation of Direct Catachine Brown was studied for fixed concentrations of hydrogen peroxide (367 mg L\(^{-1}\)) and ferrous sulphate (100 mg L\(^{-1}\)) at optimum concentrations obtained from figure 3.13 and 3.17 and for varying dye concentrations. Experiments were carried out for the dye concentrations of 50, 100, 200, 300 and 400 mg L\(^{-1}\). The results are depicted in figure 3.21.

The results obtained indicate that oxidation of the dye is more efficient at higher concentrations than for dilute solutions. When the concentration of dye was 50 mg L\(^{-1}\) (the lowest concentration studied) a ferrous sulphate concentration of 100 mg L\(^{-1}\) and a hydrogen peroxide concentration of 367 mg L\(^{-1}\) could oxidize 43 mg L\(^{-1}\) of the dye. However, for the same concentration of the Fenton's reagent, 272 mg L\(^{-1}\) of the dye could be oxidized for a concentration of 400 mg L\(^{-1}\). The results obtained clearly indicate that the oxidation efficiency is enhanced at higher dye concentrations. However, this trend is likely to approach a limit.

This behavior can be explained on the basis of the self-scavenging action of hydroxyl radicals at low concentrations of the dye. As the dye concentration increases there is an increase in the concentration of these radicals reacting with the dye rather than reacting among themselves. This reaches a maximum stoichiometric limit when \([\text{H}_2\text{O}_2]:[\text{Dye}]\) reaches 0.9.

In order to determine whether a higher concentration of the dye could be oxidized even at lower concentrations of ferrous sulphate by increasing the concentration of hydrogen peroxide, experiments were
carried out by choosing a particular concentration of the dye and then varying both ferrous sulphate and hydrogen peroxide, maintained at a constant mole ratio of 1:15. The results are summarized in Table 3.1.

Table 3.1. Conditions of experiments carried out to determine the optimum for the oxidation of Direct Catachine Brown - dye concentration of 150 mg/L and varying concentrations of the Fenton’s reagent, mole ratio of ferrous sulphate to hydrogen peroxide 1:15.

<table>
<thead>
<tr>
<th>Dye mg/L</th>
<th>FeSO₄ mg/L</th>
<th>FeSO₄ mM/L</th>
<th>H₂O₂ mg/L</th>
<th>H₂O₂ mM/L</th>
<th>Fe₂H₂O₂ Mole ratio</th>
<th>Amount of Dye oxidized, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>20</td>
<td>0.072</td>
<td>36.7</td>
<td>1.08</td>
<td>1:15</td>
<td>20</td>
</tr>
<tr>
<td>150</td>
<td>40</td>
<td>0.14</td>
<td>73.4</td>
<td>2.16</td>
<td>1:15</td>
<td>42</td>
</tr>
<tr>
<td>150</td>
<td>60</td>
<td>0.21</td>
<td>110.1</td>
<td>3.24</td>
<td>1:15</td>
<td>45</td>
</tr>
<tr>
<td>150</td>
<td>80</td>
<td>0.29</td>
<td>146.8</td>
<td>4.32</td>
<td>1:15</td>
<td>84</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>0.36</td>
<td>183.5</td>
<td>5.39</td>
<td>1:15</td>
<td>108</td>
</tr>
<tr>
<td>150</td>
<td>120</td>
<td>0.43</td>
<td>220.2</td>
<td>6.47</td>
<td>1:15</td>
<td>104</td>
</tr>
<tr>
<td>150</td>
<td>140</td>
<td>0.5</td>
<td>256.9</td>
<td>7.55</td>
<td>1:15</td>
<td>120</td>
</tr>
<tr>
<td>150</td>
<td>160</td>
<td>0.58</td>
<td>293.6</td>
<td>8.63</td>
<td>1:15</td>
<td>122</td>
</tr>
<tr>
<td>150</td>
<td>180</td>
<td>0.65</td>
<td>330.3</td>
<td>9.71</td>
<td>1:15</td>
<td>123</td>
</tr>
<tr>
<td>150</td>
<td>200</td>
<td>0.72</td>
<td>367</td>
<td>10.8</td>
<td>1:15</td>
<td>126</td>
</tr>
</tbody>
</table>

The amount of dye oxidized increased with an increase in the concentration of the Fenton’s reagent. However, the data points out two features. First, although a ferrous sulphate to hydrogen peroxide mole ratio of 1:15 is found optimum, the ratio of the oxidant to the dye is important in driving the oxidation to completion. Secondly, when the concentration of the Fenton’s reagent is not sufficient, the data points show a random behavior. This may be due to slow reaction at reduced concentration of the reagent, where the reaction pathway changes, according to some probable reactions involving the derived species.

\[
H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^-
\]
Dye + OH* → Colorless dye

at low concentrations of $\text{H}_2\text{O}_2$, or when $\text{Fe}^{2+}$ is depleted the reaction switches over to

$$\text{Fe}^{3+} + \text{HO}_2^* \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2$$

Both ferrous ions and hydrogen peroxide are integral components of Fenton's reagent generating hydroxyl radicals. Lower concentrations of either of them would result in decreased generation of the free radical thereby leading to a decrease in rate of the reaction resulting in the poor dye removal.

Walter and Huang (1996) evaluated the effect of the chlorine content of chlorinated phenols on their oxidation kinetics by Fenton's reagent. The reactivity of chlorophenols decreased with increasing chlorine substitution on the aromatic ring. They observed that at constant hydrogen peroxide and ferrous concentrations, initial dechlorination rates did not change significantly. This suggests that the generation of hydroxyl radical was the rate-limiting step.

From table 3.1 it is observed that there is an increase in the amount of the dye oxidized with increase in the concentration of the Fenton's reagent. However, beyond a ferrous sulphate concentration of 140 mg L$^{-1}$ and a hydrogen peroxide concentration of 256.9 mg L$^{-1}$ the increase was not significant. A comparison of the second order rate coefficients obtained for the different concentrations of the Fenton's reagent shows that beyond a ferrous sulphate concentration of 180 mg L$^{-1}$ and a hydrogen peroxide
concentration of 330 mg L\(^{-1}\), increase in the concentration of the Fenton’s reagent decreased the rate of oxidation of the dye. This indicates scavenging of the hydroxyl radicals by excess ferrous ions.

Table 3.1 shows that at a ferrous sulphate concentration of 100 mg L\(^{-1}\) and a hydrogen peroxide concentration of 183.5 mg L\(^{-1}\), the amount of dye oxidized was 108 mg L\(^{-1}\). Table 3.2 summarize the results of the experiments to show that the oxidation efficiency could also be increased by increasing the concentration of hydrogen peroxide even for low concentrations of ferrous sulphate.

Table 3.2. Influence of increased hydrogen peroxide concentration.

<table>
<thead>
<tr>
<th>Dye mg L(^{-1})</th>
<th>FeSO(_4) mg L(^{-1})</th>
<th>FeSO(_4) mM L(^{-1})</th>
<th>H(_2)O(_2) mg L(^{-1})</th>
<th>H(_2)O(_2) mM L(^{-1})</th>
<th>Fe:H(_2)O(_2) Mole ratio</th>
<th>Amount of Dye oxidized mg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>100</td>
<td>0.36</td>
<td>367</td>
<td>10.8</td>
<td>1:30</td>
<td>120.0</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>0.36</td>
<td>550</td>
<td>16.2</td>
<td>1:45</td>
<td>123.0</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>0.36</td>
<td>735</td>
<td>21.6</td>
<td>1:60</td>
<td>124.5</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>0.36</td>
<td>917.5</td>
<td>27.0</td>
<td>1:75</td>
<td>124.5</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>0.36</td>
<td>1101</td>
<td>32.4</td>
<td>1:90</td>
<td>124.5</td>
</tr>
</tbody>
</table>

A comparison of Tables 3.1 and 3.2 show that the lower concentration of ferrous sulphate is offset by increasing the concentration of hydrogen peroxide, leading to an increased oxidation of the dye. This means that both ferrous sulphate and hydrogen peroxide are integral components of the Fenton’s reagent. Reduced concentration of any one of them would result in decreased production of the hydroxyl radicals. Hydrogen peroxide is the oxidant and ferrous ions being required in an optimum stoichiometry. Kinetic studies have been carried out at a fixed
concentration of ferrous sulfate (100 mg L\(^{-1}\)) and the hydrogen peroxide concentration at 367 mg L\(^{-1}\).

The effect of dye concentration on Fenton’s oxidation of Reactive Yellow was determined by fixing the concentration of hydrogen peroxide at 110 mg L\(^{-1}\) and ferrous sulphate concentration at 60 mg L\(^{-1}\) (optimum concentrations obtained from figure 3.14 and 3.18) for varying concentrations of the dye. The concentrations chosen ranged from 25 to 125 mg L\(^{-1}\). The results obtained are shown in figure 3.22 and indicate that the oxidation efficiency of Fenton’s reagent is higher at higher concentrations of the dye. When the initial dye concentration was 25 mg L\(^{-1}\), 21.3 mg L\(^{-1}\) of dye was oxidized at a ferrous sulphate concentration of 60 mg L\(^{-1}\) and a hydrogen peroxide concentration of 110 mg L\(^{-1}\). The same concentration of Fenton’s reagent resulted in oxidizing 116.7 mg L\(^{-1}\) of the dye at a concentration of 125 mg L\(^{-1}\). This indicates that it was difficult to oxidize lower dye concentrations than concentrated solutions. The observations are summarized in Table 3.3.

Table 3.3. Optimum stoichiometric concentrations of the Fenton’s reagent for various dye concentrations.

<table>
<thead>
<tr>
<th>Dye (mg L(^{-1}))</th>
<th>FeSO(_4) (mg L(^{-1}))</th>
<th>H(_2)O(_2) (mg L(^{-1}))</th>
<th>mg H(_2)O(_2) / mg dye</th>
<th>Exposure (h)</th>
<th>mg of dye oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>60</td>
<td>110</td>
<td>4.40</td>
<td>2</td>
<td>21.3</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>110</td>
<td>2.20</td>
<td>2</td>
<td>44.7</td>
</tr>
<tr>
<td>75</td>
<td>60</td>
<td>110</td>
<td>1.50</td>
<td>2</td>
<td>67.0</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
<td>110</td>
<td>1.10</td>
<td>2</td>
<td>80.7</td>
</tr>
<tr>
<td>125</td>
<td>60</td>
<td>110</td>
<td>0.88</td>
<td>2</td>
<td>116.7</td>
</tr>
</tbody>
</table>

The oxidation efficiency of Fenton’s reagent for various dye concentrations is shown in figure 3.22.
Effect of dye concentration on Fenton’s oxidation of Methylene Blue was determined for a fixed concentration of both hydrogen peroxide and ferrous sulphate at 60 and 40 mg L\(^{-1}\) respectively. The dye concentrations were varied and the concentrations studied ranged from 0 to 20 mg L\(^{-1}\). Results are shown in figure 3.23. The results reveal that Fenton’s oxidation is more efficient at higher rather than for lower dye concentrations. The results obtained are summarized in Table 3.4.

Table 3.4. Optimum stoichiometric concentrations of Fenton’s reagent for various dye concentrations.

<table>
<thead>
<tr>
<th>[Dye] (mg L(^{-1}))</th>
<th>FeSO(_4) (mg L(^{-1}))</th>
<th>[H(_2)O(_2)] (mg L(^{-1}))</th>
<th>mg H(_2)O(_2)/mg dye</th>
<th>Exposure (h)</th>
<th>mg of dye oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>40</td>
<td>60</td>
<td>15</td>
<td>2</td>
<td>2.7</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>60</td>
<td>7.5</td>
<td>2</td>
<td>7.5</td>
</tr>
<tr>
<td>12</td>
<td>40</td>
<td>60</td>
<td>5.0</td>
<td>2</td>
<td>11.5</td>
</tr>
<tr>
<td>16</td>
<td>40</td>
<td>60</td>
<td>3.8</td>
<td>2</td>
<td>14.8</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>60</td>
<td>3.0</td>
<td>2</td>
<td>18.9</td>
</tr>
</tbody>
</table>

Figure 3.23 and table 3.4 further strengthen the view that Fenton’s reagent is effective for treating concentrated rather than dilute dye solutions. This observation has an attractive practical implication, as it is cost effective to treat the concentrated effluent followed by a second treatment of the residual dye and finally dilution with non-colored stream. Increased oxidation efficiency at higher dye concentrations indicate that deactivation of hydroxyl radical is an important mechanism lowering the treatment efficiency at low dye concentration while, at higher dye concentrations the reaction between hydroxyl radical and dye molecules dominate resulting in an observed increase in treatment efficiency.
Effect of dye concentration on Fenton's oxidation of Acid orange was studied by maintaining the concentration of ferrous sulphate and hydrogen peroxide at 40 mg L\(^{-1}\) and 91.7 mg L\(^{-1}\) respectively (optimum concentrations obtained in figures 3.16 and 3.20), and for varying concentrations of the dye. Dye concentrations chosen included the range up to which it followed Beer-Lamberts law. Results of the experiment are summarized in table 3.5.

### Table 3.5: Optimum stoichiometric concentrations of the Fenton's reagent for various dye concentrations.

<table>
<thead>
<tr>
<th>[Dye] (mg L(^{-1}))</th>
<th>FeSO(_4) (mg L(^{-1}))</th>
<th>[H(_2)O(_2)] (mg L(^{-1}))</th>
<th>mg H(_2)O(_2)/mg dye</th>
<th>Exposure (h)</th>
<th>mg of dye oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>40</td>
<td>91.7</td>
<td>4.6</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>91.7</td>
<td>2.3</td>
<td>2</td>
<td>38.5</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>91.7</td>
<td>1.5</td>
<td>2</td>
<td>56.7</td>
</tr>
<tr>
<td>80</td>
<td>40</td>
<td>91.7</td>
<td>1.1</td>
<td>2</td>
<td>75.5</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
<td>91.7</td>
<td>0.9</td>
<td>2</td>
<td>92.5</td>
</tr>
</tbody>
</table>

For the same concentration of Fenton's reagent, when the dye was completely decolorized at a concentration of 20 mg L\(^{-1}\); there was a progressive increase in the amount of dye oxidized at all higher concentrations. This indicates that the Fenton oxidation is a process that works best at higher dye concentrations. This observation is of much practical utility in onsite conditions.

The oxidation efficiency of the Fenton's reagent for various concentrations of Acid Orange is shown in Figure 3.24 which indicates a linear increase in amount of dye oxidized for the same concentration of Fenton's reagent irrespective of its initial concentration and decreased oxidant consumption at increased dye concentrations support the
observation that it is economical to treat concentrated rather than dilute dye solutions.
3.6. Kinetic Studies

The kinetic experiments have been carried out with the objective of elucidating the influence of the concentration of the of the following on the oxidation kinetics of the dye:

(i) Hydrogen peroxide
(ii) Ferrous sulfate
(iii) Dye

The experimental approach is described in section 3.3.2.

The integral method is usually adopted only under isolation condition i.e., when the parameter that is to be monitored is kept at very low concentrations, so that the rate of the reaction would be dependent upon this isolated parameter. However, since, both ferrous sulphate and hydrogen peroxide are critical components of the Fenton’s system if the concentration of any one of the constituents is made too low the reaction would not proceed. Hence, it is not possible to isolate either hydrogen peroxide or ferrous sulphate to study the reaction mechanism. Under such conditions the differential method (initial rate) is applied.

In the initial rate method the rate of the reaction is determined directly from the concentration versus time plots considering only the first few points after the start of the experiment.

In our studies the kinetic data has been interpreted using the initial rate method where rather than following the reaction to completion, observations are based on the first few initial points of decrease i.e., for the first half of the experiment. This takes into account only the reactions
before secondary reactions begin to have any discernible effect on oxidation of the dye.

A common feature observed in all experiments is that there is a first initial dip immediately on addition of hydrogen peroxide. The intensity of this initial dip can be pronounced and can achieve from less than 10% to 100% oxidation instantaneously, depending on the concentration of hydrogen peroxide and ferrous sulphate chosen for the experiment. However, it is after this initial dip, that the reaction begins to show interpretable trends. The Initial concentration was determined after pH correction of the reaction mixture containing the desired concentration of ferrous sulphate. This point does not take into account the effect on addition of hydrogen peroxide. Moreover, it has been observed that when the trend line is extrapolated to the Y-axis from the point of first measurement, the intercept on Y-axis suggest that a considerable portion of the dye gets oxidized immediately on addition of hydrogen peroxide. Farley and Hunter (1996) made similar observation during the Fenton oxidation of 1,2,3-trichloropropane. The oxidation kinetics followed pseudo first order after an initial period of higher and variable reaction kinetics.

Sun and Pignatello (1993) investigated the mineralization of 2,4-dichlophenoxy acetic acid (2,4-D) by Fe$^{3+}$/H$_2$O$_2$/UV system. They reported that the oxidation occurred in two stages. The first stage was attributed to reaction of free radicals generated under irradiation. In subsequent reaction the hydroxyl radical does not play any significant role. The reaction is exclusively due to photolysis or due to decarboxylation of Fe$^{3+}$ complexes
of degradation intermediates. The study reveals that the hydroxyl radical is ineffective in oxidizing the organic intermediates remaining after the first stage. This is most likely due to the lower reactivity of the highly oxygenated intermediates toward the hydroxyl radical or competitive consumption of hydroxyl radicals by other solutes. This argument is not tenable in the present context since there is a significant concentration of the dye in the medium at this point. The hydroperoxyl radical \((\text{HO}_2^*)\) produced by the reaction between hydrogen peroxide and the ferrous ion is less reactive than hydroxyl radicals. The slow acting residual hydroperoxide radical may also give such slow reaction.

Lu et al. (1997) studied the oxidation of Dichlorvos insecticide by Fenton's reagent. They observed that the oxidation was a two-stage reaction. The first stage is a rapid decomposition, which is over within 30s. This stage was attributed to a \(\text{Fe}^{2+}/\text{H}_2\text{O}_2\) reaction leading to the formation of hydroxy radicals. The second much slower stage was attributed to the \(\text{Fe}^{3+}/\text{H}_2\text{O}_2\) reaction.

Ince and Tezcanli (1999) studied the treatability of textile dye-bath effluents by advanced oxidation and its preparation for reuse. They found that the reaction occurs in two stages, a fast step followed by a slow step. The slow step reaction followed first order kinetics.

Anat and Deshpande (1996) studied the decolorization of wastewater containing reactive dyes by Fenton's reagent and found that the initial step is instantaneous. They attributed this to the rapid cleaving of
the dye molecule. However, they did not provide any proof as to the pattern cleavage.

Working on the oxidation of p-chlorophenol by Fenton's reagent Gun et al. (1999) reported that the process involved two steps. A fast initial stage, which obeyed first order rate law and a second slow stage which is attributed to the depletion of Fe$^{2+}$ by Fe-organic complex formation. Here also no proof was provided.

Kwon et al. (1999) studied the oxidation of p-chlorophenol by Fenton's reagent. They observed that the oxidation was a two-step process. The initial step was fast and resulted in significant oxidation within a few minutes. This was followed by a slow step. The initial fast rate was found first order with respect of p-chlorophenol. The slow phase was attributed to the depletion of ferrous ions caused by the formation of Fe – organic complex.
3.6.1. Influence of hydrogen peroxide on oxidation kinetics

The influence of hydrogen peroxide concentration on the rate of oxidation of the dye has been studied by maintaining a constant concentration of dye and ferrous sulphate but for varying concentrations of hydrogen peroxide. Five different concentrations of hydrogen peroxide were tried. The concentrations have been fixed in such a manner that there were two concentrations above optimum (as obtained from preliminary experiments), one concentration at the optimum and two concentrations below optimum. The results are depicted in figure 3.25.

Balanosky et al. (2000) studied the performance of a reactor in the oxidative degradation of textile waste. He also confirmed hydrogen peroxide was effective only in the presence of ferrous or ferric ions, and at lower hydrogen peroxide concentrations the reaction proceeded only slowly.

Figure 3.25 show that the initial rates for the decolorization reaction increased linearly with an increase in the concentration of hydrogen peroxide up to 390 mg L\(^{-1}\) beyond which there was a drop in the initial rates. This is because high hydrogen peroxide concentrations results in recombination of hydroxyl radicals among themselves to form hydroperoxyl radicals, according to the following reactions:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{OH}^* &\rightarrow \text{H}_2\text{O} + \text{HO}_2^* \\
2 \text{OH}^* &\rightarrow \text{H}_2\text{O}_2
\end{align*}
\]

Although hydroperoxyl radical is an oxidant it is much less reactive than the hydroxyl radicals (Legrini et al., 1993).
The results support the view that increased hydrogen peroxide concentrations decrease the rate of oxidation of the dye beyond an optimum value.

A plot of the initial rate against dye concentration is linear passing through the origin indicating that the reaction is first order with respect to hydrogen peroxide.

Kang et al. (2002) studied the pre-oxidation and coagulation of textile wastewater by the Fenton process observed 95% decolorization with in five minutes.

The influence of hydrogen peroxide on oxidation kinetics of Reactive Yellow was studied for a fixed ferrous sulphate concentration of 60 mg L\(^{-1}\) and a dye concentration of 75 mg L\(^{-1}\). Concentrations of hydrogen peroxide chosen for the experiment were 90, 100, 110, 120 and 130 mg L\(^{-1}\). The results obtained are shown in figure 3.26 and indicate that the initial rates were found to increase linearly with an increase in hydrogen peroxide concentration with an intercept at the origin. This indicates that the reaction is first order with respect to hydrogen peroxide. Reaction pathway followed can be represented by the following equation

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^-
\]

Similar observations have been reported by Isak et al., (1996) during the oxidation of aldehydes by Fenton's reagent.

Lindsey and Tarr (2000) studied the generation of hydroxyl radical during Fenton oxidation following a single addition of iron and hydrogen
peroxide. The authors observed a linear increase in hydroxyl radical formation with the concentration of hydrogen peroxide.

The influence of hydrogen peroxide on kinetics of Fenton oxidation of Methylene Blue was studied by fixing the concentrations of ferrous sulphate at 35 mg L\(^{-1}\) and dye at 10 mg L\(^{-1}\). The concentration of hydrogen peroxide was varied. Five concentrations of hydrogen peroxide were chosen in such a manner that there was two concentrations below optimum, one concentration at optimum and two concentrations above optimum. The variation in initial rates for different concentrations of hydrogen peroxide is shown in figure 3.27. Results indicate that an increase in the initial rate with an increase in hydrogen peroxide concentration up to 2.35 mM after which the initial rates decrease. This is probably the concentration of hydrogen peroxide where the ratios of ferrous ions to hydrogen peroxide are in balance to initiate the generation of hydroxyl radicals, which in turn oxidize the dye.

Similar observations have also been observed in the case of Acid Orange. Experiments to establish the influence of hydrogen peroxide on Fenton’s oxidation of Acid Orange was performed by fixing the concentration of dye at 50 mg L\(^{-1}\), the ferrous sulphate concentration at 40 mg L\(^{-1}\) (as obtained in the preliminary experiments) for varying the concentrations of hydrogen peroxide. Five different concentrations of hydrogen peroxide were chosen in such a manner that there were two concentrations below optimum, one concentration at the optimum and two concentrations above optimum. Thereby, obtaining influence of hydrogen
peroxide concentrations at both extremes relative to the optimum concentration. The results obtained are shown in figure 3.28.

As the concentration of hydrogen peroxide was increased the initial rates tend to increase in an exponential manner. Under such conditions the concentration of hydrogen peroxide is sufficient enough to be decomposed by the ferrous ions acting as a catalyst to generate the hydroxyl radicals. William et al., (1996) report that reaction rates appeared to be highest at the lowest peroxide to iron ratio. Gradually a stage is reached where the concentration of hydrogen peroxide exceeds the concentration of ferrous sulphate. Under such conditions the excess hydrogen peroxide would involve in non-productive internal reactions that lead to scavenging of the hydroxyl radicals (OH\(^\ast\)) to form hydroperoxyl (HO\(_2\)^\ast\)) radicals. These hydroperoxyl radicals have a lower reactivity when compared to the peroxy radicals. The reactions mediated by hydroperoxyl radicals after the hydroxyl radical has been scavenged, results in lowering the initial rates. This accounts for the curvature observed in figure 3.27 and 3.28.

Lloyd et al. (1997) studied the origin of hydroxyl radical O\(_2\) in the Fenton reaction and report that hydroxyl radical was derived exclusively from H\(_2\)O\(_2\). However, at higher hydrogen peroxide concentrations there is an excess of hydrogen peroxide over the ferrous ions. Excess peroxide involves in non-productive internal reactions that leads to scavenging of the hydroxyl radicals (OH\(^\ast\)) by formation of hydroperoxyl radicals (HO\(_2\)^\ast\)). Compared to the hydroxyl radical, the hydroperoxyl radical has a much
lower reactivity. After hydroxyl radicals are scavenged which is the most likely situation at hydrogen peroxide concentrations above 2.35 mM, oxidation of the dye is promoted by hydroperoxyl radical. The hydroperoxyl radical being of lower reactivity results in a decrease in the initial rates. Scott et al. (1998) measured Hydroxyl radical activity in soil slurry using the spin trap agent α-(4-Pyridyl-1-Oxide) – N-tert-butylnitrone. They observed that non-productive reactions involving hydrogen peroxide (those that did not contribute to the production of hydroxyl radicals) represented a significant source for the overall decrease in reaction efficiency.

Sun and Pignatello, (1993) studied the oxidation of 2,4-D by Fe$^{3+}$/H$_2$O$_2$/UV system and reports similar observations. The authors report that the hydroxyl radical is ineffective in oxidizing organic intermediates remaining after completion of the first stage. This was attributed to the low reactivity of highly oxygenated intermediates to hydroxyl radical and competition for the hydroxyl radical by other solutes. The hydroperoxyl (HO$_2^*$) radical was incapable of producing any CO$_2$ from the ring, indicating its poor reactivity in comparison to Hydroxyl radical (OH$^*$).

Liao et al. (1999) studied the removal of COD and color from dye manufacturing process wastewater using Photo-Fenton oxidation process. The author’s reported that increased concentration of hydrogen peroxide does not necessarily mean increased removal rates of COD and color.

Ince and Stefan (1997) studied the degradation and toxicity reduction of a textile azo dye Remazol Black – B using UV/H$_2$O$_2$. The
authors observed that beyond an effective concentration, the influence of hydrogen peroxide was found inhibitory.

Sychev and Isak (1995) studied iron compounds and the mechanisms of homogeneous catalysis. They report that higher peroxide concentrations could be detrimental to degradation kinetics since after initiation step, the propagation step would be hindered by excess hydrogen peroxide acting as a scavenger of the hydroxyl radical.

Huston and Pignatello. (1999) used photo-assisted Fenton reaction to degrade selected pesticide active ingredients in water. The authors state that at longer reaction time, higher initial peroxide concentration could result in greater mineralization. As mineralization proceeds the carbon acquires higher oxidation states, however, the organic compounds remaining in solution typically become less reactive with the hydroxyl radicals. This results in the decay of hydroxyl radical through scavenging by hydrogen peroxide or self-reaction or scavenging by ferrous ion.

A plot of the initial rates against hydrogen peroxide concentration fit well into a second order polynomial expression giving a curve as shown in Figures 3.27 and 3.28; indicating that there is a possible chance for complexation with hydrogen peroxide.

Fung et al. (1999) studied the treatability of organic and colour removal in desizing/dyeing wastewater by UV/US system combined with hydrogen peroxide. The authors observed that increasing the amount of hydrogen peroxide could enhance the oxidation efficiency. However high concentrations had little positive effects on dye removal due to the
competitive reaction of hydrogen peroxide with the hydroxyl radicals. The
dye was found to follow pseudo-first order kinetics at different pH and
hydrogen peroxide concentrations. The rate constants were linearly
correlated with pH but fitted better into a second order polynomial
expression.

One way of confirming this observation is by a double reciprocal plot
in which the inverse of initial rates is plotted against inverse of hydrogen
peroxide concentration. Such a plot is presented in figure 3.29 and 3.30.

The double reciprocal plot for Methylene Blue at different
concentrations of hydrogen peroxide is shown in figure 3.29. The resulting
plot is linear up to the limiting concentration with a positive intercept at the
Y-axis confirming the involvement of a complexation step in Fenton
oxidation of Methylene Blue. Since, concentrations of ferrous sulphate and
the dye were maintained constant for varying concentrations of hydrogen
peroxide, complexation between hydrogen peroxide and the dye is most
likely.

Figure 3.28 show that the variation in initial rates fits a second order
polynomial expression representing a curve in the case of Acid Orange.
The observation is similar to that of Fung et al., (1999) where the rate
constants fitted better into a second order polynomial expression. The
curve is an indication of complexation with hydrogen peroxide. A double
reciprocal plot can prove this observation. Figure 3.30 suggest a linear
variation in the double reciprocal of the initial rate against the hydrogen
peroxide concentration with an intercept at the Y-axis. Since,
concentrations of ferrous sulphate and the dye were maintained constant for varying concentrations of hydrogen peroxide, the observation confirms the involvement of a complexation step with hydrogen peroxide during Fenton oxidation of Acid Orange.

Salem and Maazawi (2000) studied the kinetics and mechanism of color removal of Methylene Blue with hydrogen peroxide catalyzed by supported alumina surfaces. The authors observed that at low hydrogen peroxide concentrations, the reaction was first order, which becomes zero order with increase in hydrogen peroxide concentration before becoming negative. They observed the formation of colored intermediate on the surface of the catalyst. Pignatello et al. (1999) showed evidence for an additional oxidant in photo assisted Fenton reaction. The authors observed that hydrogen peroxide formed a complex with iron, Fe (O₂H)²⁺, that absorbs in the visible region, which could be the precursor of ferryl complex.
Figure 3.25
Direct Catachine Brown
Variation of initial rates with hydrogen peroxide concentration
[DCB] = 150 mg L⁻¹, [FeSO₄] = 100 mg L⁻¹, pH 2, vol. 1L, stirring rate 75 rpm,
[H₂O₂] = varied 300, 330, 367, 390 and 420 mg L⁻¹
Figure 3.26
Reactive Yellow (RY)
Variation of initial rates with hydrogen peroxide concentration
[RY] = 75 mg L⁻¹, [FeSO₄] = 60 mg L⁻¹, pH 2, vol. 1L, stirring rate 75 rpm,
[H₂O₂] = varied 2.3, 2.94, 3.23, 3.53 and 3.82 mM L⁻¹
Figure 3.27
Methylene Blue (MB)
Variation of initial rates with hydrogen peroxide concentration
[MB] = 10 mg L$^{-1}$, [FeSO$_4$] = 35 mg L$^{-1}$, pH 2, vol. 1L, stirring rate 75 rpm,
[H$_2$O$_2$] varied 0.59, 1.18, 1.76, 2.35 and 2.94 mM L$^{-1}$
Figure 3.28
Acid Orange (AO)
Variation of initial rates with hydrogen peroxide concentration
[AO] = 50 mg L$^{-1}$, [FeSO$_4$] = 40 mg L$^{-1}$, pH 2, vol. 1L, stirring rate 75 rpm,
[H$_2$O$_2$] = varied 0.88, 1.76, 2.7, 3.53 and 4.4 mM L$^{-1}$
Figure 3.29
Methylene Blue (MB)
Double reciprocal plot of initial rates and hydrogen peroxide concentration
[MB] = 10 mg L\(^{-1}\), [FeSO\(_4\)] = 35 mg L\(^{-1}\), pH 2, vol. 1 L, stirring rate 75 rpm,
[H\(_2\)O\(_2\)] = varied 0.59, 1.18, 1.76, 2.35 and 2.94 mM L\(^{-1}\).
Figure 3.30
Acid Orange (AO)
Double reciprocal plot of initial rates and hydrogen peroxide concentration:
[AO] = 50 mg L⁻¹, [FeSO₄] = 40 mg L⁻¹, pH 2, vol. 1L, stirring rate 75 rpm,
[H₂O₂] varied 0.88, 1.76, 2.7, 3.53 and 4.4 mM L⁻¹
3.6.2. Influence of ferrous sulphate on the oxidation kinetics

The influence of ferrous sulphate concentration on the oxidation of Direct Catachine Brown was studied by fixing the concentrations of hydrogen peroxide and the dye at 367 mg L⁻¹ and 150 mg L⁻¹ respectively. The concentration of ferrous sulphate was varied. The results are shown in figure 3.31. Variation of initial rates with Ferrous sulphate concentration gives a linear plot passing through the origin indicating that the reaction is first order with respect to ferrous sulphate.

Results indicate that the initial rates increased linearly with increasing ferrous sulphate concentration up to 120 mg L⁻¹. Further increase resulted in a decrease in the initial rates. Since, the concentration of ferrous sulphate was varied at a constant concentration of hydrogen peroxide, the fall in initial rates could be due to the hydrogen peroxide concentration becoming limiting. This results in an increased accumulation of ferrous ions in solution. Of the two it is hydrogen peroxide, which is the de facto oxidant. Ferrous ions only function as catalyst that facilitates the homolysis of hydrogen peroxide. The excess ferrous ions would react with hydrogen peroxide at a very fast rate to yield hydroxyl radicals until all the hydrogen peroxide present in the reactor is utilized. It is up to this point that the rate coefficient values would continue to increase with an increase in the concentration of ferrous ions. Beyond a certain limit further increase in ferrous sulphate concentration leads to accumulation without an active role for catalysis.
The influence of ferrous sulphate on the oxidation kinetics of Reactive Yellow was studied by fixing the concentration of dye at 75 mg L\(^{-1}\) and hydrogen peroxide at 110 mg L\(^{-1}\) for varied concentrations of ferrous sulphate. The ferrous sulphate concentrations chosen for the experiments were 40, 50, 60, 70 and 80 mg L\(^{-1}\). The results are shown in figure 3.32.

From figure 3.32 it can be seen that as the concentration of ferrous sulphate is increased there is a linear increase in the initial rate up to a concentration of 70 mg L\(^{-1}\) after which the initial rates show a decrease. This indicates the negative influence of excess ferrous sulphate concentration. Bandara et al., 1996 investigated the degradation of Orange II by Fenton type reagent aided by sunlight. They observed that stable iron complexes in combination with hydrogen peroxide and the near surface radical formation are processes actively responsible for abatement of the dye. A plot of initial rates against the concentration of ferrous sulphate is a linear up to the limiting concentration indicating that the reaction is first order with respect to ferrous sulphate.

This indicates that when the concentration of ferrous ions is lesser than that of hydrogen peroxide concentration the decomposition of hydrogen peroxide will be catalyzed by ferrous ions generating hydroxyl radicals. Under such conditions hydroxyl radicals would mediate oxidation of the dye. This is indicated by an increase in the initial rates. This phenomenon would continue up to an optimum ferrous sulphate concentration. However, as the concentration is raised above the optimum, ferrous ions begin to exceed the concentration of hydrogen peroxide. The
small amounts of hydrogen peroxide present would be immediately decomposed by ferrous ions and the remaining excess ferrous ions would accumulate in the medium. This is undesirable, as excess ferrous ions are known to scavenge hydroxyl radicals to form hydroperoxyl radicals of lower reactivity. These hydroperoxyl radicals resulting in a decrease in the initial rates would now mediate oxidation of the dye. Ferric ions produced by the oxidation of ferrous ions can also scavenge hydroperoxyl radicals.

Influence of ferrous sulphate on Fenton's oxidation of Acid Orange was studied by fixing the concentration of hydrogen peroxide at 91.7 mg L\(^{-1}\) (obtained optimum) and the dye at 50 mg L\(^{-1}\), for varying concentrations of ferrous sulphate. The ferrous sulphate concentration was varied in such a manner that there was one concentration below the observed optimum, one concentration at the optimum and three concentrations above the optimum. Figure 3.33 shows the variation in initial rates with concentration of ferrous sulphate.

From the figure (3.33) it can be seen that the initial rate increases with an increase in the concentration of ferrous sulphate up to a limiting concentration of 60 mg L\(^{-1}\) after which a further increase results in a decrease in the initial rates. Indicating that at high ferrous sulphate concentrations the excess ferrous ions scavenge the hydroxyl radicals. This is similar to the observation made by Tang and Huang (1996), who state that because both Fe\(^{2+}\) and H\(_2\)O\(_2\) can react with OH\(^+\), so neither of them should be overdosed if the maximum reaction rate is to be achieved. Wang et al., (1998) observed a decrease in the dechlorination rate of tetra
chloroethene with time during Fenton oxidation. This was attributed to the conversion of Fe (II) to Fe (III).

Up to an optimum ferrous sulphate concentration of 60 mg L\(^{-1}\), the initial rates increased linearly with the regression line passing through origin indicating that the reaction is first order with respect to ferrous sulphate.

Fig. 3.33 indicates that both low and high ferrous sulphate concentrations can have a negative impact on oxidation rate of the dye. This is because when the concentration of ferrous sulphate is lower than the concentration of hydrogen peroxide, ferrous ions would catalyze the decomposition of hydrogen peroxide to form highly reactive hydroxyl radicals. These hydroxyl radicals in turn oxidize the dye. Under such conditions, rate of the reaction would show an increase with an increase in the ferrous sulphate concentration up to an optimum (which is at 60 mg L\(^{-1}\)). Further increase would result in the concentration of ferrous ions exceeding that of hydrogen peroxide. So initially hydrogen peroxide would be rapidly decomposed by ferrous ions, after which the remaining ferrous ions would simply accumulate in the reaction mixture. This increased accumulation of ferrous ions is undesirable as they lead to scavenging of hydroxyl radicals and form hydroperoxyl radicals thereby decreasing the reaction rate (Huston and Pignatello., 1999) according to the equation.

\[
\text{Fe}^{2+} + \text{OH}^* \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}
\]
From Fig. 3.33 it can be seen that the initial rates increased linearly with an increase in ferrous sulphate up to a limiting concentration of 60 mg L\(^{-1}\). The plot is linear and passes through origin indicating that the reaction is first order with respect to ferrous sulphate.

One common feature observed irrespective of the dye class (Direct, Reactive and Acid dye) is that although there is an initial increase in the rate of oxidation with an increase in ferrous sulphate concentration, beyond an optimum, the increased concentration was found to negatively influence the rate of reaction by actually decreasing the reaction rate for further increase. These observations made with respect to the three dyes namely Direct Catachine Brown, Reactive Yellow and Acid Orange can be accounted for by considering observations made by other authors working in similar or related fields.

Yoon et al. (2001) investigated the reaction pathway of OH radicals produced by Fenton oxidation in wastewater treatment. They observed that high concentrations of ferrous ions enhanced the production of hydroxyl radicals that led to faster consumption of hydrogen peroxide. A possible drawback associated with such a system is the scavenging of hydroxyl radical by the ferrous ions. They did not report the optimal concentrations.

On the basis of the above discussion the probable mechanism followed could be summarized as

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^*
\]
This step would continue up to an optimum concentration of ferrous ions. Under conditions of an excess of ferrous ions the hydroxyl radicals formed are scavenged according to the reaction

\[ \text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \cdot \text{OH} \]

Or, the hydroxyl radical can undergo a dismutation reaction

\[ 3\cdot \text{OH} \rightarrow \cdot \text{HO}_2 + \text{H}_2\text{O} \]

Or, the hydroperoxyl radical may be scavenged by the ferrous ions according to the reaction

\[ \text{Fe}^{2+} + \cdot \text{HO}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{O}_2 \]

The ferric ions may be recycled to ferrous ions by the reaction

\[ \text{Fe}^{3+} + \cdot \text{HO}_2 \rightarrow \text{Fe}^{2+} + \cdot \text{H} + \text{O}_2 \]

These reactions can contribute to a decrease in the initial rates at excessive concentrations of ferrous ions.

Wang et al. (1998) investigated the effect of pyrophosphate on the dechlorination of tetrachloroethene by Fenton’s reagent. A decrease in the dechlorination rate was observed with time. This was attributed to the conversion of Fe (II) to Fe (III) and complexation of Fe (III) with pyrophosphate.

Kang et al. (1999) applied Fenton’s reagent to degrade 2,4-dinitrophenol. At low dosages of ferrous ions and hydrogen peroxide, a linear increase in the initial removal rate of DNP is observed while at higher dosages of ferrous ions (>1mM) the effect was insignificant.
Liao et al. (1999) studied the effects of ferrous, hydrogen peroxide and pH on the oxidation of effluents from a dye-manufacturing unit. Oxidation increased with concentration of ferrous ions during the initial reaction periods. However as the reaction progressed with an increase in the ferrous ions the removal profiles leveled off due to the lack of hydrogen peroxide residue.

The influence of ferrous sulphate on oxidation kinetics of Methylene Blue was studied by fixing the concentrations of hydrogen peroxide at 60 mg/L and dye concentration at 10 mg L\(^{-1}\). The concentration of ferrous sulphate was varied from 10 to 50 mg L\(^{-1}\).

The variation in initial rates for different ferrous sulphate concentrations is shown in figure 3.34.

Kang et al. (1999) observed a linear increase in the initial degradation rates of DNP and color at low dosages of ferrous ions and hydrogen peroxide. At High concentration of ferrous ions (>1mm) the response was insignificant.

Liao et al. (1999) observed that during the initial reaction periods the rate of oxidation process increased at higher intensity of radiation and concentration of ferrous ions. As the reaction progressed with an increase in the ferrous ions the removal profiles leveled off due to the lack of hydrogen peroxide residue.

Wang et al. (1998) studied the Fenton oxidation of tetrachloroethene and observed a decrease in the dechlorination rate with time. This was attributed to the conversion of Fe (II) to Fe (III).
Figure 3.34 indicates that the initial rates increased with an increase in the concentration of ferrous sulphate up to 0.14 mM after which the initial rates leveled off. This trend indicates that a further increase in the ferrous sulphate concentration could lead to a decrease in the initial rates. Isak et al. (1996) studied the oxidation kinetics of aldehydes by Fenton's reagent and observed that Fe$^{2+}$ played the role of a catalyst dissociating H$_2$O$_2$ to OH$^-$ and OH$^·$. Liao et al. (1999) studied the use of Photo-Fenton oxidation for the removal of COD and color from dye wastewater. The oxidation process was enhanced for increased concentration of ferrous ions during the initial reaction periods. However as the reaction progressed, with an increase in the ferrous ions the removal profiles leveled off due to the lack of hydrogen peroxide residue. This is a very likely phenomenon, as ferrous sulphate at high concentrations decrease the rate of oxidation of the dye by scavenging hydroxyl radicals. Initially, ferrous sulphate added would catalyze the oxidation of hydrogen peroxide in the medium. Yoon et al., (2001) investigated the reaction pathway of OH radicals produced by Fenton oxidation in wastewater treatment. The authors found that high concentrations of ferrous ions enhanced the production of hydroxyl radicals and led to faster consumption of hydrogen peroxide. An increase in the ferrous sulphate concentration beyond an optimum leads to undesirable and excessive accumulation of ferrous ions in the reaction mixture. These ferrous ions scavenge the hydroxyl radical through the following equation

$$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^-$$
The little of the hydroperoxyl radical that is formed would also react with the excess of ferrous ions according to the following reaction and get scavenged.

\[ \text{Fe}^{2+} + \text{HO}_2^* \rightarrow \text{Fe}^{3+} + \text{HO}_2 \]

Fe$^{3+}$ formed in the above step can also scavenge the hydroperoxyl radical according to the following equation

\[ \text{Fe}^{3+} + \text{HO}_2^* \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \]

The Fe$^{3+}$ formed can also react with hydrogen peroxide according to the equation

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \]

However, the hydroperoxyl radical formed has a lower reactivity. Ferrous ions are generated in low concentrations and the absence of hydroxyl radical does not permit any reaction to take place between the two. This could lead to a decrease in the initial rates.

The initial rates when plotted against ferrous sulphate concentrations fitted well into a second order polynomial expression representing a curve as shown in figure 3.34. This indicates that there could be a complexation step involved with respect to ferrous sulphate also. Therefore, a double reciprocal plot was carried out. The results are shown in figure 3.35.

The double reciprocal plots of initial rates for oxidation of Methylene Blue at different concentrations of ferrous sulphate are shown in figure 3.35. Where \( r_0 \) is the initial rates obtained for different ferrous concentrations and \([\text{FeSO}_4]\) is the initial ferrous sulphate.
concentration. The plot was found to be linear with a positive intercept. Since, the concentration of hydrogen peroxide and the dye was maintained constant for varying concentrations of ferrous sulphate a complexation between ferrous sulphate and the dye is most likely. Figure 3.35 confirms complexation with ferrous sulphate.

Joseph J. Pignatello. (1992) studied photo assisted Fenton to catalyze the degradation of chlorophenoxy herbicides. The authors observed that scavenging of the active oxidant and complexation with Fe$^{3+}$ could inhibit the reaction.

Herve et al. (1998) studied oxidation of Atrazine by Fe (II)/H$_2$O$_2$ system. They suggested that the reaction of hydrogen peroxide with ferrous ion involves an intermediate which leads to the formation of another intermediate which reacts with Fe (II) to give Fe (III) without the formation of OH$^*$. Sedlak and Andren. (1991) studied the oxidation of chlorobenzene with Fenton’s reagent. The authors suggest that complexes of aromatic intermediate compounds with iron and oxygen may play a role in regulating the reaction pathways.

Herrera et al. (1998) studied photo-oxidation of concentrated p-coumaric acid in homogeneous solution and report that Fenton’s reagent form precursor intermediates that are susceptible to degradation under light.

Alexei and Kiwi (1997) studied transient intermediate species active during the Fenton – mediated degradation of Quinoline. The authors report
formation of intermediates having a transient lifetime of less than 4μs. The intermediates were affected by reagent concentration, concentration of the oxidant and pH.

Tachiev et al. (2000) studied the Kinetics of hydrogen peroxide decomposition with complexed and “free” iron catalysts. At low pH the ferrous iron was mostly uncomplexed and in the free form, while high pH ranges (6 - 9) resulted in the formation of Fe (III) complexes.

Kwon et al. (1999) studied the oxidation of p-chlorophenol by Fenton's reagent. Occurrence of the slow phase was attributed to depletion of ferrous ions caused by the formation of Fe – organic complex.

Nadtochenko and Kiwi (1997) studied photo induced adduct formation between orange II and Fe^{3+} (aq) or Fe(OX)_{3}^{3-}H_{2}O_{2} using steady state and pulsed laser photolysis. They reported that the excited states of Fe(OX)_{3}^{3-} or the (FeIII)-Orange II) complexes are the active species during the decolorization of the dye. Based on a radical theory of Fenton catalysis and direct evidence obtained from laser spectroscopy, the authors established the formation of OH* adducts for Orange II as the initial degradation step leading to observed oxidation of the dye.

Herrera et al. (1999) studied the photochemical decolorization of Remazol Brilliant Blue and Uniblue A in the presence of Fe^{3+} and H_{2}O_{2} through Laser flash photolysis. The authors report that electron transfer between the excited dye and Fe^{3+} was found to be the initiating step, either as a bimolecular process (D* + Fe^{3+} = D^{0+} + Fe^{2+}) or through a dye - iron complex (D* + Fe^{3+} = D...Fe^{3+}) which again forms (D^{0+} + Fe^{2+}). A radical
chain reaction is observed between Fe$^{3+}$/ H$_2$O$_2$ during the initiation step. Photo dissociation reaction of the D....Fe$^{3+}$complex is found to be more important in the initiation of chain reaction rather than bimolecular quenching between D$^*$ and Fe$^{3+}$.

Esther et al. (1995) studied the Reactions of low transition metal complexes with hydrogen peroxide. The results indicated the formation of an Iron (II) peroxide intermediate complex which at pH < 5.5 decompose to yield free hydroxyl radical. This indicated that the non-participating ligand-L had an appreciable effect on the reaction mechanism of the metal center with hydrogen peroxide.

Sawyer (1997) studied Metal Hydro peroxide induced activation of dioxygen (O$_2$) for the ketonization of hydrocarbons by Fenton reagent. The authors established that Fenton chemistry involves the formation of hydro peroxide (ROOH) adducts of reduced transition metals [Fe (II), Cu (I) and Co (II)] via nucleophilic addition. These reactive intermediates react with excess catalyst to form L$_x$Fe$^{III}$OH (R) or with excess ROOH to form O$_2$, H$_2$O and ROH or with excess hydrocarbon (RH) to form ROH (Fenton chemistry) or with ambient dioxygen to form adduct [L$_x$' [Fe$^{II}$]- OOR, BH$^+$].
Figure 3.31
Direct Catachine Brown (DCB)
Variation of initial rates with ferrous sulphate concentration
[DCB] = 150 mg L⁻¹, [H₂O₂] = 367 mg L⁻¹, pH 2, vol. 1L, stirring rate 75 rpm,
[FeSO₄] = varied 0.32, 0.36, 0.40, 0.43 and 0.47 mg L⁻¹
Figure 3.32
Reactive Yellow (RY)
Variation of initial rates with ferrous sulphate concentration
\([\text{RY}] = 75 \, \text{mg} \, \text{L}^{-1}, [\text{H}_2\text{O}_2] = 110 \, \text{mg} \, \text{L}^{-1}, \text{pH} 2, \text{vol.} \, 1\text{L}, \text{stirring rate} \, 75 \, \text{rpm}, \]
\([\text{FeSO}_4] = \text{varied} \, 0.14, 0.18, 0.21, 0.25 \, \text{and} \, 0.29 \, \text{mM} \, \text{L}^{-1}\)
Figure 3.33
Acid Orange (AO)
Variation of initial rates with ferrous sulphate concentration
[AO] = 50 mg L\(^{-1}\), \([\text{H}_2\text{O}_2]\) = 91.7 mg L\(^{-1}\), pH 2, vol. 1L, stirring rate 75 rpm,
[Fe\(\text{SO}_4\)] = varied 0.11, 0.14, 0.18, 0.21 and 0.25 mM L\(^{-1}\)
Figure 3.34
Methylene Blue (MB)
Variation of initial rates with ferrous sulphate concentration
[MB] = 10 mg L⁻¹, [H₂O₂] = 60 mg L⁻¹, pH 2, vol. 1L, stirring rate 75 rpm,
[FeSO₄] = varied 0.035, 0.072, 0.11, 0.14 and 0.18 mM L⁻¹
Figure 3.35
Methylene Blue (MB)
Double reciprocal plot of initial rate against ferrous sulphate concentration
\([\text{MB}] = 10 \text{ mg L}^{-1}, [\text{H}_2\text{O}_2] = 60 \text{ mg L}^{-1}, \text{pH } 2, \text{vol. } 1\text{L, stirring rate 75 rpm,}\]
\([\text{FeSO}_4] \text{ varied } 0.035, 0.072, 0.11, 0.14 \text{ and } 0.18 \text{ mM L}^{-1}\)
3.6.3. Influence of dye concentration on oxidation kinetics

Influence of concentration of the dye on kinetics of Fenton's oxidation of Direct Catachine Brown was studied by fixing the concentration of hydrogen peroxide at 367 mg L\(^{-1}\) and ferrous sulphate at 100 mg L\(^{-1}\). The concentrations of the dye ranged from 50 to 400 mg L\(^{-1}\). The variation in initial rates for different concentrations of Direct Catachine Brown is shown in figure 3.36.

The initial rates were found to increase linearly with an increase in the concentration of the dye up to 300 mg L\(^{-1}\). However, the observed decrease in initial rates when the concentration of the dye was raised to 400 mg L\(^{-1}\) could be due to inhibition of the hydroxyl radical formation due to the reaction between ferrous ions and hydrogen peroxide.

The influence of dye concentration on the Fenton oxidation of Reactive Yellow has been established by fixing the concentration of hydrogen peroxide and ferrous sulphate at 110 and 60 mg L\(^{-1}\) (the obtained optimum concentrations) respectively for varying dye concentrations. The dye concentrations studied ranged from 25 mg L\(^{-1}\) to 125 mg L\(^{-1}\). Fig. 3.37 illustrates the results obtained. On the basis of the obtained results it is inferred that the initial rates showed a linear variation with an increase in the dye concentration. Indicating that the reaction can be considered first order with respect to the dye. This can be accounted, as at increased concentrations there is an increased collision between dye molecules and the hydroxyl radicals produced, leading to an increase in initial rates.
Influence of dye concentration on the kinetics of Fenton oxidation of Methylene Blue was studied for different concentrations of the dye ranging from 4 mg L\(^{-1}\) to 20 mg L\(^{-1}\) keeping ferrous sulphate and hydrogen peroxide concentrations fixed at the observed optimums of 40 and 60 mg L\(^{-1}\) respectively. Variation in initial rates for different concentrations of the dye is shown in figure 3.38. Results indicate that the variation in initial rates with dye concentration is linear indicating that the reaction is first order with respect to Methylene Blue.

Salem and Maazawi (2000) studied the Kinetics and mechanism of color removal of Methylene Blue with hydrogen peroxide catalyzed by supported alumina surfaces. The authors observed that Fenton oxidation was first order with respect to Methylene Blue and with respect to hydrogen peroxide and ferrous sulphate the order was found to be dependent on the concentration range.

Influence of dye concentration on Fenton's oxidation of Acid Orange has been studied by fixing the concentration of hydrogen peroxide (at 91.7 mg L\(^{-1}\)) and ferrous sulphate (at 40 mg L\(^{-1}\)) as obtained through the optimization experiments for varying concentrations of the dye. Concentration range chosen for the experiment ranged from 0 to 100 mg/L. Fig. 3.39 illustrates the influence of concentration of Acid Orange on Fenton oxidation. The study indicated that the initial rates increased linearly with dye concentration up to 80 mg L\(^{-1}\).

One common feature observed irrespective of the dye class, is that the initial rates increased linearly with an increase in the dye
concentration. This can be accounted for by the collision theory, according to which, with an increase in the dye concentration there would be an increased collision between the dye molecules and hydroxyl radicals leading to an increase in the rate of the reaction. However exceptions have been observed in the case of Direct Catachine Brown and Acid Orange where although at lower dye concentrations the increase in the rate of the reaction is linear, at higher dye concentrations (300 and 80 mg L$^{-1}$ respectively), a decrease in rate of the reaction with an increase in the dye concentration has been observed. This could be because, increased dye concentrations probably interferes with the reaction between ferrous ions and hydrogen peroxide thereby inhibiting the activity of hydroxyl radicals.
Figure 3.36
Direct Catachine Brown
Variation of initial rates with hydrogen peroxide concentration
$[\text{H}_2\text{O}_2] = 367 \text{ mg L}^{-1}$, $[\text{FeSO}_4] = 100 \text{ mg L}^{-1}$, pH 2, vol. 1L, stirring rate 75 rpm,
[DCB] varied 0.048, 0.096, 0.19, 0.29 and 0.38 mM L$^{-1}$
Figure 3.37
Reactive Yellow
Variation of initial rates with hydrogen peroxide concentration
\([H_2O_2] = 110\ \text{mg L}^{-1}\), \([\text{FeSO}_4] = 60\ \text{mg L}^{-1}\), pH 2, vol. 1L, stirring rate 75 rpm,
\([\text{RY}] = \text{varied 0.063, 0.12, 0.18, 0.25 and 0.31 mM L}^{-1}\)
Figure 3.38
Methylene Blue (MB)
Variation of initial rates with hydrogen peroxide concentration
\([\text{H}_2\text{O}_2] = 60 \text{ mg L}^{-1}, [\text{FeSO}_4] = 40 \text{ mg L}^{-1}, \text{pH} 2, \text{vol. 1L, stirring rate} \text{ 75 rpm,} [\text{MB}] = \text{varied 0.0125, 0.025, 0.0375, 0.05 and 0.0625 mM L}^{-1}\)
Figure 3.39  
Acid Orange (AO)  
Variation of initial rates with hydrogen peroxide concentration  
\([H_2O_2] = 60 \text{ mg L}^{-1}, [\text{FeSO}_4] = 40 \text{ mg L}^{-1}, \text{ pH 2}, \text{ vol. 1L}, \text{ stirring rate 75 rpm,} \)

\([\text{AO}] = \text{varied 0.04, 0.08, 0.12, 0.16 and 0.20 mM L}^{-1}\)
3.6.4. Reaction mechanisms

(i) Where the reaction is first order with respect to [Dye], [H₂O₂] and [FeSO₄]

If we assume that the reaction comprises of two equations. Equation (1) represents the fast step and equation (2) represents the slower one.

\[
\begin{align*}
\text{Rate} &= k_1 k_2 [A][B][0] \\
\text{Rate} &= K[A][B][D]
\end{align*}
\]

Where [A] represents concentration of ferrous sulphate
[B] represents concentration of hydrogen peroxide
[C] represents concentration of hydroxyl radical formed as a result of the reaction between [A] and [B]
[D] represents dye concentration
\(k_1\) and \(k_2\) represents rate constants
K represents equilibrium constant.
(ii) Where there is complex formation both with respect to \([H_2O_2]\) and \([FeSO_4]\) but first order with respect to dye

\[
\begin{align*}
  & k_1 \\
  & A + B \rightarrow C \quad (1) \\
  & K \\
  & C + D \rightarrow CD \quad (2) \\
  & k_2 \\
  & CD \rightarrow \text{products} \quad (3)
\end{align*}
\]

\[
\text{Rate} = k[C]_e = kK[C]_e[D]_e
\]

\[
K = \frac{[CD]_e}{[C]_e[D]_e}
\]

\[
[D]_t = [D]_e + K[C]_e[D]_e
\]

\[
[D]_e = \frac{[D]_t}{1 + K[C]_e}
\]

\[
\text{Rate} = kK[C]_e[D]_t \quad \left\{1 + K[C]_e\right\}
\]

\[
\text{Rate} = kK k_1 [A][B][D] \quad 1 + k_1 K[A][B]
\]

At constant D and B

\[
\text{Rate} = \text{const.} [A] \quad 1 + \text{const.} [A]
\]

At constant D and A

\[
\text{Rate} = \text{const.} [B] \quad 1 + \text{const.} [B]
\]

\[\text{Where} \ [A] \text{ represents concentration of ferrous sulphate} \]
\[\text{[B] represents concentration of hydrogen peroxide} \]
\[\text{[C] represents concentration of hydroxyl radical formed as a result of the reaction between [A] and [B]} \]
\[\text{[D] represents dye concentration} \]
\[\text{[E]}_e \text{ represents an intermediate complex} \]
\[k_1 \text{ and } k_2 \text{ represents rate constants} \]
\[K \text{ represents equilibrium constant.} \]
(iii) Where there is complex formation with respect to \([H_2O_2]\) and first order with respect to \([FeSO_4]\) and dye

\[
\begin{align*}
A + B & \rightarrow C & (1) \\
K & \\
D + B & \leftrightarrow E & (2) \\
k & \\
E + C & \rightarrow \text{products} & (3)
\end{align*}
\]

\[
\begin{align*}
[C] &= k_1[A][B] \\
[E]_e &= K[D]_e[B]_e \\
\text{Rate} &= k[E]_e[C]_e \\
\text{Rate} &= kK[D]_e[B]_e[C] \\
[D]_i &= [D]_e + [E]_e \\
&= [D]_e + K[D]_e[B]_e \\
&= [D]_e(1 + K[B]_e) \\
[D]_e &= [D]_i \\
&= [D]_i \\
&= [D]_i(1 + K[B]_e) \\
\text{If } [B] \text{ is large, } [B]_e &= [B]_i \\
[D]_e &= [D]_i \\
&= [D]_i(1 + K[B]_i) \\
\text{Rate} &= kK k_1[D]_i[B]_i[C] \\
&= kK k_1[D]_i[B]_i[C] \\
&= [D]_i(1 + K[B]_i) 
\end{align*}
\]

Where \([A]\) represents concentration of ferrous sulphate
\([B]\) represents concentration of hydrogen peroxide
\([C]\) represents concentration of hydroxyl radical formed as a result of the reaction between \([A]\) and \([B]\)
\([D]\) represents dye concentration
\([E]_e\) represents an intermediate complex
\(k_1\) and \(k_2\) represents rate constants
\(K\) represents equilibrium constant.
3.6.5. Conclusions

1. Findings reported on kinetic profile during oxidation of dyes with Fenton’s reagent are in good agreement with observations of earlier workers on other organic substrates. This work goes a step further. Critical concentration of the dye at which the reaction mechanism undergoes transition has been identified. Fenton oxidation of all the dyes studied occurred in two distinct stages:

(i) An initial fast step where the percentage decolorization can range from less than 10% to 100% depending on the concentration of ferrous sulphate and hydrogen peroxide chosen for the experiment. This part of the reaction was too rapid to be effectively monitored.

(ii) A slow step, which begins from the point of initial dip and then takes the reaction to completion at a rate that is slower and can be controlled by a judicious choice of ferrous sulphate and hydrogen peroxide concentrations. This slow step can be monitored.

2. The oxidation of Reactive Yellow showed that the initial rates for decolorization increased linearly with an increase in hydrogen peroxide concentration over the range studied. Since the initial rates increased linearly with an intercept at origin, the oxidation reaction was considered to follow first order kinetics. In the case of Direct Catachine Brown the initial rates although increased linearly at lower
hydrogen peroxide concentrations, beyond an optimum concentration resulted in a decrease in the initial rates, as excessive hydrogen peroxide concentrations results in a decrease in the oxidation rate due to scavenging of hydroxyl radicals. However up to the point of increase the initial rates increased linearly with an intercept at the origin indicating that the reaction is first order with respect to hydrogen peroxide. In the case of Acid Orange and Methylene Blue the variation in initial rates fitted a first order polynomial representing a curve, which in turn gave a linear fit for the double reciprocal plot with a positive intercept. These observations confirm that of a complexation step is involved in the Fenton oxidation of Acid Orange and Methylene Blue.

3. Fenton oxidation of all dyes except Methylene Blue showed that the initial rates increased linearly with an in the ferrous sulphate concentration. This increase was observed only up to an optimum concentration beyond which further increase resulted in a decrease in the initial rates. Variation of initial rates with Ferrous sulphate concentration resulted in a linear plot passing through the origin indicating that the reaction is first order with respect to ferrous sulphate. However in the case of Methylene Blue the initial rates when plotted against ferrous sulphate concentrations fitted well into a second order polynomial expression representing a curve. This indicates that there could be a complexation step involved with
respect to ferrous sulphate. A linear plot with positive intercept in the double reciprocal plot of initial rates against hydrogen peroxide concentration confirmed complexation.

4. Fenton oxidation is first order with respect to the dye concentration irrespective of the dye class, as a linear increase in initial rates with increase in dye concentration was observed. However a few exceptions have been noticed. In the case of Reactive Yellow and Methylene Blue when the initial rates increased with increase in the dye concentration over the entire concentration range chosen for the experiments, in the case of Direct Catachine Brown and Acid Orange although a linear increase in initial rates was observed at low dye concentrations, higher concentrations were found to inhibit the activity of hydroxyl radicals and thereby resulting in a decrease in the initial rates.