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Degradation of azo dyes in aqueous solution by $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{Fe}$

Sangeeta Dhulashia
Florida International University

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

**DEGRADATION OF AZO DYES IN AQUEOUS SOLUTION BY
 $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ AND $\text{H}_2\text{O}_2/\text{Fe}$**

**A thesis submitted in partial satisfaction of the
requirements for the degree of**

MASTER OF SCIENCE

IN

ENVIRONMENTAL ENGINEERING

by

Sangeeta Dhulashia

1998

**To: Dean Gordon R. Hopkins
College of Engineering**

This thesis, written by Sangeeta Yashik Dhulashia, and entitled Degradation of Azo dyes in Aqueous Solutions by $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{Fe}$, having been approved in respect to style and intellectual content, is referred to you for your judgement.

We have read this thesis and recommend that it be approved:

Hector R. Fuentes

Wolfgang F. Rogge

Steven C. McCutcheon

Walter Z. Tang, Major Professor

Date of Defense: March 26, 1998

The thesis of Sangeeta Y. Dhulashia is approved.

**Dean Gordon R. Hopkins
College of Engineering**

**Dr. Richard L. Campbell
Dean of Graduate Studies**

Florida International University, 1998

DEDICATION

To my loving husband Yashik, whose consistent support, understanding and help made this work possible, and to my wonderful parents, Ramnik and Kamala, for their love, inspiration and immense faith in my capabilities.

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ABSTRACT OF THE THESIS

DEGRADATION OF AZO DYES IN AQUEOUS SOLUTION BY $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ AND $\text{H}_2\text{O}_2/\text{Fe}$

by

Sangeeta Dhulashia

Florida International University, 1998

Miami, Florida

Professor Walter Z. Tang, Major Professor

An advanced oxidation process, which uses Fenton's Reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), is studied in the destruction of three different classes of azo dyes. The optimal pH and stoichiometry for H_2O_2 and Fe^{2+} in the oxidation of the azo dyes were investigated; an experimental optimal ratio was also compared to a theoretical optimal ratio of H_2O_2 to Fe^{2+} . The optimal oxidation of monoazo and disazo dyes is at pH 3 and pH 4, respectively. The optimal ratio for monoazo and disazo dyes ranged from 1 to 10. The experimentally determined optimal ratios are in excellent agreement with theoretically predicted optimal H_2O_2 to Fe^{2+} ratio of 11. Complexation was observed in oxidation of trisazo dye Direct Blue 71. A lower optimal ratio of H_2O_2 to Fe^{2+} for trisazo dye than ratios required for mono and disazo dyes, is due to a larger amount of Fe^{2+} associated with Fe complexation of chromophore.

Due to a relatively large amount of sludge, which is generated by the common Fenton's Reagent, this study was expanded to characterize the performance of a novel

H₂O₂ and Fe powder system. This system decolorizes the same dyes from Fenton's treatment. Kinetics and mechanism of the reaction were studied. The kinetics followed pseudo-first order and Fenton's Reagent was the major mechanism. The degradation rate depends upon both numbers of azo bonds and auxiliary groups. The rate of decolorization of the dye decreases as the pH level increases. Hydrogen peroxide and iron powder system resulted in higher color removal, at lower sludge production, for selected dyes at lower pH than the Fenton's Reagent treatment option.

Keywords: Azo dyes, Fenton's Reagent, Hydrogen Peroxide, Zero Valent Iron, Hydroxyl Radical, Advanced Oxidation Process, Oxidation, and Optimal Ratio of H₂O₂/Fe²⁺.

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DEGRADATION OF AZO DYES IN AQUEOUS SOLUTION BY $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ AND $\text{H}_2\text{O}_2/\text{Fe}$

GENERAL INTRODUCTION

Dyeing and finishing are the major sources of pollution in the textile industry. In a typical dyeing and finishing mill, about 100 L of water are consumed for every ton of textiles processed (Internal Technical Report, 1994). In the dyeing process, the reactions necessary to fix dye onto textiles do not always go to completion as designed. Ten to 15% of the dye is lost in the dyeing process effluent (Vaidya and Datye, 1982). Therefore, the removal of color from non-biodegradable dyes in wastewater is of significant concern to the textile industry. This effluent is either discharged directly to a watercourse or to a sewer, which is then partially treated by municipal sewage treatment plants. The other major pollutants in textile wastewater include high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, acidity and basicity, and other soluble substances. If a textile wastewater is not properly treated, dyes and other process chemicals undergo chemical as well as biological changes by consuming dissolved oxygen in the stream, which impact the balanced ecosystem necessary for aquatic life. Based on the chemical structure of the chromophoric group, synthetic dyes are classified as azo dyes, anthraquinone dyes, triarylmethane dyes, etc. (Allen, 1971).

Azo dyes are used in greater quantity than any other (Zollinger, 1987). Azo bonds have the general formula of $-\text{N}=\text{N}-$ which is known as an azo group. Dyes are classified

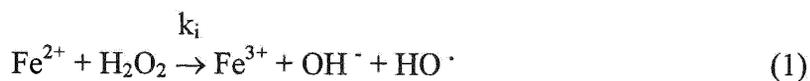
as monoazo if there is one azo group, disazo if there are two azo groups and trisazo if there are three azo groups present. Several mono-substituted azo dyes, including 4-phenylazoaniline and N-methyl- and N, N-dimethyl-4-phenylazoanilines, are mutagenic as well as carcinogenic (McCann and Ames, 1975). Carcinogenicity of an azo dye may be due to the dye itself or to aryl amine derivatives generated during the reductive biotransformation of the aryl linkage. In mammals, azo dyes are reduced to the aryl amines by cytochrome P-450 (Fujita and Peisach, 1977) and by a flavin dependent cytosolic reductase (Huang et al., 1979). Aryl amines in mammals can be oxidized to corresponding N-hydroxy derivatives, which are subsequently transformed to reactive electrophiles capable of forming covalent linkages with DNA (Tarpley et al., 1980). Because of the carcinogenicity and mutagenicity, some European countries have banned azo dyes (Perenich, 1996).

Conventional treatment technologies used to decolorize textile wastewater include adsorption by activated carbon (Porter, 1972; McKay, 1980), electrochemical treatment (Lin and Peng, 1994), biological treatment, and ozonation (Sinder and Porter, 1977). However, activated carbon adsorption does not destroy the dye molecules. Ozonation has high operation and maintenance cost. Synthetic dyes often containing substitutions such as azo, nitro, and sulfo groups are resistant to aerobic degradation by bacteria. The strong electron-withdrawing character of the azo group stabilizes these aromatic pollutants against conversions by oxygenases (Flores et al., 1997). Several treatment alternatives such as ultrafiltration, electrochemical treatment, and membrane filtration are currently

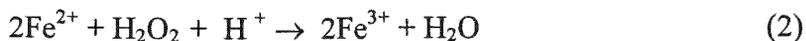
under investigation so that effective and economic treatment technologies can be developed for the textile wastewater treatment.

One of the research areas includes advanced oxidation processes. Several advanced oxidation processes seem to be very effective in destruction of azo dyes. Hydrogen Peroxide and Fe^{2+} (Kuo, 1992), UV/ H_2O_2 , and TiO_2/UV (Tang et al., 1995; Cunningham et al., 1992; and Tang et al., 1996) have been used to destroy dye in textile wastewater at a laboratory scale. Also, Fenton's reagent, a mixture of hydrogen peroxide and ferrous sulfate has been used to (Kuo, 1992; Lin and Peng, 1995) decolorize and reduce the COD content of the textile wastewater's that contain various types of reactive, direct, basic, acid, and disperse dyes. Fenton's reagent is relatively economical, and easy to apply, compared to other oxidation processes (Venkatadri et al., 1993). In fact, Fenton's reagent is effective in treating several different types of industrial wastewater (Barbeni et al., 1987; Watts et al., 1990; Sedlak and Andren, 1991; Porter and Roth, 1993; Venkatadri and Peters, 1993).

Fenton's reagent is a combination of any ferrous salt and H_2O_2 solutions, described as follows:



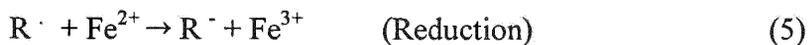
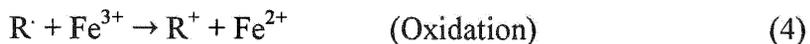
where k_i is the initiation rate constant of hydroxyl radical generation that has a value of $51 \text{ M}^{-1} \text{ s}^{-1}$. Walling (1975) simplified the overall Fenton chemistry by taking the dissociation of water into consideration:



This equation shows that an acidic environment is required in order to produce a maximum amount of hydroxyl radicals (Tang and Huang, 1996). In the presence of organic substrates such as dye molecules RH, hydroxyl radicals, and ferrous ions at low pH can produce organic free radical R[·],



The organic free radical may then be oxidized by Fe³⁺, reduced by Fe²⁺, or dimerized (Kuo, 1992), according to the following reactions:



Another competitive reaction is that excessive Fe²⁺ can scavenge hydroxyl radicals through the following reaction:



Where k_{t2} has a value of $3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, in addition to this, excessive H₂O₂ also consumes hydroxyl radicals as shown by:



Where k_{13} has a value of $2.7 * 10^7 \text{ M}^{-1}\text{s}^{-1}$. The reactions in equations 3, 7 and 8 demonstrate that there is a competition for hydroxyl radical by Fe^{2+} , H_2O_2 and the azo dye, which leads to the nonproductive decomposition of hydrogen peroxide and limits the production of hydroxylated organic compounds. Therefore, it is necessary to establish a stoichiometric relationship among H_2O_2 , Fe^{2+} and the dye to maximize the degradation of azo dyes efficiently.

This thesis is presented in two main parts. Part I investigates several aspects of the conventional Fenton's treatment. These aspects include: (1) The stoichiometric requirements of Fenton's reagent in degrading different classes of azo dyes, and (2) The effect of pH on the degradation rate of each class of dyes. It also compares the theoretical optimal ratio to experimental optimal ratios. The eleven azo dyes studied in this thesis were the same group selected in previous studies that focused on the TiO_2/UV process; in addition, they were also easily available.

Part II expands on the information of Part I. Due to a relatively large amount of sludge, which is generated by the common Fenton's Reagent, this study was extended to characterize the performance of a novel H_2O_2 and Fe powder system. This system decolorizes the same dyes from Fenton's treatment. Kinetics and mechanism of the reaction is studied in Part II. Effect of the number of azo bonds, auxiliary functional

groups, and pH on degradation kinetics by hydrogen peroxide and zerovalent iron powder is also investigated. Based on the used experimental approaches, an effort was made to compare the hydrogen peroxide and iron powder treatment process with Fenton's treatment process.

PART I. DEGRADATION OF AZO DYES IN AQUEOUS SOLUTION BY $\text{H}_2\text{O}_2/\text{Fe}^{2+}$

1 INTRODUCTION

Hydrogen Peroxide (H_2O_2) catalyzed by Fe^{2+} , is called Fenton's Reagent. The process was named after Professor Fenton because he was the first person who reported a brief description of powerful oxidizing properties of a mixture of hydrogen peroxide and ferrous salts and published this unique reaction (1881). Fenton tested this mixture to oxidize different organic acids including formic, glycollic, lactic, tartronic, malic, saccharic, mucic, glyceric, benzoic, picric, dihydroxytartaric, dihydroxymaleic, and acetylenedicarboxylic (Fenton 1900). In the absence of ferrous salt, the degradation of hydrogen peroxide proceeded at lower rates with little or no oxidation of the organic acids (Fenton 1899, 1900). Cross and Bevan (1898), Morrell and Crofts (1899), Bernieck (1899), Fenton (1900), and Bertelan (1920), reported enhanced degradation of hydrogen peroxide by ferrous salts. Able (1920) published the first proposed kinetic mechanism followed by the work of Bray and Livingston (1923). Early studies were conducted by Martinon (1885), and Goldhammer (1927), to see the effect of Fenton's Reagent on phenols. Manchot and Lehmann (1928), carried out some experiments and found that for each equivalent of Fe^{2+} , three equivalents of H_2O_2 were decomposed. They also noted that in concentrated hydrogen peroxide solutions, each Fe^{2+} decomposed twenty-four equivalents of hydrogen peroxide.

Haber and Weiss (1931), were the first who proposed that free radicals existed as intermediates during the chemical reactions in a solution. In 1932, Haber and Weiss published a paper proposing that Fenton chemistry was the result of chain reactions dependent on concentration of the reactants. The paper disproved the original theory of Fenton's reaction, which was explained through the interaction of six-valent iron-oxygen compounds with hydrogen peroxide. In 1934, Haber and Weiss proposed that Fenton's Reagent was actually the result of a chain mechanism and free radical reaction resulting in highly reactive intermediate compounds. The concentration of free hydroxyl radical was determined to be directly proportional to the concentration of hydrogen peroxide. It was also noted by them that breaking of chain length was increased at lower pH so that the propagation cycle was extended before termination.

Baxendale et al. (1946) concluded that in an oxygen-free environment, Fenton's Reagent initiated very rapid polymerization of methyl acrylate, methacrylic acid, methyl methacrylate, acrylonitrile, and styrene. The reaction was a function of formation of hydroxyl radicals. In the presence of oxygen, no polymerization occurred. In 1949, Barb et al., concluded an extensive investigation of Fenton's Reagent chemistry. When $[H_2O_2]/[Fe^{2+}]$ ratios are low, the reaction rate is the second order and stoichiometry is $2[Fe^{2+}] \cong [H_2O_2]$, but in the presence of polymerizable vinyl compound the reaction remained second order and the stoichiometry changed to $[Fe^{2+}] \cong [H_2O_2]$. Thus, they concluded that the polymerization of vinyl compound results in a polymer with terminal hydroxyl groups. They also suggested inhibition effect of hydroxyl radical due to higher concentration of hydrogen peroxide. To explain this mechanism it was proposed that

hydroxyl radicals react with hydrogen peroxide to form hydrogen dioxide. This reaction takes place over the ferrous iron and hydrogen peroxide reaction and significantly decreases hydroxyl radical formation. Hydrogen dioxide was not a strong oxidizing agent to break the bonds of vinyl compound or oxidize other organic substances.

Merz and Water (1949) showed that oxidation of organic compounds by Fenton's Reagent could proceed by chain as well as non-chain mechanisms, which was later confirmed by Ingles (1972). Gabriel and Stein (1951) studied the effect of Fenton's Reagent on phenol with specific interest on ferric ions. They confirmed that once ferric ions were produced, the ferric-ferric system was catalytic in nature, which accounted for relatively constant concentration of ferrous ion in solutions. It was also proposed by them that complexation inhibited aromatic oxidation. In the late seventies, there were two different theories proposed, free radical mechanism by Walling (1977) and complex formation by Kremer (1977). It was first established by Walling that Fenton's oxidation takes place by free radical mechanism, while Kremer discovered that complexation also exists. To resolve these conflicts Walling (1985) performed some experiments and proved that only free radical mechanism is dominant. Later work of Kremer (1985) suggested that one of the assumptions by Walling was significant and thus concluded that both mechanisms occur simultaneously.

During the late seventies, a simultaneous effort was made to see the application of Fenton's Reagent in the field of environment. Various contaminants were studied in the laboratory and several optimum conditions examined. Practical applications of Fenton's

Reagent to treat contaminants are also examined by pilot plants and continuous treatment systems in textile wastewater's, etc. From the early nineties, Bigda (1994) has made an effort to design a reactor for Fenton's Reagent to treat various contaminants. In order to design a reactor specific to a contaminant, the study of optimal stoichiometric ratios of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ for a contaminant needs to be studied (Bigda, 1994).

Part I of this thesis investigates several important fundamental factors. These include: (1) The stoichiometric requirements of Fenton's Reagent in degrading different classes of azo dyes, and (2) The effect of pH on the degradation rate of each class of dyes. It also compares the theoretical optimal ratio to experimental optimal ratios.

2 FUNDAMENTAL THEORY

2.1 Hydrogen Peroxide

The compound hydrogen peroxide, H_2O_2 , was first identified by Thenard in 1818 (Schumb et al., 1955). Commercially available since the middle of 19th century, large-scale production and industrial use has increased rapidly since 1925, when electrolytic processes for production were introduced and applications in industrial bleaching became increasingly important. Commercially, H_2O_2 is handled as an aqueous solution with a wide range of concentration. The important properties and uses of hydrogen peroxide result from the covalent oxygen-oxygen bond. Hydrogen peroxide is a liquid at normal

temperatures; melting point, -0.43°C ; boiling point at 760 mm, 15.2°C . Most constants are related to aqueous solutions used commercially instead of the pure compound.

2.1.1 Molecular Structure

The four atoms in the hydrogen peroxide molecule are structurally joined by simple covalent bonds, H-O-O-H, in a non-polar structure. The structure can be defined by four parameters: the O-O distance, the O-H distance the O-O-H angle, and the angle between two planes, each of which is defined by the two oxygen atoms and one of the hydrogen atoms. The best values in the solid state are O-O distance: $1.453 \pm 0.007 \text{ \AA}$; O-H distance, $0.988 \pm 0.005 \text{ \AA}$; O-O-H angle $102.7 \pm 0.3 \text{ \AA}$; and dihedral angle between the O-O-H planes: $90.2 \pm 0.6 \text{ \AA}$. The dihedral angle appears sensitive to surrounding and thus may be different in the vapor phase or in other crystals containing H_2O_2 (Kirk Othmer, 1979).

2.1.2 Speciation of Hydrogen Peroxide

The coordinates for the solid-liquid phase diagram recommended from a critical study are listed in Table 1.

Table 1. Recommended Coordinates of Solid-Liquid Phase Diagram for the Hydrogen Peroxide Water System (Kirk Othmer, 1979)

H ₂ O ₂ concentration, wt %	Freezing pt, °C	H ₂ O ₂ concentration, wt %	Freezing pt, °C
0	0	50	-52.2
10	-6.4	60	-55.5
20	-14.6	61	-56.1 ^a
30	-25.7	65	-49
35	33	70	-40.3
40	41.4	80	-24.8
45	51.7	90	-11.5
45.2	52.2 ^a	100	-0.43
48.6	52 ^b		

^a Eutectic

^b Compound, H₂O₂·2H₂O

The eutectics exist at 45.2 and 61.2 wt % H₂O₂, and that the compound H₂O₂·2H₂O (48.6 wt % H₂O₂) exists in the solid state. Solid solutions are not formed in this system although it is extremely difficult to obtain water free of solid H₂O₂. The recommended value for the heat of fusion of H₂O₂ is 87.84 cal/g. For liquid-vapor phase relationship for aqueous hydrogen peroxide, partial pressures of the vapors over the liquid are lower than the calculated value for ideal solutions but there are no azeotropes. Table 2 shows atmospheric boiling points and related liquid and vapor compositions interpolated.

Table 2. Atmospheric Boiling Points of Hydrogen Peroxide Solutions

(Kirk-Othmer, 1979).

Liquid composition, wt % H ₂ O ₂	Boiling point, ° C	Vapor composition, Wt % H ₂ O ₂
0	100	0
10	101.7	0.9
20	103.6	2.1
30	106.2	4.2
35	107.9	5.8
40	109.6	7.6
50	113.8	13.0
60	119	20.8
70	125.5	33.4
80	132.9	51.5
90	141.3	75.0
100	150.2	100

The heat of vaporization of aqueous hydrogen peroxide at 25° C and 60° C is listed in table 3.

Table 3. Total Heat of Vaporization of Aqueous H₂O₂ (Kirk Othmer, 1979).

H ₂ O ₂ Concentration, wt %	Heat of vaporization cal/g solution	
	25° C	60° C
0	582.1	563.2
20	543.5	526.4
40	503.1	487.4
60	460.4	446.0
80	414.1	401.3
100	362.7	351.3

2.1.3 Thermodynamics of Hydrogen Peroxide

The values for the number of thermodynamic functions of H₂O₂ can be obtained from the handbook of chemical engineering data. However, some of these values are based on the interpretation of infrared spectra, some modifications should be made based on the latest absorption spectra data. The average heat capacity from 25 to 60° C for 100 % H₂O₂ is 0.628 cal/(g) (°C). The heat of mixing of H₂O₂ and (100%) water ranges from -590 cal/mole H₂O₂ at 0° C to -1110 cal/mole H₂O₂ at 75° C. The heat of formation H₂O₂ from the reaction



at 25°C has been calculated at -32.52 kcal/mole (K&M). The free energy of formation of anhydrous H₂O₂ liquid at 25°C is calculated as -28.78 kcal/mole. The heat of decomposition of pure liquid H₂O₂ to water and oxygen at 25°C is -23.44 kcal/mole.

2.1.4 Reaction Mechanism

Depending on the usage, hydrogen peroxide is a versatile and effective oxidizing agent as a source of active oxygen compared to molecular oxygen resulting from simple decomposition. The reactions can be simplified to five general types:

1) Decomposition



2) Molecular Addition



3) Substitution



or



4) H_2O_2 as a reducing agent



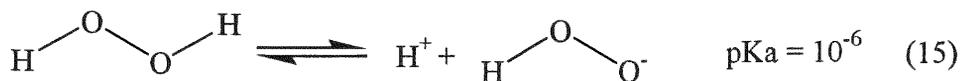
5) H_2O_2 as an oxidizing agent



Undergoing these reactions, hydrogen peroxide may react as a molecule, be ionized, or be dissociated into free radicals. The mechanism is very complex in many cases and may depend on the type of catalyst and reaction conditions.

2.1.4.1 Ionization

Hydrogen peroxide exhibits a weakly acidic character, having a dissociation constant of about 1.5×10^{-12} . Thus, pure aqueous solutions of hydrogen peroxide have pH values below 7. The activation hydrogen peroxide might be natural as it exhibits weakly acidic character in aqueous solutions.



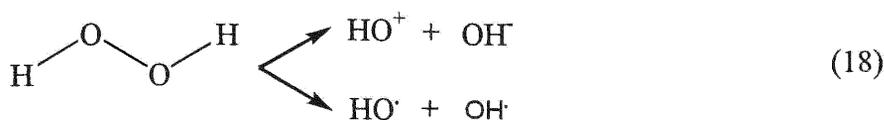
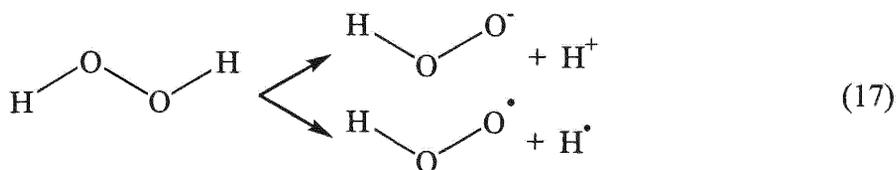
Depending on the pH of the medium, chemist will be able to generate in huge concentrations, ionic species having either nucleophilic character (pH>7) or electrophilic character (pH <7). In alkaline medium, it reacts with hydroxyl anions to give perhydroxyl anions HOO⁻ according to the following equilibrium equation.



This equilibrium is shifted to the right when the basicity of the medium increases. This emphasizes the nucleophilic character of the peroxidic linkage O-O, due to formation of HOO⁻ anion. This perhydroxyl anion is considered as a supernucleophile as its reactivity is about two hundred times higher than that of HO⁻ anion.

2.1.4.2 Free Radical Formation

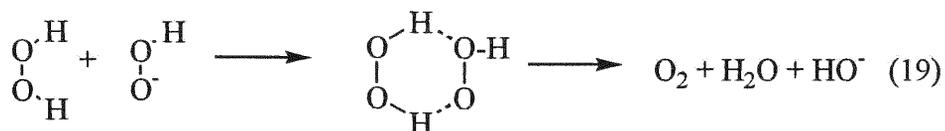
Hydrogen peroxide can dissociate into free radicals by breaking either an H-O bond or the O-O bond.



Depending on the fact whether the electron pair of the broken bond is shared or not by the two new entities, the reaction sequence will involve either an ionic or a free radical pathway as shown in equation 17 and 18. The heat for reaction in equation 17 is 88 kcal/mole and for reaction in equation 18 is about 50 kcal/mole. The later reaction predominates in uncatalyzed vapor-phase decomposition and photochemically initiated reactions.

2.1.4.3 Decomposition.

The reaction shown by equation 1 is very important because the stoichiometry must be controlled at all times when hydrogen peroxide is being manufactured, stored, shipped and used. In a few application cases, it is necessary to decompose the peroxide under controlled conditions but in rest cases it is necessary to minimize decomposition as the release of oxygen, and heat causes safety problems and results in poor efficiency of utilization. In the absence of any reagent, the HOO^- anion is able to oxidize another molecule of hydrogen peroxide, by an unstable transition complex that decomposes with release of molecular oxygen.



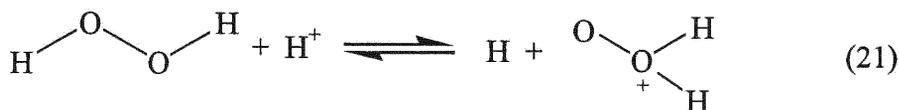
This decomposition reaction can be completely over ridden in the presence of an electrophilic substrate. One of the main industrial applications is the synthesis of aliphatic amine-oxides, which are used in manufacturing of detergents.

Aminohydroperoxides and aminoperoxides can also be formed very easily at room temperature starting from ammonia, hydrogen peroxide and a carbonyl derivative.

In acidic medium, hydrogen peroxide is more stable as equilibrium is completely shifted to the left.



Due to solvation of protons by hydrogen peroxide oxonium structure is observed as in equation 21, this structure changes the nature of the peroxide bond and thus increases its stability.



When the reaction medium contains a substrate, which is more powerful nucleophile such as and acid, alcohol, ketone or oxometal group protonation occurs on the latter and a new electrophilic intermediate is generated and reacts with hydrogen peroxide. This is a very important pathway where peroxidic linkage O-O is conserved and transferred into a new disymmetric molecule, which is, called “peroxycompound”. These reactions are carried out on large scale in industry to manufacture performic acid or peracetic acid leading to various kinds of epoxides such as soybean oil, linseed oil etc.

2.1.4.4 H₂O₂ as a Reducing Agent.

Hydrogen peroxide will reduce strong oxidizing agents as chlorine, hypochlorites, potassium permanganate and ceric sulfate



2.1.4.5 H₂O₂ as an Oxidizing Agent

Hydrogen peroxide is a strong oxidant with standard oxidation potential of 1.8 V and 0.87 V at pH 0 and 14 respectively. Hydrogen peroxide oxidizes large number of organic and inorganic compounds. However the mechanism varies greatly with the reductive substrate, the catalyst used and other reaction conditions. Compounds oxidized range from iodide ions to organic color bodies of unknown structure in cellulose fibers. Numerous applications of hydrogen peroxide in removal of organic contaminants including prevention of odors of sulfides from wastewater collection and treatment units, removal of sulfites, hypochlorites, nitrites, cyanides, and chlorine are available. It is also useful to treat gaseous pollutants such as sulfur oxides and nitrogen oxides by conversion to corresponding acids.

2.2 Fenton's Reagent

2.2.1 Reaction Mechanism

2.2.1.1 Fenton's Kinetic Model

Fenton (1894) first studied the oxidizing capacity of ferrous salt and hydrogen peroxide. In studying the behavior of tartaric and racemic acids, a violet color in caustic alkali was observed. The color disappeared if acid was added. It was noticed that fresh external air is more active than the room air.

Fenton performed different experiments using different amounts of ferrous salt (Fe^{2+}) and hydrogen peroxides and proposed that iron has a catalytic action on this reaction, and small amount of iron is sufficient to determine oxidation of unlimited amounts of tartaric acid. In tartaric acid, he proposed that two atoms of hydrogen are removed from a molecule of acid with a result in production of dihydroxymaleic acid. The most oxidizing agent was hydrogen peroxide (others such as chlorine, potassium permanganate, atmospheric oxygen and electrolysis were also compared).

Fenton's work was extended to alcohols (1899), and organic acids (1910). While oxidizing monohydric alcohols, they failed to detect aldehyde, which was later explained by Goldschmidt and Pauncz that Fenton used an excess of hydrogen peroxide in the work. Attempts to identify the intermediates and products of several organic acids and

alcohols were made, but there was no explanation as to why the phenomenon was taking place.

2.2.1.2 Chain Reaction Mechanism by Merz and Waters (1947)

Goldschmidt and Pauncz (1933), showed that the reaction was not due to peroxides of iron and considered that the process was a chain reaction involving the same reactive intermediate as the one concerned in the catalytic decomposition.

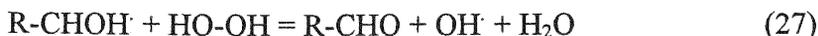


It was also showed that the ratio (alcohol oxidized/ Fe^{2+} oxidized) could be greater than unity. Baxendale, et al., (1957) showed that hydroxyl radical concerned in initiating the chain polymerization of olefins by hydrogen peroxide was identical with that which effects the rapid oxidation of glycollic acid. It was confirmed by Merz and Waters (1947), that the simple water soluble alcohols are oxidized rapidly by Fenton's Reagent, the primary alcohols oxidized to aldehydes which further oxidized at comparable rates by exactly the same mechanism. Merz and Waters (1947), proposed the mechanism of oxidation of alcohol's and aldehydes with sodium persulphate, hydrogen peroxide and excess of ferrous salt as follows:

1) Chain Starting:



2) Reaction Chain:



3) Chain ending at low substrate concentration:



4) Chain ending at high substrate (alcohol) concentration:



In 1949, Merz and Waters determined the values for ratio of rate constants k_2/k_3 that indicated which particular radical reduced hydrogen peroxide. They grouped compounds in three classes, those reacting by chain process, where only small amount of reducing agent is required, those reacting by nonchain process, where all oxidation is effected by hydroxyl radical and there is considerable loss of hydroxyl radical and those reacting negligibly with Fenton's Reagent. The rate of reaction of organic radical for chain reaction was given as follows:

$$d[\text{H}_2\text{O}_2]/d[\text{RH}] = 1 + k_2[\text{Fe}^{2+}]/k_3[\text{RH}] \quad (30)$$

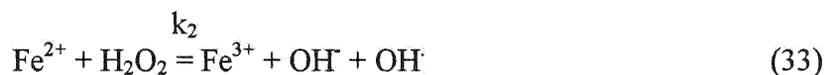
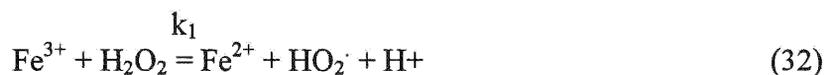
and for non chain reaction was given as follows:

$$d[\text{H}_2\text{O}_2]/d[\text{RH}] = 2 + k_2[\text{Fe}^{2+}]/k_3[\text{RH}] \quad (31)$$

They were able to determine values for the ratio of rate constants k_2/k_3 and to indicate whether a particular radical reduced hydrogen peroxide from intercept of their graphs.

2.2.1.3 Redox Formulation by Barb et al (1951)

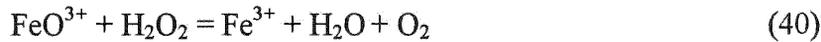
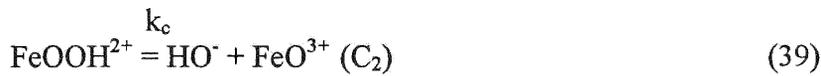
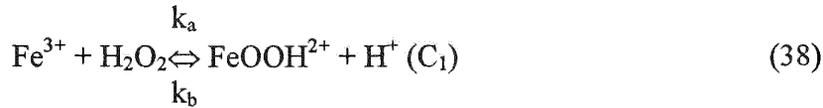
Barb et al. (1951) gave the redox formulation, which involved the reaction sequence as follows:



where k_1 and k_2 showed inverse $[\text{H}^+]$ dependence.

2.2.1.4 Complex Mechanism by Kremer and Stein (1963)

The scheme presented by Kremer and Stein (1959), was elaborated by Kremer (1963), which involved the following sequences:



where $\text{C}_1 = \text{H}^+$ and $\text{C}_2 = \text{FeO}^{3+}$ and k_a and k_d showed inverse $[\text{H}^+]$ dependence and $k_b \gg k_a \gg k_c$, so C_1 could be taken as a low concentration intermediate to a good approximation

$$[\text{C}_1] = K[\text{H}_2\text{O}_2] [\text{Fe}^{3+}], \quad K = k_a/k_b \quad (41)$$

$$[\text{Fe}^{3+}]_t = [\text{C}_2] + [\text{Fe}^{2+}] \quad (42)$$

$$-d[\text{H}_2\text{O}_2]/dt = k_c K [\text{Fe}^{3+}]_t [\text{H}_2\text{O}_2] + (k_d - k_c K) [\text{C}_2] [\text{H}_2\text{O}_2] \quad (43)$$

$$d[\text{O}_2]/dt = k_d [\text{C}_2] [\text{H}_2\text{O}_2] \quad (44)$$

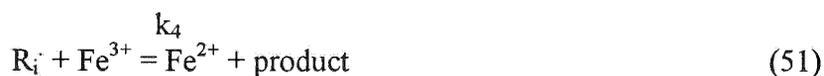
$$d[\text{C}_2]/dt = k_c K [\text{Fe}^{3+}]_t [\text{H}_2\text{O}_2] - (k_d + k_c K) [\text{C}_2] [\text{H}_2\text{O}_2] \quad (45)$$

$[\text{C}_2]$ rises continually during reaction approaching a saturation value $k_c K [\text{Fe}^{3+}]_t / (k_c K + k_d)$ and $-d[\text{H}_2\text{O}_2]/dt$ will always be greater than twice $d[\text{O}_2]/dt$. At the end of the reaction

some hydrogen peroxide will be stored as C₂, less than one-half mole of O₂ will be liberated per mole of H₂O₂ decomposed.

2.2.1.5 Walling's Modified Kinetic Model

Walling and Kato (1971), modified this reaction mechanism model proposed by Mertz and Waters (1949) as follows:



where k's in L/mol.sec from literature. The reaction conditions were chosen to minimize the competing processes as follows:



Thus the stoichiometry was given as follows:

$$R = 2ar(1-R) + b \quad (56)$$

where $R = \Delta[\text{Fe}^{2+}]/2\Delta[\text{H}_2\text{O}_2]$, $r = [\text{Fe}^{2+}]/2[\text{RH}]$, $a = k_2/\Sigma k_3$, $b = (k_{3j} + 2k_{3k})/2\Sigma k_3$

This mechanism is referred as 'Free Radical Mechanism'.

2.2.1.6 Ingles Approach

In 1972, Ingles studied Fenton's Reagent using redox titration and supported Kremer's 'complex' mechanism theory. It was concluded that when suitable complexes are formed, substrates are not oxidized by free radicals. A new mechanism involving electron transfer was proposed.

Fenton's reaction scheme was modified by Ingles when substrate was present in large amounts in the form of substrate-iron-peroxide complexes, and suggested that electron transfer occurs within this complex. All substrates were considered to compete as ligands in iron complexes and to modify the reaction characteristics of each other and of the complex. The reaction in equation 41 yields hydroxyl radical thus sequence of free radical mechanism previously proposed by Walling appears to be possible. However, the

3 LITERATURE REVIEW

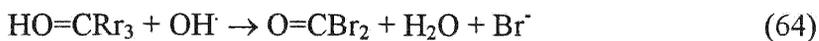
3.1 Oxidation Kinetics and Mechanisms of Aliphatic Organic Pollutants

3.1.1 Trihalomethanes (THM)

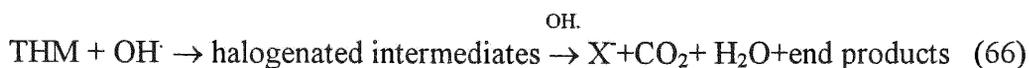
Trihalomethanes (THMs) are priority pollutants listed by EPA. They are recalcitrant in nature, thus their destruction is difficult. The most commonly encountered THMs in drinking water concerned to human health are chloroform, bromodichloromethane, dibromochloromethane and bromoform. Tang and Tassos (1997) studied oxidation kinetics and mechanisms of trihalomethanes. This study mainly focused on the above mentioned four THMs.

Effect of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ on oxidation kinetics, oxidation kinetics of THM mixtures, and effect of number of chlorine atom in a THM on its oxidation was investigated. Since bromoform is among the easiest to be oxidized of the four THMs, it was used to study the effect of Fenton's Reagent ratio on the oxidation kinetics. Bromoform concentrations used were 49.2, 98.3 and 295 $\mu\text{g/L}$. It was observed that as the ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ increased the removal increased at equilibrium, with increasing initial concentration of bromoform. This may indicate the hydroxyl radical had a preference towards organic compound resulting in proportionally less scavenging effect by $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ and MeOH. For higher $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ratio of 10:1, the amount of bromoform removal appeared to show dependence on initial bromoform concentration. As initial organic substrate

concentration increases, less scavenging of OH[·] Occurs. It was observed that at H₂O₂:Fe²⁺ ratio of 100:1 bromoform removal was only 25%, while at a ratio of 5:1, 83% removal was observed. As the ratio decreased from 5:1 to 2:1, no increase in removal of bromoform was observed. Thus, optimum ratio needs to be maintained to achieve maximum degradation. Both H₂O₂ and Fe²⁺ are able to scavenge hydroxyl radicals generated through Fenton's Reagent, if any one of them is not present in optimum dosage it has an ability to scavenge hydroxyl radicals and reduce its availability to the substrate. Oxidative destruction of THM is more difficult because THM is a saturated aliphatic and has only one C-H bond, so oxidation is solely due to hydrogen abstraction, which is more difficult than hydroxylation in reacting with unsaturated compounds. This may require a higher concentration of hydroxyl radicals, which implies that higher concentrations of Fe²⁺ and hydrogen peroxide are needed. Hydroxyl radicals are also scavenged by organic compounds as well as chloride and bromide ions, which could be shown by the following reactions:



The inhibitory effect of chloride and Bromide ions is not significant unless free ion concentration exceeds a range from 1×10^{-2} to 5×10^{-2} M. Dehalogenation is believed to be a slower process than oxidation of the parent compound, the proposed general reaction is as follows:



There were fluctuations in bromoform concentration even after triplicate runs this was explained by recombination of bromoform radical as follows:



This recombination requires either the presence of hydrogen radicals (H^\cdot) or the presence of both H^+ and e^\cdot . As the experiments were carried out in acidic conditions ($\text{pH}=3.5$), electron transfer was possible because Fenton's chemistry does not generate hydrogen radical Huang et al. (1993).

During the kinetic studies of THMs, it was found that the oxidation rates for bromoform were slower than the oxidation rates of unsaturated chlorinated aliphatic compounds such as TCE, because the hydroxylation rate constant of TCE was $10^9 \text{M}^{-1}\text{s}^{-1}$ and hydrogen abstraction of bromoform was $1.1 \times 10^8 \text{M}^{-1}\text{s}^{-1}$. Hydroxyl radicals react with aromatics and alkenes through hydroxyl addition to double bonds, while hydrogen atom abstraction of saturated organic compounds is slower than hydroxylation. No

oxidative destruction of chloroform by Fenton's Reagent was experimentally observed, because both H_2O_2 and Fe^{2+} had about one magnitude higher rate constant with respect to hydroxyl radicals than chloroform.

The effect of number of chlorine atoms in a THM molecule on its oxidation was studied by Tang and Tassos (1997). It was observed once again that oxidative destruction decreases as the number of chlorine atoms present in substrate molecule increases. It was found that the relationship between removal rate and number of chlorine atoms was linear. This phenomena was contributed by the fact that the bromine substituents were better leaving groups than chlorine substituents (Solomons, 1988). Another consideration was electronegativity and bond energy. An equation in which bond energy between atoms A and B is given as a function of electronegativity is given by Sharp (1990) as follows:

$$D_{AB} = 0.5 (D_{AA} + D_{BB}) + 23 (X_A - X_B)^2 \quad (69)$$

where D_{AB} , D_{AA} , and D_{BB} are the bond energies between A and B, A and A, and B and B respectively. Bond energy decreases as electronegativity decreases. Thus ease of dehalogenation of an organic compound is directly proportional to bond energy between carbon and halogen atoms, 95 and 67 Kcal/mol for C-Cl and C-Br bonds, respectively. Therefore, brominated compounds were more easily oxidized than those containing proportionately more chlorine (Tang, and Tassos, 1997).

3.1.2 Hydroxymethanesulfonic acid

Hydroxymethanesulfonic acid (HMSA) is a complex formed from formaldehyde and S(IV) in solution, it has a high resistance to oxidation, such as oxidation towards hydrogen peroxide and oxygen as well as ferric ions and oxygen. It was found in atmospheric liquids, i.e., rain and snow. Martin et al. (1989), first studied oxidation of HMSA. It was proposed by Graedel et al. (1985) that Fenton's type reactions are possible in atmospheric liquid water.

Martin et al. (1989) studied the oxidation of HMSA by Fenton's Reagent to look at the decomposition of hydrogen peroxide, decomposition of HMSA, estimation of absolute rate of reaction with hydroxyl radical. In the laboratory experiments, it was shown that decomposition of hydrogen peroxide was the first order processes and was measured by oxygen evolution. The decomposition of hydrogen peroxide can be kinetically described as follows:

$$-d(\text{H}_2\text{O}_2)/dt = k (\text{Fe}^{2+}) (\text{H}_2\text{O}_2) \quad (70)$$

where k was $0.044 \text{ M}^{-1} \text{ s}^{-1}$ at pH 2 and temperature 25°C .

The actual oxidation rate by free radicals was established by subtracting the rate of formation of SO_4^{-2} (from decomposition of HMSA) from the observed Fenton's rate. The rate of decomposition of HMSA was observed to be the first order and the shape of

the curve suggested that doubly ionized HMSA decomposed more readily than singly ionized HMSA. The rate levels off until second ionization is complete and this would occur at high pH. Similar experiment was performed for acetaldehyde-bisulfite complex HESA and it was seen that acetaldehyde complex, HESA, should not be as effective as HMSA at protecting S(IV) from oxidation. Fenton's Reagent studies were carried out at different pH of 1, 2, 3 and 4. Results showed that the oxidation was a first order process with respect to different initial Fe^{2+} concentration and different pH at 10^{-1}M H_2O_2 and 10^{-2} M HMSA. At higher concentrations of iron ion, there was a slight fall off that was attributed to less hydrogen peroxide and thus less hydroxyl radicals in the system. Similar experiments were carried out at different initial hydrogen peroxide concentrations and the oxidation was seen to be of first order, but at larger concentrations it deviated from first order due to lesser amount of Fe^{2+} . With the pH studies, it was observed that maximum oxidation rate occurred at pH 3.5.

The data from pH 1 to 3 were approximated by an empirical rate law as follows:

$$-d(\text{HMSA})/(\text{HMSA}) dt = k (\text{Fe}^{2+}) (\text{H}^+)^{-1} (\text{H}_2\text{O}_2)^{2/3} \quad (71)$$

with $k=1.4 \pm 0.2 \times 10^{-3} (\text{l/mol})^{2/3} \text{ s}^{-1}$, thus if assumed that 10^{-5}M H_2O_2 and 10^{-6} M Fe are present at pH 3, the oxidation rate was $2.3 \times 10^{-4} \% \text{ h}^{-1}$ (very low).

Oxidation of HMSA was studied relative to pinacol to estimate absolute rate of oxidation of HMSA with OH radicals in solution. Pinacol oxidizes to acetone in

Fenton's oxidation. The rate of reaction of OH radicals with pinacol ($k=3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) and acetone ($k=4.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) were reported by Anbar and Neta (1967). Oxidation rates of pinacol (10^{-2}M), pinacol-HMSA (10^{-2} M each) and HMSA alone, with $\text{Fe}^{2+} = 10^{-4} \text{ M}$, $\text{H}_2\text{O}_2 = 0.1 \text{ M}$ and pH of 2 was studied. Oxidation rates for each molecule were different in separated and mixed reactions as steady state concentration of free radicals depends on chemistry of organic substrates in solution. Thus, the work was concluded on basis of the assumption that HMSA is more reactive than pinacol by factor of 3.9 ± 0.8 . Thus, if absolute rate of reaction of pinacol with OH radicals was taken as $3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ then:



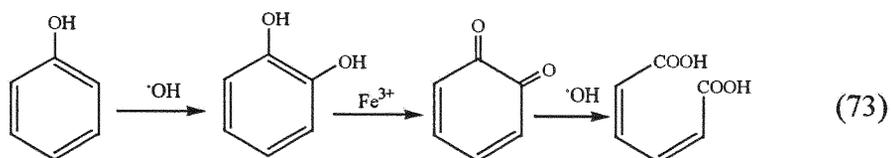
and $k = 1.25 \pm 0.25 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. This rate constant suggested that HMSA may be consumed fairly rapidly in tropospheric clouds as OH from other sources should be abundant to give a large reaction rate.

3.2 Oxidation Kinetics and Mechanism of Aromatic Organic Pollutants

3.2.1 Phenolic Waste

Phenolic wastes are one of the most prevalent forms of chemical pollutants in industry. The major sources of phenolic waste are insulation, fiberglass manufacturing, petroleum refineries, textile mills, steel making, plywood, hardboard, organic products

manufacture, paint stripping, and wood preservatives. Eisenhauer (1964) first studied the oxidation of phenolic wastes with Fenton's Reagent. It has been demonstrated that the oxidation phenol involves the intermediate formation of catechol and hydroquinone which are formed by ferric ion formed to corresponding quinones (Merz et al., 1949; Stein et al., 1951 and Wieland et al., 1928). Catechol can be oxidized in high yield to muconic acid by hydrogen peroxide and ferrous salt (Pospisil, 1957). Thus Eisenhauer showed that phenol oxidation proceeds according to the following equation:



Preliminary experiments were carried out with pure phenol solutions in distilled water at a concentration of 50 ppm. Experiments were carried out at pH 3 and at a temperature of 10 °C. It has been demonstrated that oxygen, provided by bubbling air through the reaction mixture plays a major role in reaction, by increasing reaction rate and driving the reaction to completion. As noted in table 1, optimum results were obtained when reaction was carried out using one mole of ferrous salt and three moles of hydrogen peroxide per mole of phenol. Optimum results were obtained in pH range of 3 to 4 as seen in Figure 1.

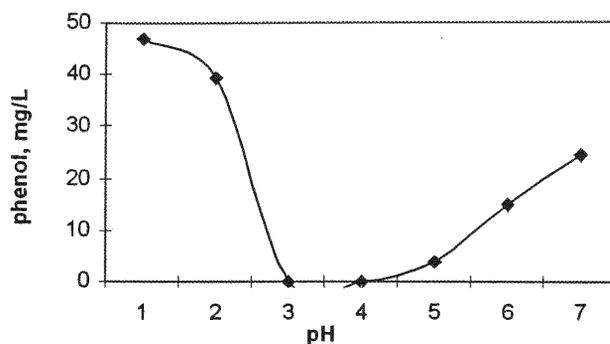


Figure 1. Effect of pH on Oxidation of phenol with Fenton's Reagent

(Eisenhauer, 1964)

Substituted Phenols

The oxidation of a number of substituted phenolic wastes by Fenton's Reagent was first studied by Eisenhauer (1964), and was carried out in the same manner as for phenol. It was observed that the greater the degree of substitution, the slower was the rate of reaction, especially when substituents were ortho and para directing. When all available positions were blocked, as in case of pentachlorophenol, no reaction occurred. Halophenols were rapidly oxidized, and the reaction rate in decreasing order was given by $\text{Cl} > \text{Br} > \text{I}$, which is attributed to electronegativity of halogen group. Phenols containing meta-directing groups such as carboxyl and nitro groups were very rapidly oxidized by Fenton's Reagent and methyl substituted phenols (Cresols) were more resistant to oxidation. Effluents from refinery, steel plant and insulation plant were treated. Refinery effluent was stripped and the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was 9:1 per mole of phenol, which completely removed the phenol. Steel plant effluent contained some

cyanide, which interfered with the reaction, and 16 moles of hydrogen peroxide per mole of phenol decreased the phenol level to 35 %. For insulation plant Fenton's Reagent was successful in reducing phenol and COD.

Edward et al. (1978) studied eighteen different phenolic compounds. The reaction was started at pH 5 to 6 as the pH decreased in the system due to the generation of protons by Fenton's Reagent. Table 4 indicates that all the mono substituted phenols were readily oxidized within one hour. The effect of oxidation of di-substituted phenols was dependent on character and position of ring substituents. Dichlorophenols, were readily oxidized than electron donating substituents of dimethyl phenols. Since Fenton's Reagent is a free radical mechanism, any substituent that increases the electron density of the ring will slow the reaction. So methyl phenol, with an electron-donating group will oxidize slowly. Variations in catalyst conditions were also studied for phenol reduction as shown in table 5 and 6.

It was recommended that catalyst concentration levels from 10-20 g/g iron ion should be used for phenolic wastewater no greater than 2000 $\mu\text{g/g}$. Higher phenol concentrations require at least 100:1 phenol: iron ratios and optimum results occur when phenol solution is initially at a pH between 5 and 6.

Table 4. Oxidation of Phenolic Compound, 3:1 Hydrogen Peroxide:Phenol, Mole Ratio (Edward et al., 1978)

Phenolic Compound	% Oxidized-1 hr (No Fe ²⁺)	% Oxidized-1 hr (with Fe ²⁺)
Phenol	0	100
2-Chlorophenol	9	100
3-Chlorophenol	50	100
4-Chlorophenol	20	100
2, 4-Dichlorophenol	0	100
2,5-Dichlorophenol	2	74
Pentachlorophenol	6	100
o-Cresol	0	100
m-Cresol	0	100
p-Cresol	6	100
2, 4-Dimethyl phenol	10	72
2, 5-Dimethyl phenol	6	0
2-Nitrophenol	34	100
4-Nitrophenol	0	100
2, 4-Dinitrophenol	2	30
2, 5-Dinitrophenol	10	73
a-Naphthol	8.5	100
b-Naphthol	9.5	100

Table 5. Variation of Catalyst Conditions (Edward et al., 1978)

Iron	Phenol:Iron	H ₂ O ₂ :Iron	% Reduction		
			15 min	30 min	60 min
50 µg/g Fe ⁺²	1:1	3:1		100	100
50 µg/g Fe ⁺³			96	100	100
50 µg/g Fe ⁺²	2:2	6:1	97	100	100
50 µg/g Fe ⁺³			92	98	100
50 µg/g Fe ⁺²	10:1	30:1	91	99+	99+
50 µg/g Fe ⁺³			94	97	99+

Initial Conditions: 50 µg/g phenol, 150 µg/g H₂O₂, pH= 5-6, T= 25° C

Table 6. Variation of Catalyst Conditions (Edward et al., 1978)

Iron	Phenol:Iron	H ₂ O ₂ :Iron	% Reduction		
			15 min	30 min	60 min
5 µg/g Fe ⁺²	100:1	300:1	85	91	95
5 µg/g Fe ⁺³			79	93	99
1 µg/g Fe ⁺²	500:1	1500:1	42	66	70
1 µg/g Fe ⁺³			21	51	70

Initial Conditions: 500 µg/g phenol, 1500 µg/g H₂O₂, pH = 5-6, T = 25 °C

Barbeni et al. (1987) studied five different chlorophenols and compared their half-life. They demonstrated that the appearance of chloride ion is independent of the disappearance of parent organic during Fenton's oxidation of 2-chlorophenol and it took 30 minutes to oxidize 50 mg/l of aqueous chloro-phenol (CP). Table 7 summarizes the time necessary to reduce the initial concentration of CP in solution by a factor of two and is a practical operational parameter, which should not be confused with kinetic parameter.

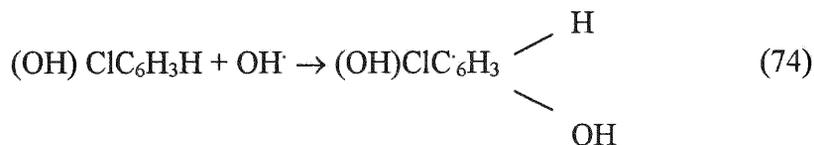
Table 7. Half lives (t/2) of Decomposition of Various Chlorinated Phenols

[Fe²⁺] = 5 X 10⁻⁵ M, [H₂O₂] = 5 X 10⁻³ M, [CP] = 3 X 10⁻⁴ M (Barbeni et al., 1987)

Compound	t/2 at 5 X 10 ⁻³ M HClO ₄ (min)	T/2 at 1.5 X 10 ⁻² M HClO ₄ (min)
3- Chlorophenol	6.5	34
2-Chlorophenol	14.5	125
4-Chlorophenol	12.5	180
3, 4-Dichlorophenol	6.3	16
2, 4, 5-Trichlorophenol	12	36

Thus, among monochlorophenols meta chloro substitution induces more rapid degradation than either of ortho or para substitution. The formation of Cl^- was slower than the disappearance of the 3, 4- DCP which suggested that chloroaliphatic intermediate(s) may be formed after the opening of benzene ring and the time lag between appearance of Cl^- ion disappearance of phenol depends on the number of chloro substituents on aromatic ring. Experiments were also carried out at different ferrous concentrations. It was found that increasing ferrous concentration in solution for a fixed hydrogen peroxide at 5×10^{-3} M increased the rate of decomposition. Similar experiments were also carried out with ferric ions. It was observed that when equimolar amount of ferrous and ferric ions were used in same reaction mixture the reaction rate ($t/2$) \sim 20 min where as it was \sim 50 min if only ferrous ions were used, thus ferric ion is an important species in the degradation process.

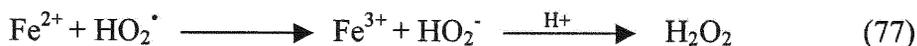
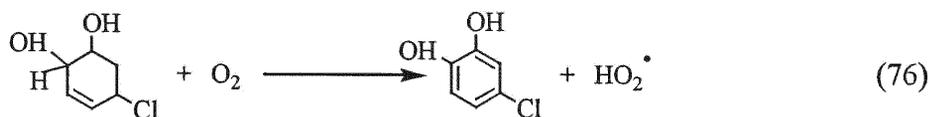
Barbeni et al. (1987) suggested that the hydroxyl radicals formed as a result of reaction between Fe^{2+} and H_2O_2 are good electrophiles. The electrophilic interaction of OH^\cdot with aromatic ring is favored by the presence of activating substituent (OH).



The degradative oxidation of chlorophenols proceeds by a hydroxylated species (reaction 74 and 75) followed by ring opening to yield aldehydes and ultimately degradation

occurs to CO_2 and Cl^- . It was suggested that the first step was the formation of radical cation by acid-catalyzed dehydration of radical formed between the interaction of OH^\cdot with chlorophenols.

Oxygen acts as radical scavenger and forms HO_2^\cdot . This HO_2^\cdot species successively reacts with either Fe^{2+} and Fe^{3+} to regenerate H_2O_2 and Fe^{2+} as shown in reaction in equations 76, 77 and 78.



Potter and Roth (1993), examined the oxidation kinetics of three monochlorophenol isomers and five of the six dichlorophenol isomers under batch and semibatch conditions. pH was maintained at 3.5 and the ultimate oxidation to CO_2 , H_2O and HCl was not reached but the extent of oxidation could be estimated from the measured parameters (Potter and Roth, 1993). The mechanism of oxidation of these species is important in determining if kinetics is feasible. The proposed reaction pathway suggested by Potter and Roth is as follows:

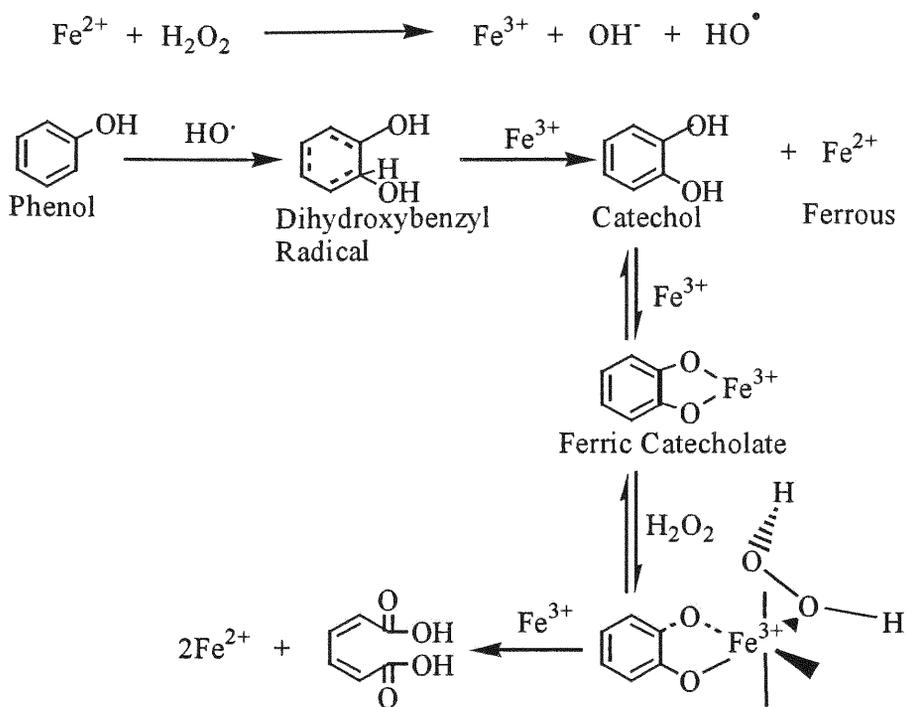


Figure 2. Reaction Pathway for Oxidation of Phenol (Potter and Roth, 1993).

Two possible pathways for mineralization of p-Chlorophenol had been proposed. First, Metilitsa (1971) proposed mineralization by substitution by hydroxyl radical. Second, Pieken and Kozarich (1989) proposed the route by elimination. Following are the proposed routes.

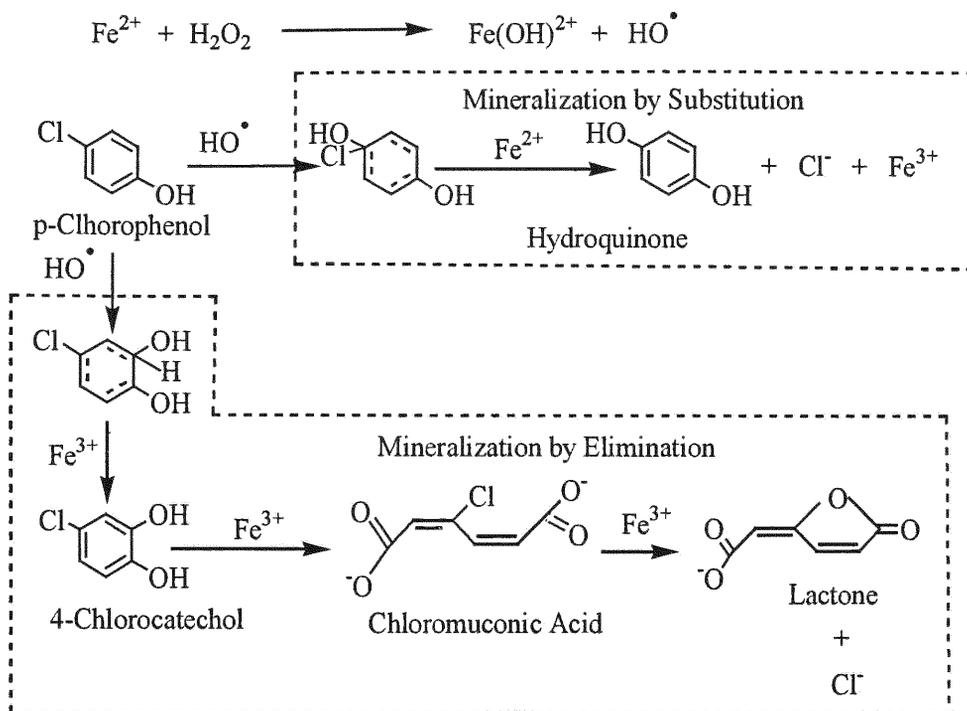


Figure 3. Two Possible Pathways for degradation of p-Chlorophenol

(Potter and Roth, 1993).

The experiments conducted by Potter and Roth showed agreement to previous work that monochlorophenols tend to mineralize to a greater extent than dichlorophenols, which was carried by Edward et al. (1978) and Barbeni et al. (1987). They showed that mineralization may be favored as the initial concentration of organic species decreases, and mineralization occurs primarily with daughter products.

Rate constants of 2, 4- Dichlorophenol (DCP) and 2, 4, 6-Trichlorophenol (TCP) were determined by competitive method by Tang and Huang (1996). The equation used to calculate the rate constants is as follows:

$$k_{HO\cdot, s} = k_{HO\cdot, R} * \ln ([S]/[S]_0) / \ln ([R]/[R]_0) \quad (79)$$

where:

$k_{HO\cdot, s}$ = rate constant between any organic compound and hydroxyl radical

$k_{HO\cdot, R}$ = rate constant between reference compound and hydroxyl radical

[S] = concentration of the substrate at any time

[S₀] = initial concentration of the substrate

[R] = concentration of the reference compound at any time

[R₀] = initial concentration of the reference compound (2-CP)

It was observed that the oxidation rate decreases with increasing degree of chlorine content according to the following order in terms of both elementary rate constants and the observed pseudo-first order rate constants as 2-CP > 2, 4-DCP > 2, 4, 6-TCP. In their work, the oxidation rate constant between hydroxyl radicals and 2, 4-DCP was $7.22 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and 2, 4, 6-TCP is found to be $6.27 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The optimum pH was found to be 3.5.

Pentachlorophenol

Pentachlorophenol, a widely used wood preservative is considered to be moderately biorefractory with a biodegradation rate constant of 3×10^{-12} L/cell.hour, a $\log K_{ow}$ of 5.01 and a vapor pressure of 1.1×10^{-4} mm Hg at 20° C. Watts et al. (1990) carried out completely mixed batch tests by treating pentachlorophenol contaminated soils with Fenton's Reagent. The soil characteristics are shown in table 8.

Table 8: Soil Characteristics (Watts et al., 1990).

Classification	Soil I Ramona soil A horizon; Fine-loamy, mixed, Thermic, typic Hplexeralfs	Soil II Ramona Soil C horizon, fine-loamy, Mixed, Thermic Hplexeralfs
Crystalline Fe Oxides (%)	0.46	0.28
PH	8.00	8.00
Organic Carbon (%)	0.58	0.05
Cation Exchange Capacity (meq/100 g)	5.34	4.32

Mineralization of PCP was studied in commercially available silica sand and two natural soils by removal of parent compound and total organic carbon with corresponding stoichiometric recovery of chloride. Figure 4 shows the rate of reaction as a function of pH.

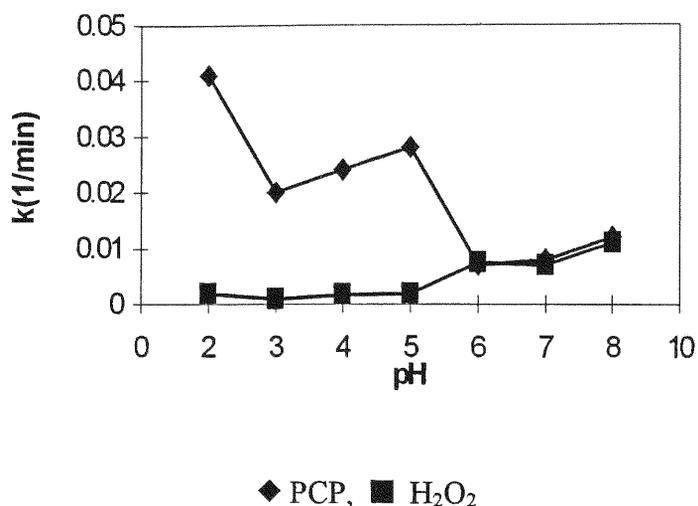


Figure 4. Effect of pH on the Rates of Fenton's Treatment of Pentachlorophenol
(Watts et al., 1990).

It was reported that the soluble iron concentration decreased over the first three hours of treatment and the concentration remained relatively constant there after. A possible mechanism for iron precipitation was defined as follows:



which has a reaction half-life of 25 minutes at neutral pH (Sung and Morgan, 1980). Hypothetically the decomposition rate of Fenton's system is zero because the production of hydroxyl radical should approach steady state. However, in this experiment the decomposition rates were not linear. Watts et al. (1990), proposed zero, first, and second order kinetic models, but concluded that first order was the best with $r^2 > 0.9$ for plots of the natural logarithm of concentration as a function of time. They observed that the

reaction occurring in Fenton's system are complex. However, the empirical fit of experimental data to the first-order model provided the most accurate means of comparing different treatment conditions. The tests also showed that organic carbon was removed rapidly after PCP degradation, which illustrates that hydroxyl radical attack on the products is more rapid than on the parent compound. It was also observed that the addition of Fe^{2+} significantly increased the degradation rate constant at low pH. Table 9 shows the results of the kinetics at different pH levels with or without soluble iron addition.

Table 9: Fenton's Reagent Treatment Efficiencies (Watts et al., 1990).

PH	$k_{\text{PCP}}/k_{\text{H}_2\text{O}_2}$						
	2	3	4	5	6	7	8
Silica + Fe	13.7	25	10.5	11.6	0.9	1.2	1.1
Soil 1 no Fe	12.5	4	6.7	0.67	0.63	0.18	0.12
Soil 1 + Fe	5	3.4	2	1.4	1	0.13	0.082
Soil 2 no Fe	8	17.6	2	11	4.5	1.1	0.36
Soil 2 + Fe	7.3	11.3	8.2	4.6	3.7	0.72	0.3

Based on the first order rate constant for PCP degradation, at pH 3 five hours were required for 99% PCP degradation with Fe^{2+} addition, and 39 hours without Fe^{2+} degradation.

Nitro Phenols

Nitrophenols are persistent pollutants and commonly found in industrial wastewater. Degradation of nitrophenols to less dangerous materials or mineralization is difficult process involving biodegradation or oxidation via natural processes. Nitrophenols are commonly found in degradation of pesticides such as parathion and nitrofen. The corrosive materials found in sewage plants and are recognized as priority pollutants.

Studies conducted by Kiwi et al. (1994) showed efficient photo and dark oxidation via Fenton-like reactions on 2 and 4-nitrophenols. Photolysis of acidic solutions of H_2O_2 give OH^\cdot radicals as primary photoproducts (Baxendale and Wilson, 1957) as follows:



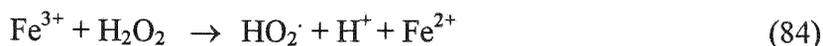
along with small amounts of HO_2^\cdot radicals:



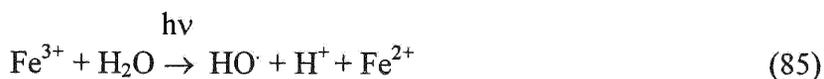
The irradiated 2-nitrophenol forms a triplet state that reacts with H_2O_2 (Kiwi, et al., 1993).



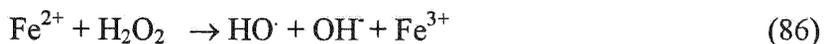
Irradiation results showed that photoproducts were formed as hydroquinones, benzoquinones and nitrophenols. Under experimental conditions Fe^{3+} ion is known to promote decomposition of H_2O_2 as follows:



or according to the mechanism

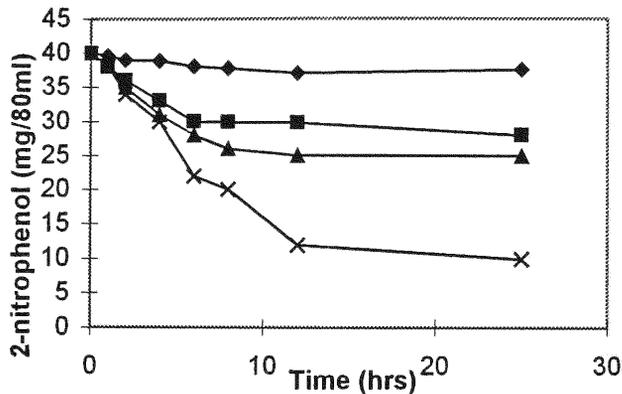


with Fe^{2+} ion additionally producing $\text{OH}\cdot$ radicals as follows:



Degradation of 2-nitrophenol using different conditions as direct photolysis, some Fe^{3+} as catalyst, H_2O_2 /dark and H_2O_2 /light was studied and the results are shown in Figure 5. The effect of temperature was studied and was found to be beneficial on light activated degradation. The time was reduced by 40% for dark processes and 50% for similar processes under light. 2-nitrophenol degradation could be induced by sunlight where temperatures above 30°C are available in nature under favorable conditions. Light

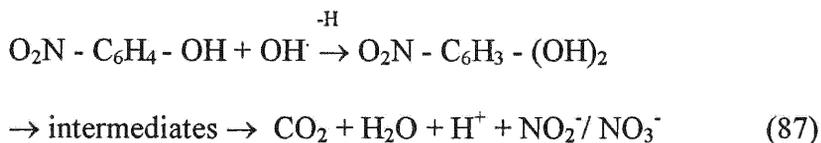
improves reaction 86 of the system $\text{Fe}^{2+}\text{-H}_2\text{O}_2$ significantly. The degradation of 2-nitrophenol seems to favor the regeneration of Fe^{2+} -ions in reaction in equation 87. Fe^{2+} produces OH^\cdot radicals than the dark Fenton system where $\text{Fe}^{2+}:\text{OH}^\cdot$ Ratio is 1:1.



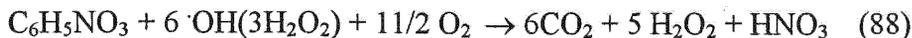
◆ Direct light, ■ Fe-ion light, ▲ H₂O₂ dark, ✕ H₂O₂ light.

Figure 5. Photodegradation of 2- nitrophenol (Kiwi et al., 1994)

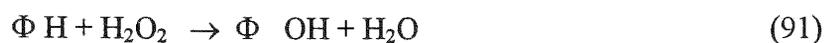
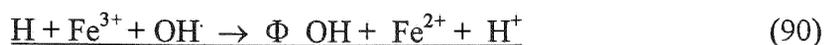
The overall oxidation of 2-nitrophenol by OH^\cdot radicals could be expressed as follows:



the overall reaction is written as follows:



Reaction in equations from 84 to 88 show that only H₂O₂ is consumed during the light degradation process present in the following reactions:



It was observed that two processes were taking place side by side leading to the degradation of 2-nitrophenol. This process is represented by Kiwi et al. (1993) in Figure 5. It was considered that the overall rate for TOC or DOC degradation at 60° C in the first 2 hours was 10 times faster than the rate subsequently observed for this reaction between 2 and 5 hours. It was also observed that under light, 4-nitrophenol degradation proceeded two times faster than 2-nitrophenol. The rates of OH[·] oxidation are about the same for both compounds. In a benzoic ring the nitro withdrawing effect is preferentially marked in ortho and para positions and in 2-nitrophenol hydroxylation of 6 position leads to dihydroxy compound as shown in figure 6. In case of hydroxylated 4-nitrophenol, the two bonds between adjacent-OH groups might undergo easy oxidative scission but in 2-nitrophenol only one bond of this type is found in hydroxylation. This explains why the photo-Fenton degradation observed for 2-nitrophenol proceeds at about half the rate than the homologue 4-nitrophenol.

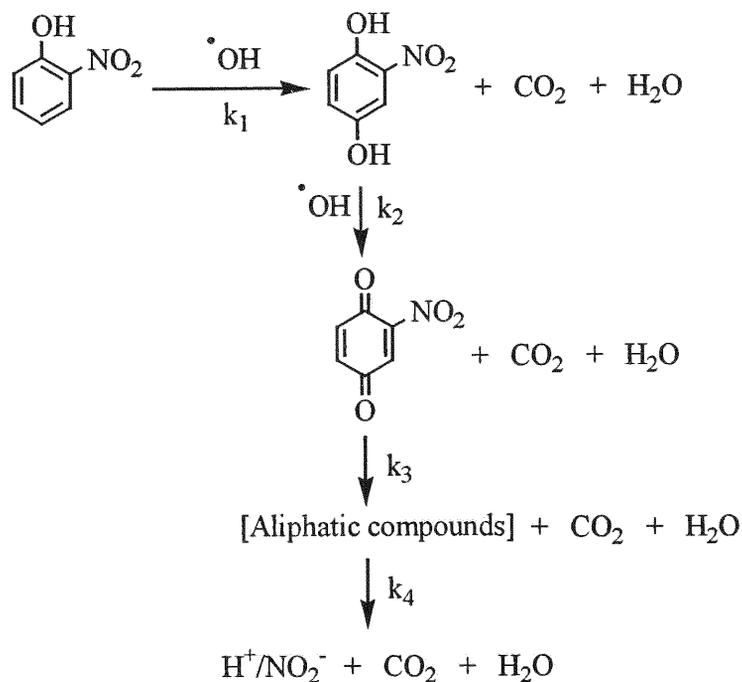


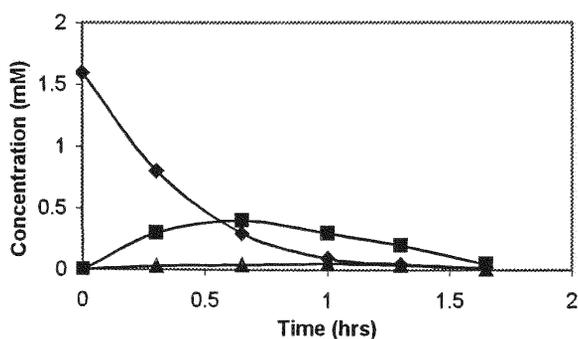
Figure 6. Degradation pathway of Nitrophenol (Kiwi et al., 1994)

3.2.2 Benzenes

Chlorobenzenes have been widely used as solvents, degreasing agents, pesticides, and dielectric fluids and as industrial precursors in production of phenols, DDT, aniline and dyestuff intermediates. Chlorobenzenes represent a unique class of compounds because their hydrophobicity increases with chlorine substitution, while the rates of hydroxyl radical attack on the ring are nearly equal regardless of the degree of chlorination (Watts, et al., 1997). Sedlak and Andren (1991) investigated the degradation of chlorinated aromatic hydrocarbons (CAHs) by Fenton's Reagent using bench scale experiments. Twelve different intermediates identified during oxidation were 2-

Chlorophenol, Chlorobenzoquinone, 3-Chlorophenol, 4-Chlorophenol, 2, 2'-DCB, 2, 3'-DCB, 2, 4'-DCB, 3, 3'-DCB, 3, 4'-DCB, 4, 4'-DCB, MHCIBps and DHCIBps. Figure 7 shows the result of oxidation of chlorobenzene by Fenton's Reagent at Ferrous concentration of 0.5 mM and pH of 3.

Chlorobenzene and all intermediate products (Figure 8) disappeared in the first 2 hours of reaction. The experiment was conducted in the presence of oxygen at pH 3, and approximately 5 mol of H_2O_2 / mol of chlorobenzene was required to completely remove the aromatic intermediates from solution. Reactions in the absence of oxygen yielded much higher concentrations of dichlorobiphenyls when compared to those in air. DOC analysis indicated that the aromatic intermediates undergoes ring cleavage prior to mineralization. The reaction almost ceases after approximately 4 hrs, this is shown by stabilization of DOC concentration, pH, and Fe^{2+} and can be due to the inability of many ring-cleavage intermediates to regenerate Fe^{2+} . The reaction mechanism is shown in Figure 9.



Chlorobenzene, ■ Total Chlorophenols, ▲ Chlorobenzoquinone

Figure 7. Oxidation of Chlorobenzene with Fenton's Reagent

(Sedlak and Andren, 1991)

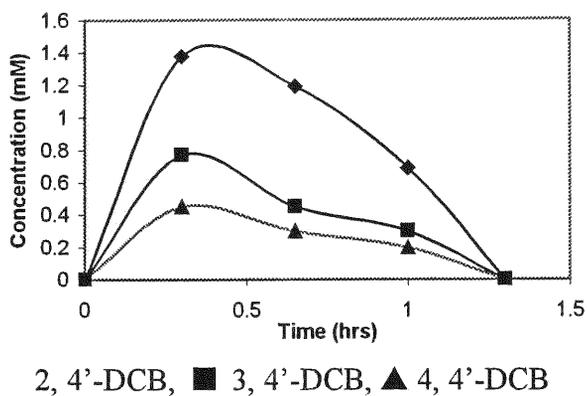


Figure 8. Formation of Three Dichlorobiphenyl Isomers during Oxidation of Chlorobenzene (Sedlak and Andren, 1991)

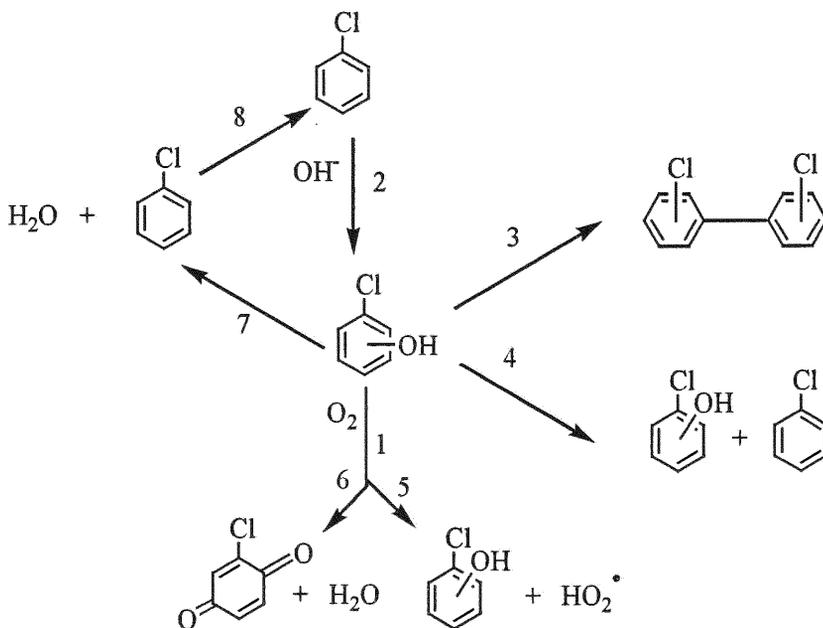


Figure 9. Proposed Reaction Pathway for Oxidation of Chlorobenzene by Fenton's Reagent (Sedlak and Andren, 1991)

The first step in this sequence is the hydroxyl radical attack on chlorobenzene (reaction 2), which likely results in the formation of chlorohydroxycyclohexadienyl (ClHCD) radical I (Dorfman et al., 1962, and Eberhardt and Yoshida, 1973). This may undergo one of several possible further reactions. In the absence of strong oxidants, two predominant reactions are dimerization to produce dichlorobiphenyls (reaction 3) and bimolecular disproportionation to produce chlorophenol and chlorobenzene (reaction 4). Both reactions showed the stoichiometry of 2 mol of H₂O₂/mol of chlorobenzene oxidized. In the presence of oxygen or strong oxidants several additional reactions contribute to product formation. Reactions of oxidant with ClHCD radical (reactions 5 and 6) predominates because they are first order with respect to ClHCD radical, whereas reactions 3 and 4 are second order with respect to the radical. The presence of oxygen or other strong oxidants favors the more direct oxidation pathway and follows a stoichiometry in which less hydrogen peroxide is required to degrade the CAHs. The oxidation of chlorobenzene and chlorophenol isomers is most likely attributable to the formation of phenolic polymers. Disappearance of broad band absorption and dimers as the reaction progressed suggests that these polymers and dimers are ultimately amenable to oxidation.

Watts et al. (1997) investigated the effects of hydrogen peroxide concentration and desorption rates on oxidation of series of four chlorobenzene on hematite which is a naturally occurring iron oxide found in soils and subsurface systems. The focus was to look at the relationship between desorption and oxidation of chlorobenzene sorbed on hematite. Hydrogen peroxide concentrations from 0.1 to 5% were used and the rates of

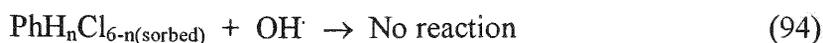
oxidation and were compared with rates of desorption. The desorption experiments showed that 0.1 mmol/Kg 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene partitioned on hematite. Desorption followed first order kinetics with respect to each chlorobenzene, and rate constants were inversely proportional to chlorine substitution and octanol-water partition coefficient.

This study indicated that degradation of 1,3,5-trichlorobenzene with initial concentrations of 0.1, 1, 2, and 5% H₂O₂ in relation to deionized water control, trichlorobenzene desorption and H₂O₂ consumption. The data suggested that oxidation occurred at least in the sorbed state with hydrogen peroxide concentrations $\geq 2\%$. Several studies have shown that the optimum oxidation rate is reached at 2% H₂O₂, because 2% is the minimum H₂O₂ concentration capable of oxidizing sorbed contaminants. These experiments showed that although the rate constants for hydroxyl radical attack on chlorobenzene are nearly equal, degradation rates decreased from lower to higher chlorine substitution. Chlorobenzene oxidation by hematite catalyzed Fenton-like reactions was highly dependent on desorption rate. Hexachlorobenzene was not desorbed or oxidized, which shows that hydroxyl radicals do not degrade even reactive substrates while sorbed on the surface of hematite.

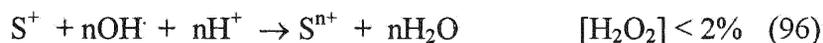
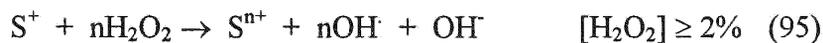
The reaction mechanism was explained as follows. Reaction 92 shows the heterogeneous decomposition of H₂O₂ (Kitajima et al., 1978).



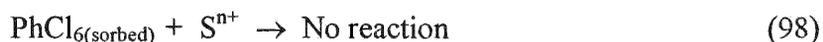
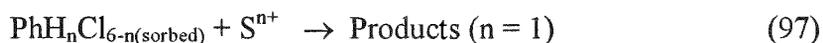
where S is mineral surface and S⁺ is oxidized region of surface. Hydroxyl radicals generated by above reaction reacts with all four chlorobenzenes in aqueous phase (not sorbed) and oxidizes them.



Higher concentrations of H₂O₂ increases hydroxyl radicals or higher system redox potential may increase the oxidation state on mineral surfaces (Sⁿ⁺), which might lead to oxidation of sorbed 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene and pentachlorobenzene.



Where Sⁿ⁺ is a more oxidized mineral surface relative to S⁺, this is capable of degrading chlorobenzenes with at least one C-H bond but not perhalogenated hexachlorobenzene.



Thus, mineral-catalyzed Fenton-like reactions are controlled by desorption, H₂O₂ concentration and contaminant structure. Watts et al. (1994) also studied sorption and degradation of hexachlorobenzene on goethite as iron catalyst.

3.2.3 Toluene

2,4-Dinitrotoluenes (DNT) are generated from ammunition factories and other chemical industries. It is used in making 2,4 diaminotoluene for isocyanate production. They are also used for production of dyes, explosives, and organic synthesis and as a propellant additive. Mothanty and Wei (1993) carried out experiment to study the effect of H₂O₂/DNT ratio on removal, rate of DNT removal, effect of temperature and effect of sequential addition on oxidation. They also compared Fenton's Reagent with UV/H₂O₂ system to see which process is more effective way to generate hydroxyl radicals.

The effect of H₂O₂:DNT ratio was studied using the ratios from 5:1 to 80:1. The ratio of Fe²⁺/H₂O₂ was 0.024, the initial pH varied from 4 to 5. Figure 10 shows average removal of DNT with variation of H₂O₂:DNT ratio for contact time of 1 hour.

The concentration of by-products decreased with increasing H₂O₂. The consumption of H₂O₂ increased with the amount of DNT applied. At higher H₂O₂ concentrations, there was greater amount of self decomposition as the OH[·] generated would react with H₂O₂ and hence reaction in equation 99 would be prominent.



Figure 10 shows that greater than 99% of DNT is removed at a ratio of 20. The rate of removal of DNT was seen to follow a pseudo first order reaction with a rate coefficient of 0.035/min at a molar ratio of 15:1:1.8 of H₂O₂:DNT:Fe²⁺. To study the effect of sequential addition, three different experiments were performed.

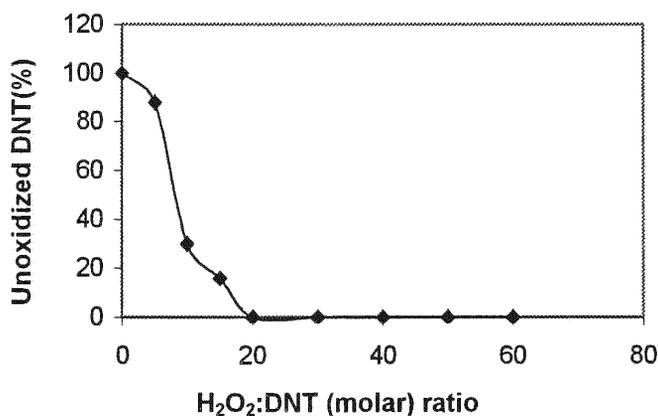


Figure 10. Removal of 2, 4-DNT with Change in H₂O₂:DNT Ratio

(Mohanty and Wei, 1993)

TOC, H₂O₂ and pH were monitored during the course of experiment as seen in table 10. During reaction, there is an excess of Fe²⁺ and hence reaction in equations 100 and 101 dominates as the ratio of substrate to H₂O₂ is high, thus reaction in equation 1 becomes unimportant.

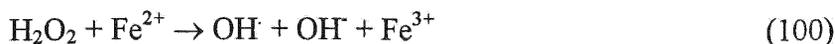


Table 10. Experimental conditions for sequential addition (Mohanty and Wei, 1993)

Exp.	Initial DNT mM/L	H ₂ O ₂ :DNT:Fe ²⁺	Comments
1	0.42	20:1:2.5	H ₂ O ₂ in 20 equal steps
2	0.42	20:1:2.5	Fe ²⁺ in 20 equal steps
3	0.42	20:1:2.5	H ₂ O ₂ and Fe ²⁺ applied initially in a single dose

Sequential dosing of H₂O₂ had lower concentration of reaction by-products when compared with experiment without sequential dosing. The retention time of these byproducts was higher than their parent compounds. One of these by-products might be a dimer. If there is excess of H₂O₂ available, reaction in equations 99, 100, and 102 gain importance.



The removal of TOC was minimum which indicated losses of H₂O₂ and showed the importance of reaction (99). No removal of TOC was observed during the first 30 minutes, this was due to lower Fe²⁺ concentration and thus low hydroxyl radical availability for oxidation of organics. In the presence of oxygen the rate of degradation and extent of oxidation increased dramatically, but there was no major difference in

removal of TOC and COD. The reaction was also run at three different temperatures; 21° C, 30° C and 40° C with all other conditions constant. Figure 11 shows that temperature affects the reaction rate considerably.

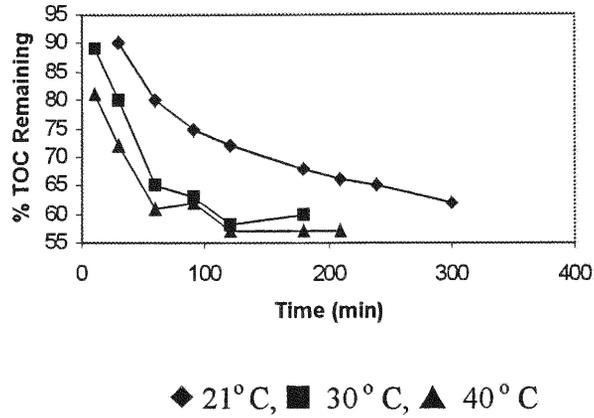
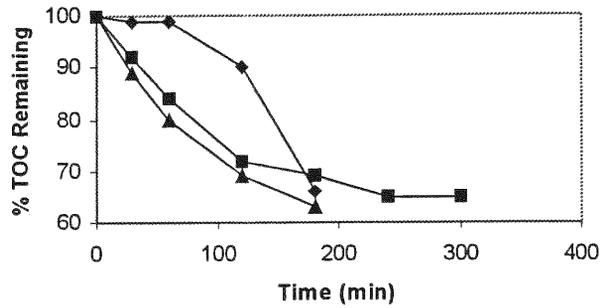


Figure 11. Effect of Temperature on Removal of TOC

(Mohanty and Wei, 1993)

Hydrogen peroxide was depleted in 5, 4 and 2.5 hours for the reactions at temperatures of 21° C, 30° C and 40° C, respectively. TOC removal was also greater at higher temperatures. Initial presence of Fe^{3+} and Cu^{2+} enhanced the evolution of oxygen in the absence of substrates. Figure 12 shows the result of effect of Fe^{3+} and Cu^{2+} on degradation.



◆ $\text{H}_2\text{O}_2:\text{DNT}:\text{Fe}^{2+}=20:1:2.5$, ■ $\text{H}_2\text{O}_2:\text{DNT}:\text{Fe}^{2+}:\text{Fe}^{3+}=20:1:2:0.5$,
 ▲ $\text{H}_2\text{O}_2:\text{DNT}:\text{Fe}^{2+}:\text{Cu}^{2+}=20:1:2:0.5$

Figure 12. Effect of Metals on Removal of TOC (Mohanty and Wei, 1993)

The rate of removal of DNT was pseudo first order and the behavior of rate of removal was a straight line with regression coefficient of 0.98.

Benzene, Toluene and Xylene (BTX)

Benzene, toluene and xylene (BTX) is highly soluble in water and are found in oil-contaminated groundwater. It was found by Garrogunino et al. (1992) that the toxicity of contaminated ground water is primarily due to BTX. BTX present in ground water in dilute concentrations present a challenge to drinking water supply resources. The most common source of point source pollution is underground oil storage tanks and is distributed around the regions as in petroleum stations, factories and oil-refinery-plants. Owing to large amount and location in a densely populated area of these tanks, the adverse effect is significant to human beings if a leakage occurs.

Lou and Lee (1995) oxidized BTX in a batch reactor using Fenton's Reagent to simulate the fuel hydrocarbon-contaminated groundwater from a spill site. Change of BTX concentration with time, pH, H₂O₂, Fe²⁺ optimum ratio of H₂O₂: BTX: Fe²⁺, and rate expression of BTX was reported. Results were obtained in terms of destruction efficiency of BTX, which is expressed as follows:

$$\text{DRE \%} = \frac{C_0 - C_t}{C_t} \times 100 \quad (103)$$

where C₀ is the initial concentration of BTX (mg/L) and C_t is the concentration of BTX after t minutes (mg/L). At H₂O₂: BTX: Fe²⁺ ratio of 2.4:1:12 (mg/L) the removal of BTX is significantly oxidized by Fenton's Reagent, benzene and toluene removal was about 86% and xylene removal was 80 %. After about ten minutes, the concentration of BTX remained almost unchanged and had reached 90-94% removal after 60 minutes. The destruction efficiencies of BTX as a function of pH is shown in Figure 13. When H₂O₂ was 120 mg/L, Fe²⁺ was 600 mg/L, and BTX 50 mg/L.

The DRE of BTX decreased with increasing pH value for pH ≥ 4. At pH < 4, the DRE of benzene, toluene and xylene changed insignificantly with values about 87%, 88% and 83%, respectively. The relation between DRE of BTX and H₂O₂ is shown in Figure 14 and shows that at a fixed pH and Fe²⁺, the DRE of BTX increased almost linearly with increasing H₂O₂ concentration till 60 mg/l, and with an increase in concentration of H₂O₂ the DRE of BTX remained at 80% to 90%, showing zero order reaction.

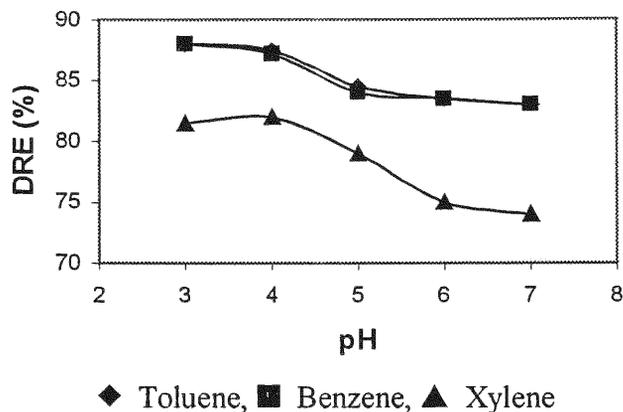
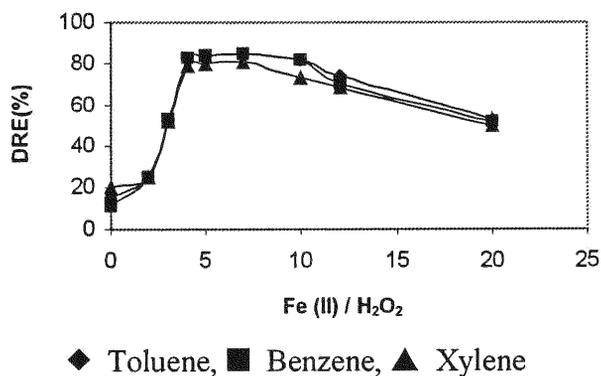


Figure 13. Effect of pH on Destruction Efficiency of BTX (Lou and Lee, 1995)



$H_2O_2=0-150$ mg/L, $Fe^{2+}=0-700$ mg/L, BTX=50 mg/L, pH=4

Figure 14. Effect of H₂O₂/ Fe²⁺ Concentration Ratio on Destruction of BTX

(Lou and Lee, 1995)

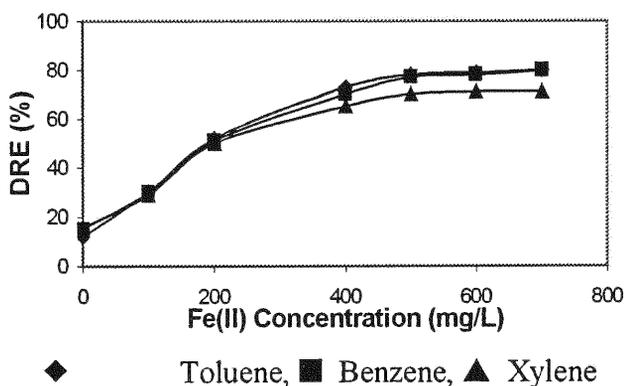
As proposed by Harber and Weiss (1934), which may be due to the fact that at lower H₂O₂ concentrations and fixed Fe²⁺, the oxidation approaches second order. But

when the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ increases, the reaction kinetics approach zero order and the reaction process depends on the competition between hydroxyl radical and superoxide radical. If there is excess of hydrogen peroxide, reaction in equations 99, 100, and 102 are dominant for 2, 4-Dinitrotoluene. The amount of H_2O_2 was consumed rapidly, thereby indicating the importance of equation 99. Figure 14 indicates that DRE of BTX was small, which indicated the lack of H_2O_2 and shows the importance of reaction in equation 99.

Figure 15 shows the effect of Fe^{2+} on DRE of BTX, it indicated that at zero Fe^{2+} the DRE of BTX oxidized by H_2O_2 was below 20%, and it increased with increasing concentration of Fe^{2+} . At $\text{Fe}^{2+} > 600$ mg/L, the DRE of BTX reached the maximum value of approximately 82% for benzene and toluene and 73% for xylene. Lou and Lee (1995), found that the DRE of BTX caused by Fenton's Reagent cannot be further raised due to lack of available H_2O_2 , the H_2O_2 was consumed rapidly and DRE of BTX were minimum, thus it suggests that reaction in equation 99 is very important.

To study the optimal ratio of H_2O_2 : BTX: Fe^{2+} , the concentration of BTX was kept at 50 mg/L and pH was varied from 4 to 5. The range of the ratio studied was from 0 to 20. After 10 minutes of contact period, the DRE of BTX with change in ratio was indicated as in fig 14, which showed that the DRE increased with an increase in the ratio in range from 0 to 5, but further increase in the ratio actually decreased the DRE of BTX and the optimal ratio was found to be 0.2. Effect of H_2O_2 : BTX ratio on removal was also studied by varying this ratio from 2.4 to 12. The ratio of H_2O_2 : Fe^{2+} for this was 0.2.

The destruction of BTX versus H_2O_2 : BTX ratio revealed that the optimal DRE of BTX was found to be around 98% to 100% for xylene and benzene & toluene, respectively, when H_2O_2 : BTX ratio was 12:1. Lou and Lee concluded that benzene, toluene and xylene can be effectively oxidize at H_2O_2 : BTX: Fe^{2+} ratio of 12:1:60 (mg/L) in less than ten minutes. The results of chromatograms indicated that the concentration of by-product was insignificant and very low. The plot of reaction time with BTX concentration showed the rate to follow a pseudo first-order reaction at 20°C. At an applied concentration ratio of 2.4:1:12 (H_2O_2 : BTX: Fe^{2+}), the rate coefficients of benzene, toluene and xylene were calculated to be 4.03 (h^{-1}) and 2.91 (h^{-1}) respectively.



H_2O_2 = 60 mg/L, BTX = 50 mg/L, pH = 4

Figure 15. Effect of Fe^{2+} Concentration Ratio on Destruction of BTX

(Lou and Lee, 1995)

Removal of BTX was found to be pseudo first order. The coefficient of linear regression was found to be 0.991 and 0.994 for xylene and for benzene & toluene, respectively. The rate expression for benzene and toluene was given as follows:

$$\ln C = 3.92 - 4.03 (t) \quad (104)$$

for Xylene as follows:

$$\ln C = 3.89 - 2.91 (t) \quad (105)$$

where C was concentration of benzene, toluene and xylene after t hours in ppm, t is reaction time in hours.

3.2.4 Polychlorinated Biphenyls (PCBs)

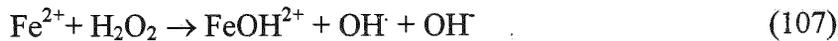
In most wastes and wastewater, PCBs are found in aqueous phase as well as in association with particulate matter. The fraction of PCB associated with each phase depends on the hydrophobicity of the congener and the congeners containing more chlorine substituents have a stronger tendency to associate with particulate. PCBs sorbed to surfaces as diatomaceous earth are not oxidized by aqueous OH⁻ at an appreciable rate, relative to the rate of reaction of OH⁻ with solution phase PCBs. To evaluate quantitatively the effect of sorption to particulate matter on PCB oxidation by OH⁻ a study was performed by Sedlak and Andren (1994). Transformations of three PCB

cogeners, 2-monochlorobiphenyl (MCIBp), 2,2',5-trichlorobiphenyl (TrClBp), 2,2',4,5,5'-pentachlorobiphenyl (PeClBp) were studied at an initial concentration of 1 μ M of each of them, expressed as if all of the PCB was in solution. Data from the experiments were compared with predictions from quantitative kinetic models that used independently determined data on reaction rates and OH \cdot concentrations.

Hydroxyl radicals were generated through the photo-Fenton reaction. The first step in reaction was photoreduction of ferric hydroxy complex by radiation from a black light.



Ferrous iron produced is then oxidized by H₂O₂ in Fenton's reaction



Reaction 107 was significantly faster than reaction 106.

The consumption rate of H₂O₂ and the OH \cdot production was directly related to total iron concentration. The concentration of hydroxyl radical produced by the reaction in equations 106 and 107 were controlled by the rate of reaction with dissolved constituents. Rate constants for adsorption (k_a) and desorption (k_d) of PCBs from particles were determined. Desorption rate constants were calculated by regression of data from 1.5 to 5

h. Adsorption rate constants were estimated from equation 108 assuming that the partitioning observed between 2 and 5 h in the experiments without OH⁻ could be used for calculation of equilibrium partition coefficients (K_p).

$$K_p = k_a / k_d \quad (108)$$

K_p were calculated by averaging the partitioning data collected after 2 h in the experiments conducted in the absence of OH⁻. Equation 108 may be employed to model partitioning kinetics over short time intervals for the particles used in these experiments as equilibrium models may not adequately predict partitioning over extended time intervals for many types of particles. Partitioning data and reaction rate constants calculated for 2,2',5-trichlorobiphenyl and 2,2',4,4',5-pentachlorobiphenyl by Sedlak and Andren (1994) is shown in table 11.

Table 11. Partitioning Data and Reaction Rate Constants Calculated for 2, 2', 5-Trichlorobiphenyl and 2,2',4,4',5-Pentachlorobiphenyl (Sedlak and Andren, 1994)

Variable	2,2'5-Trichlorobiphenyl	2,2',4,5,5'-Pentochlorobiphenyl
$k_d^* (X 10^4 s^{-1})$	2.04 (± 0.10)	4.53(± 0.03)
$k_a(1 g^{-1}s^{-1})$	0.39 (± 0.15)	1.41(± 0.34)
$K_p (1 g^{-1})$	1860 (± 615)	31,600($\pm 5,400$)
$k_{OH} (X 10^9 cm^3 mol^{-1} s^{-1})$	6.9	4.6

Sedlak and Andren (1991,b) modeled hydroxyl radical reaction kinetics in the presence of particulate. They found that the reaction kinetics for PCB oxidation in presence of particulate resulted from the complex interplay between solution-phase OH[•] reactions and reversible adsorption-desorption reactions. A model predicting kinetics of reactions must at least consider following reactions:



where PCB=S = particle-associated PCB concentration (mol/g)

PCB= dissolved PCB concentration(M)

S= particle concentration(g/L)

[OH[•]] = steady-state hydroxyl radical concentration(M)

PCB-OH = hydroxylated PCB concentration (M)

There were several possible options for modeling reaction in equations 109 and 110, and the choice of an appropriate model depended on the relationship between the rate constants and degree of accuracy desired. When the compound of interest was not strongly associated with the solid phase or when the reaction rate was much lower than the desorption rate, it was possible to model the transformation as a pseudo-first order

process, this was based on the assumption that reaction in equation 109 was insignificant relative to reaction 110 (i.e. $[\text{PCB}] = \text{PCB}_{\text{tot}}$). The transformation rate was then approximated by equation 111.

$$- d[\text{PCB}] / dt = k_{\text{OH}} [\text{OH}^-] [\text{PCB}] \quad (111)$$

where k_{OH} is the second order reaction rate constant ($\text{M}^{-1}\text{s}^{-1}$)

With an assumption that the steady-state OH^- concentration was constant, transformation of the solute could be modeled as a pseudo-first-order process with an apparent first-order rate constant of $k_{\text{OH}}[\text{OH}^-]$. This model was applied to results for MCIBp, good predictions were obtained of transformation rates of PCB. Results suggested that the pseudo first order model can be applied only a small fraction of total PCB present was associated with particulate-phase. The main advantage of this model was that accurate predictions of reaction rates could be made without determination of adsorption-desorption rate constants, since particle associated PCB concentrations were low and desorption rates fast adsorption-desorption kinetics were not necessary.

When a larger fraction of HOC was associated with particulate phase, numerical solution of equations 109 and 110 were required to predict PCB transformation rates. The instantaneous concentration of dissolved PCB was estimated by incorporating the terms $[\text{S}]$ and $[\text{OH}^-]$ into the rate constant expressions for reaction in equations 111 and 112.

$$[\text{PCB}] = \frac{k_d [\text{PCB}]_o [e^{-\alpha t} - e^{-\beta t}]}{\beta - \alpha} \quad (112)$$

where $[\text{PCB}]_o$ = initial total PCB concentration

$$\alpha\beta = k_d k_{\text{OH}} [\text{OH}^\cdot]$$

$$\alpha + \beta = k_d + k_a [\text{S}] + k_{\text{OH}} [\text{OH}^\cdot]$$

The rate of PCB transformation by OH^\cdot was then calculated using equation 112 at discrete time intervals using the dissolved PCB concentrations predicted by equation 110. The predictions of the numerical solution model were compared with experimental data for TcClBp. The model was in good agreement with the data, the measured concentrations were within approximately $\pm 10\%$ of the predicted values. Transformation rates were much more sensitive to changes in k_d than OH^\cdot . The strong affinity of PeClBp for the particulate phase prevented the transformation of significant amounts of PeClBp over the time period considered in these experiments.

These experiments provided valuable insight into the nature of HOC transformations in the presence of particles. Pseudo-first-order models adequately predicted transformation rates when only a small fraction of solute was associated with the particulate phase. When a substantial fraction of HOC was associated with particulate phase, more complex models based on solution of kinetic expressions describing reversible sorption and OH^\cdot transformation reactions, were required to predict

transformation kinetics. HOC, which were almost completely associated with particulate phase, underwent transformation reactions at very slow rates.

3.2.5.9 Pesticides

Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)- s-triazine) is one of the most commonly used pesticides in the United States and its usage accounts for 12% of the pesticides. Arnold et al. (1995) studied the effects of different reaction conditions on the efficacy of Fenton's Reagent for degrading atrazine. Atrazine degradation and product formation rates were determined as a function of FeSO_4 and H_2O_2 concentrations and the ratios and solution pH. The ratios of $\text{FeSO}_4 : \text{H}_2\text{O}_2$ were used at 1:1, 1:200 and 2:1 at concentrations from 0.1 to 25 mM. FeSO_4 and H_2O_2 ratio of 1:1 and its effect on Atrazine degradation was studied. During this study seven major products were identified such as CDIT, CIAT, CDET, CEAT, ODIT, CDAT and CAAT (Abbreviations with chemical structures, common name and chemical name is shown in table 12).

It was observed that at concentrations of 2.69, the reaction mixtures were depleted of the CDIT, CIAT, CEAT, and ODIT. But CDAT, CAAT and six minor unidentified atrazine derivatives persisted at Fenton's Reagent concentrations up to 25 mM. Fenton's Reagent treatment was ineffective in degrading CDAT and CAAT due to the low reactivity of oxidized products toward OH. At low $\text{FeSO}_4 : \text{H}_2\text{O}_2$ ratio, a complete treatment was achieved with lower Fe^{2+} concentrations as compared to 2.69 mM treatment, but increasing H_2O_2 concentration 100-fold lowered the reactions efficiency

since larger amounts of chlorinated products (CDAT and CAAT) remained. Excess of hydrogen peroxide might have lead to dealkylation, thus decreasing dechlorination. Increase in Fe^{2+} concentration lowered reaction efficiency as excess Fe^{2+} reacts with OH⁻ at $\text{FeSO}_4 : \text{H}_2\text{O}_2$ of 2:1.

Table 12. Names and Abbreviations of Atrazine and Fenton's Reagent-Generated Degradation Products (Arnold et al. (1995))

Common Name	Chemical Name	Abbreviation
Atrazine	2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine	CIET
Atrazine Amide	2-acetamido-4-6-(isopropylamino)-s-triazine	CDIT
Diethylatarazine	2-amino-4-chloro-6-(isopropylamino)-s-triazine	CIAT
Simazine amide	2-acetamido-4-chloro-6-(ethylamino)-s-triazine	CDET
Deisopropylatrazine	2-amino-4-chloro-6-(ethylamino)-s-triazine	CEAT
Hydroxyatrazine amide	2-acetamido-4-hydroxy-6-(isopropylamino)-s-triazine	ODIT
Deisopropylatrazine amide	2-acetamido-4-amino-6-chloro-s-triazine	CDAT
Chlorodiamino-s-triazine	2-chloro-4,6-diamino-s-triazine	CAAT
Ammeline	2,4-diamino-6-hydroxy-s-triazine	OAAT

Atrazine degradation rates were studied at an Atrazine concentration of 132 μM with Fenton's Reagent (1:1) in range of 1.06-2.69 mM. Almost 98% of Atrazine was removed in less than 30 seconds. The remaining atrazine degradation was slow and after 24 hour 1% of the initial amount remained. Using Fenton's Reagent with concentrations greater than or equal to 1.42 mM, atrazine was degraded in less than 30 seconds below detection limits. Fenton's Reagent with concentrations of 2.69 mM showed that atrazine transformation products accounted for less than 5% each of initial atrazine concentration and were depleted within 3 h. After 11.5 h of treatment only products remained were CDAT and CAAT. Excess H_2O_2 resulted in slower degradation of atrazine and followed pseudo-first-order kinetics. The half-life ($t_{1/2}$) of atrazine in 1:100, FeSO_4 : H_2O_2 was 1.9 h. Table 13 lists half-life of atrazine using various technologies.

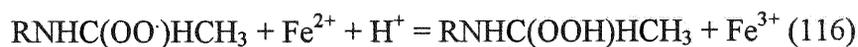
Table 13. Half-life of Atrazine from Various Technologies (Arnold et al., 1995)

Technology	Atrazine (μM)	Half-life ($t_{1/2}$) (m)	Reference
Fenton's Reagent(1.42mM;1:1)	132	0.5	Arnold et l., 1995
TiO_2/UV	116	20	Pelizzetti et al., 1990
$\text{H}_2\text{O}_2/\text{UV}$	96	1.8	Beltran et al., 1993
Ozone	465	16	Kearney et al., 1988
$\text{Fe}(\text{ClO}_4)_3$ (0.26mM)/UV	5.2	1.4	Larson et al., 1991

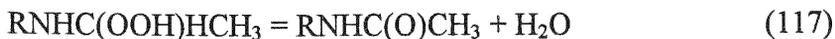
Thus as seen from Table 13, Fenton's Reagent shows the fastest depletion of atrazine. In chloride balance Arnold et al. (1995) found that OH^\cdot may react with Cl^- at

low pH to produce HOCl^- and Cl_2 causing underestimation of Cl^- concentrations, but the results suggested that Cl^- scavenging by OH^- was minimal. It was indicated by the study that dechlorination and dealkylation occur simultaneously and the batch treatment showed that dechlorination occurred more readily with alkylated s-triazines. Chlorinated products accounted for a large part of s-triazines present at end of Fenton's reaction. It is important to find the chlorinated products, as they may be as toxic as the parent compound.

Three different degradation mechanisms were proposed. In the first mechanism, the hydroxyl radical attacks atrazine by hydrogen abstraction from the secondary carbon of ethylamino side chain producing a free radical as shown in equation 113.



Molecular oxygen reacting with the free radical producing a peroxy radical of atrazine as in equation 115. This is reduced by Fe^{2+} to form a hydroperoxide. The rearrangement of the hydroperoxide forms amide through oxidation of secondary carbon with loss of a water molecule as in equation 117 (Larson et al., 1991; Kearney et al., 1988; Masten et al., 1994; and Pelizzetti et al., 1992).



The second mechanism proposed was dealkylation by hydrogen abstraction of the secondary carbon followed by introduction of an oxygen atom from either HO· or a high valent iron-oxo species forming an alcohol adjacent to electronegative nitrogen. The iron-oxo is unstable and decomposes to aldehyde and N-dealkylated s-triazine. The third mechanism is that dechlorination could occur by OH· radical attack of the s-triazine ring at the position occupied by chlorine group oxidizing the aromatic heterocyclic ring of atrazine as proposed by Potter and Roth (1993). Reduction of the ring by Fe²⁺ results in dechlorination to give hydroxylated s-triazine, Fe³⁺ and Cl⁻. The degradation pathway was proposed accounting for type and pattern of products generated in the study by Arnold et al. (1995). This is shown in Figure 16.

Reactions from a to e show that dechlorination, alkyl side chain oxidation and/or cleavage occur as parallel reactions giving CDIT, CIAT, CDET, CEAT or ODIT. Reactions f and g show that dealkylation gives CIAT and CDAT, this undergoes side chain oxidation and/or cleavage to form CDAT and/or CAAT as in reaction j, l and m. Similar reactions occur with CDET and CEAT to give CDAT and CAAT as main chloro-s-triazine compounds at end of Fenton's Reagent treatment as in reactions h, I, k, m, and n. Similar side chain cleavage is expected to occur with dechlorinated products as in reaction p.

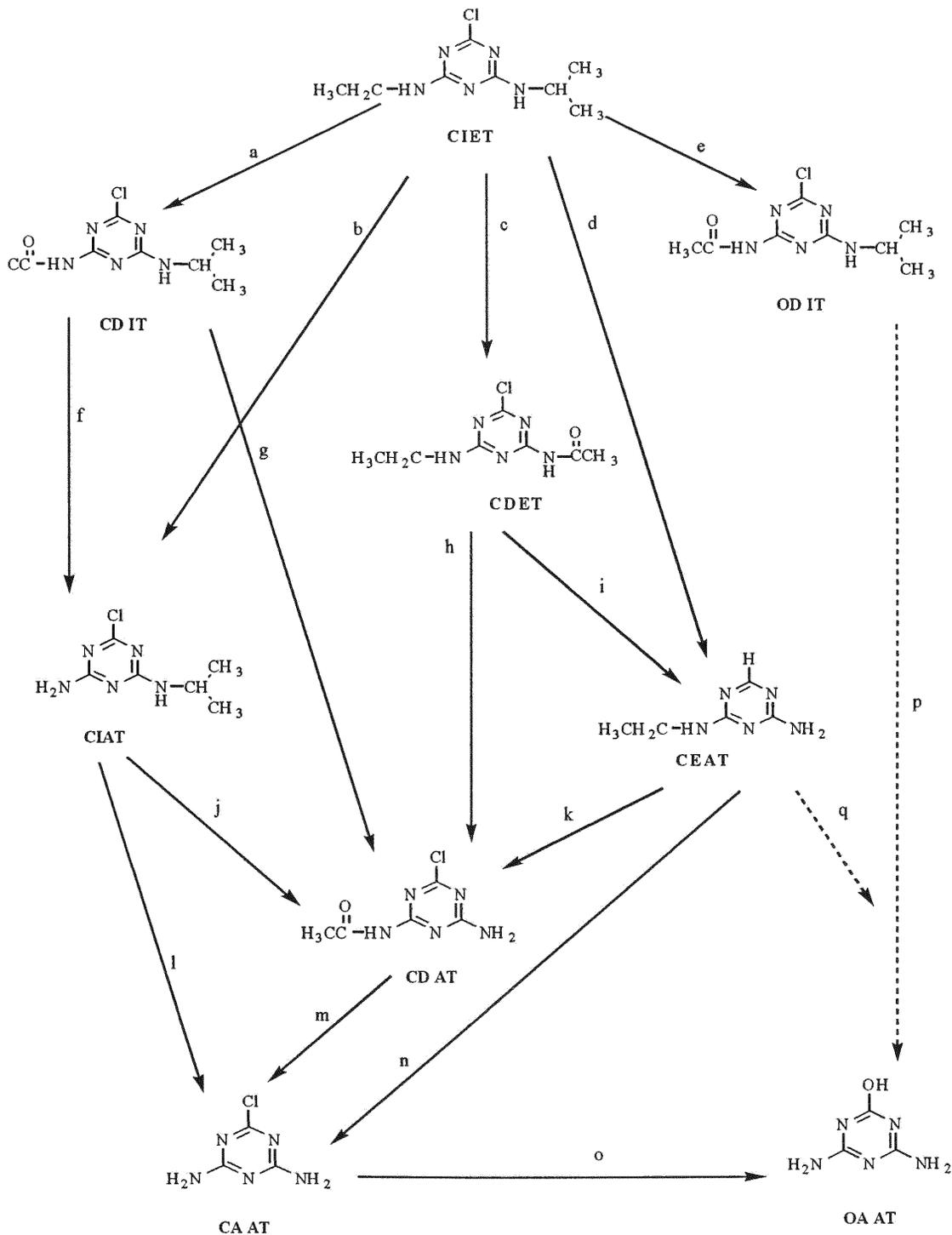


Figure 16. Degradation Pathway for Atrazine Treated with Fenton's Reagent

(Arnold et al., 1995).

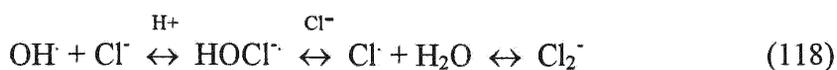
It was suggested that dechlorination of alkylated s-triazine derivatives in reaction q is most likely a sequential treatment of terminal products CDAT and CAAT resulted in only major transformation (reaction 0) to deaminated or/and dechlorinated products such as OAAT. The amide was unstable during isolation procedure CDIT, CDET and CDAT formed small amounts of CIAT, CEAT and CAAT respectively which indicated that the amide was easily cleaved.

3.2.6 Herbicides

2,4-D and 2,4-T are important post emergent herbicides, they were discontinued in U.S. in the mid-1970s. Pignatello (1992) studied their degradation and mineralization in presence and in absence of visible light containing small portion of UV component. 2,4-D in concentration of 0.1 mM was treated with $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ both greater than 1mM. 2,4-D was transformed in less than 1 min. The reaction took nearly 2 min at lower $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ concentration (0.25 mM) and gave 76-88% transformation. Transformation was independent of initial pH, but when Fe^{3+} (instead of Fe^{2+}) was used, the disappearance of parent compound was more sensitive to pH. The optimum conditions for the transformation of 2, 4-D by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in both perchlorate and sulfate solution was at $[\text{Fe}^{3+}] = 1\text{mM}$, $[\text{H}_2\text{O}_2] = 2.5\text{-}10\text{ mM}$, $\text{pH} = 2.7\text{-}2.8$, $[2, 4\text{-D}] = 0.1\text{mM}$. Transformation of 2,4,5-T at pH 2.8 was slower. It was also observed that the transformation was inhibited by methanol or chloride due to scavenging of active oxidant and by sulfate due to complexation of Fe^{3+} . The intermediates were polychlorophenols (DCP) and trichlorophenol (TCP). This reaction was sensitive to anion in solution. 2,4-

D was rapidly converted to highly hydrophilic intermediates. Herbicide concentration (0.1 vs. 0.5 mM 2,4-D) had no effect on 2,4-D mineralization. It was observed that it had no substantial effect on the extent or rate of mineralization on 2,4-D if Fe^{2+} was replaced by Fe^{3+} .

The transformation and mineralization of herbicides by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ were promoted by irradiation with visible light with small UV component. In bright $\text{Fe}^{3+}/\text{H}_2\text{O}_2/h\nu$ system transformation of 2, 4, 5-T was complete in less than 0.3 hour and mineralization was complete in less than 2 hour. The transformations were observed to be 2.7 and 1.6 times faster for 2, 4-D and 2, 4, 5-T than in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (dark) respectively. Fenton's Reagent transformed the herbicides faster than $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and was seen to be important if the removal of parent compound was required without mineralization. Retardation of 2,4-D at low pH was attributed to prior complexation of Fe^{3+} and H_2O_2 where as retardation at pH above 3 was attributed to precipitation of Fe^{3+} to amorphous oxyhydroxides ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). It was also observed that hydroxyl radicals could be scavenged by chloride and sulfate as follows:



Reaction 118 was predicted to be slower than reaction 119. Chloride strongly inhibited 2,4-D transformation which suggested that the chloride ligand had minimal effect on Fe^{3+} reactivity and inhibition of 2, 4-D was mainly due to scavenging of $\text{OH}\cdot$. Scavenging of $\text{OH}\cdot$ by chloride at pH ~ 3 would begin to be significant when $[\text{Cl}^-]$ was above few millimolar. Dechlorination occurred rapidly after herbicide transformation. Phenoxy acetic acid decarboxylated to yield phenoxyethyl radical ($\text{PhOCH}_2\cdot$). If the corresponding (aryloxy) methyl radical was produced from 2,4-D and 2,4,5-T a reaction pathway to generate phenol was oxidation-hydrolysis-elimination as follows:



Irradiation with weak intensity light above 300 nm strongly accelerated degradation, the total mineralization was observed to be as in equation 121 when 2,4-D: Fe^{3+} : H_2O_2 was consumed as 1:4:5.



Pignatello and Baehr (1994) studied herbicides 2, 4-Dichlorophenoxy acetic acid (2, 4-D) and Metolachlor. Both the herbicides showed contrasting behavior to each other in a way that metolachlor was mostly sorbed and 2, 4-D was mostly in solution. The sorption studies indicated that about 10 to 16% of total 2, 4-D was sorbed where as 89% of total metolachlor was sorbed. Reactions were carried out in lab to study the behavior of herbicide and iron (III) complexes in soil, herbicide degradation, and comparison of

iron(III)-L with iron (II). Five Fe-L for the study were gallic acid (GAL), picolinic acid (PIC), rhodizonic acid (RHO), hydroxyethyleniminodiacetic acid (NTA) were used, these structures are shown in Figure 17.

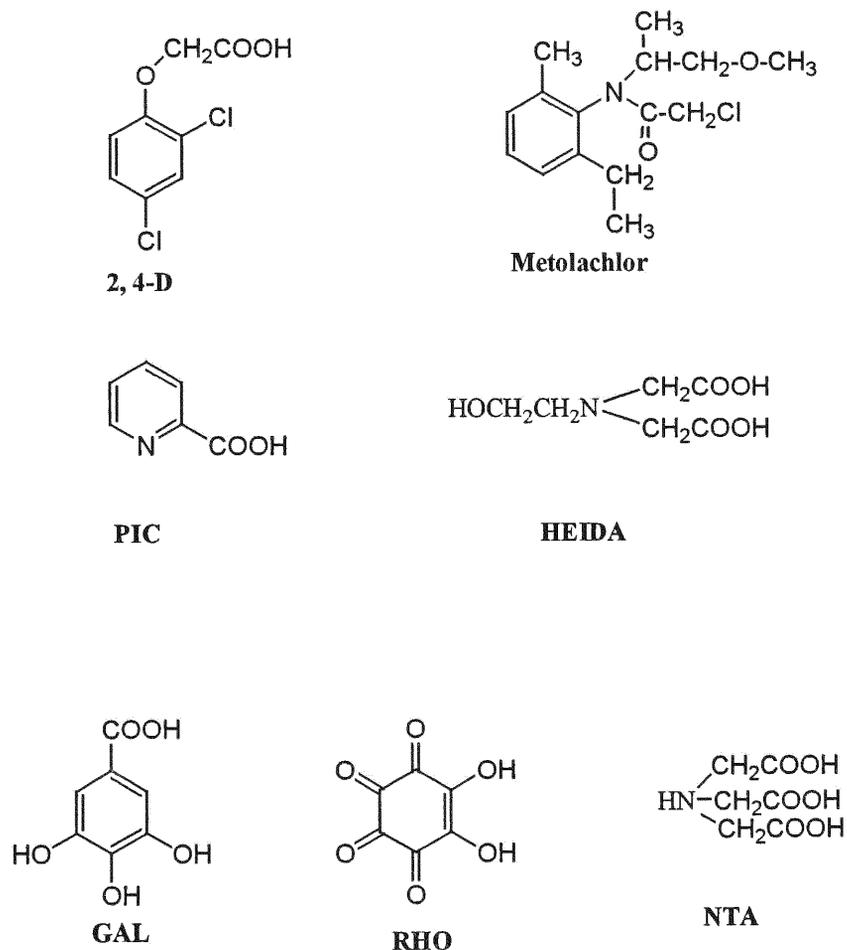


Figure 17. Molecular Structure of Ligands Studied in Degradation of Herbicides

(Pignatello and Baehr, 1994)

To study the herbicide degradation, it was assumed that the oxidation is solution phase process. Complexes Fe-GAL, -HEIDA, and -NTA were chosen to study as they

have relatively greater ability to stay in solution (due to the assumption). Studies were carried out with 2000 mg/Kg of 2,4-D equilibrated for 24 h, treated with 0.1 mol/Kg and 1×10^{-2} mol/Kg Fe-L or corresponding free ligand. It was observed that a Fe-L system was superior to free ligand alone and that free ligand did not extract enough Fe from soil to achieve practical levels of degradation. Fe-GAL was inferior to Fe-HEIDA and Fe-NTA. The complexes Fe-HEIDA and Fe-NTA gave significantly less removal at 0.1 mol/Kg hydrogen peroxide and nearly complete removal at 0.5 mol/Kg H_2O_2 . Metolachlor was treated using Fe-NTA and 0.5 mol/Kg H_2O_2 , about 92% was removed and the results indicated that even compounds that are initially mostly sorbed can react with hydroxyl radicals. It is unclear whether desorption precedes reaction or sorbed molecules are attacked. This indicated that a mass ratio of H_2O_2 to herbicide of 5.6 to 8.5 is required to remove the parent compound. The degree of ring and carboxy carbon mineralization increased in the order GAL>HEIDA>NTA. The mineralization was favored as H_2O_2 increased from 0.1 to 0.5 mol/Kg, but decreased with further increase to 1 mol/Kg. As H_2O_2 increased the extractable ^{14}C decreased in the order GAL>HEIDA>NTA. The remaining radioactivity increased with H_2O_2 concentration and followed order GAL>HEIDA>NTA.

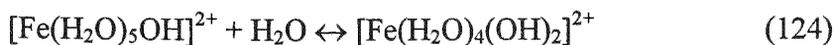
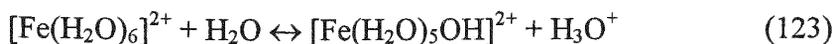
Pignatello and Baehr (1994) also compared iron (III)-L with iron (II) to remove the herbicides. Simple Fe^{2+} removed 61% of 2,4-D and 7% metolachlor, and Fe-NTA removed 99.3% of 2,4-D and 87% of metolachlor. Addition of NTA with Fe^{2+} was found to be as effective as Fe-NTA in removing metolachlor. This meant that Fe^{2+} is oxidized by H_2O_2 in milliseconds in situ to active Fe(III)-L complex.

Table 14. Phase Distribution of Herbicides in 1:1 Soil Suspension (Pignatello and Baehr, 1994)

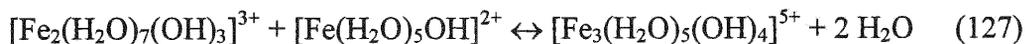
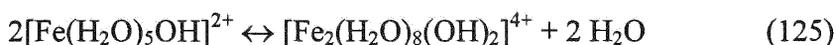
Compound	Application rate (mg/Kg)	Time (hour)	C _s /C _a (L/Kg)
2,4-D	1580	0	0.190 ± 0.02
2,4-D	1580	3	0.11 ± 0.02
Metolachlor	3020	0	8 ± 1.3

3.2.7 Dyes

The major problem with dye wastewater is the color produced by residual dyes during the dyeing process. If higher concentration of dyes and color of streams increase the transparency of streams will be reduced and thus plants in drainage would perish and ecosystem will be seriously damaged. Several amino-substituted azo dyes are mutagenic and carcinogenic. Attempt was first being made by Kuo (1992), to decolorize dye wastewater using Fenton's Reagent. It was suggested that dye decolorization was contributed to both oxidation as well as coagulation processes. During oxidation process, the hydroxyl radicals would attack organic substrate RH such as unsaturated dye molecule. The chromophore of the dye molecule would be destroyed and decolorized. Ferric ions generated from Fenton's reaction might form ferric hydroxo complexes with hydroxide ions as in reactions 123 and 124.



These complexes have a pronounced tendency to polymerize at pH 3.5-7 as in equation 125, 126, and 127:



As a result, coagulation inevitably remove portion of ferric ions. The experiments carried out showed that hydrogen peroxide and ferrous ions were more stable when pH was lower than 3.5. In basic solutions hydrogen peroxide was unstable and decomposed easily. Disperse dyes showed notable color removal above pH 9, this was attributed to coagulation generated by ferrous ions. The ferrous ions release electrons in basic solutions and forms ferric ions these ferric ions may form ferric hydroxo complexes which can coagulate the disperse dyes. Disperse dye is nonionic/insoluble dye and has very low activity to be readily reactive with hydrogen peroxide. Thus, active substance such as H_2O_2 would not deplete quickly and it would not be prompted to decompose further. Disperse dyes contain some dispersants which may react with the active substances and hydrogen peroxide is also prompted to decompose.

Ferrous sulfate was also studied and has a beneficial effect on dye degradation, because high ferrous concentration will make the redox reaction complete and increase coagulation, which improves decolorization. As for temperature effect, lower temperature reactions required longer time than higher temperature. Wastewater from dyeing and finishing mills are usually equal to 50° C. Kuo (1992) also studied five different types of dye wastewater randomly selected from mills and the results were in good agreement with those from the laboratory studies. The average percent COD removal was about 90% and average decolorization was above 97%. Kuo showed that effective pH should not be greater than 3.5. Effective dosage of H₂O₂ and ferrous sulfate was different for different types of dyes, decolorization is affected by different dye structures, the auxiliary group on the dye molecule, and temperature.

Degradation of azo dyes by Fenton's Reagent was studied by Spadaro et al., (1994). They studied different types of azo dyes and effort to identify benzene was made. The proposed mechanism by Spadaro for benzene generation is shown in fig 18. According to this mechanism, the hydroxyl radical adds to the azo linkage bearing carbon (C-4) of amine or hydroxy substituted ring. The hydroxyl radical adduct breaks to produce phenyldiazene and phenoxy radical. Hydroxyl radical or molecular oxygen can readily oxidize phenyldiazene by one electron to yield phenyldiazene radical and phenyldiazene is extremely unstable. Phenyldiazene radical is also unstable and cleaves homolytically to generate phenyl radical and molecular nitrogen. The phenyl radical might abstract hydrogen radical from ·O₂H or dye degradation products to produce benzene. Phenyl radical is not likely to be scavenged by molecular oxygen as it reacts

sluggishly with oxygen. The phenoxy radical might react with hydroxyl radical and oxygen to result in aromatic ring degradation. The study showed that there was a benzene generation with phenylazo substituted azo dyes. Benzene being priority pollutant, structure and concentration of individual azo dyes should be known before effluent is treated using process, which relies on hydroxyl radical chemistry.

Treatment of textile wastewater from a large dyeing and finishing mill by a continuous process of combined chemical coagulation, Fenton's Reagent and activated sludge process was investigated (Lin and Peng, 1995). The textile wastewater reservoir held 300 L of screened raw textile wastewater and was adjusted to pH. This was pumped into chemical coagulation tank where the front section contained polyaluminum chloride at dosage of 100 mg/L with a mixer operating at 150 rpm. Polymer was added in back section of tank at a concentration of 0.5 mg/L and mixer speed here was 50 rpm. The retention time was 2 minutes in each section. The sedimentation tank followed by chemical coagulation had a retention time of 60 minutes. This went to Fenton's reactor with a size of 25 x 25 x 88 cm. The treated textile wastewater from Fenton's reactor went to second sedimentation tank with a 60 min retention time. The top textile wastewater was finally passed to activated sludge tank where it was mixed with equal volume of activated sludge. They used a 1:1 ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$.

Decolorization of azo dyes was also studied by Solozhenko et al. (1995) by studying Active Yellow Lightfast 2KT (AYL). The kinetic measurements are shown in

Appendix A. AYL elimination depended on initial concentration of H_2O_2 , decolorization was accelerated by raising temperature or under sunlight influence.

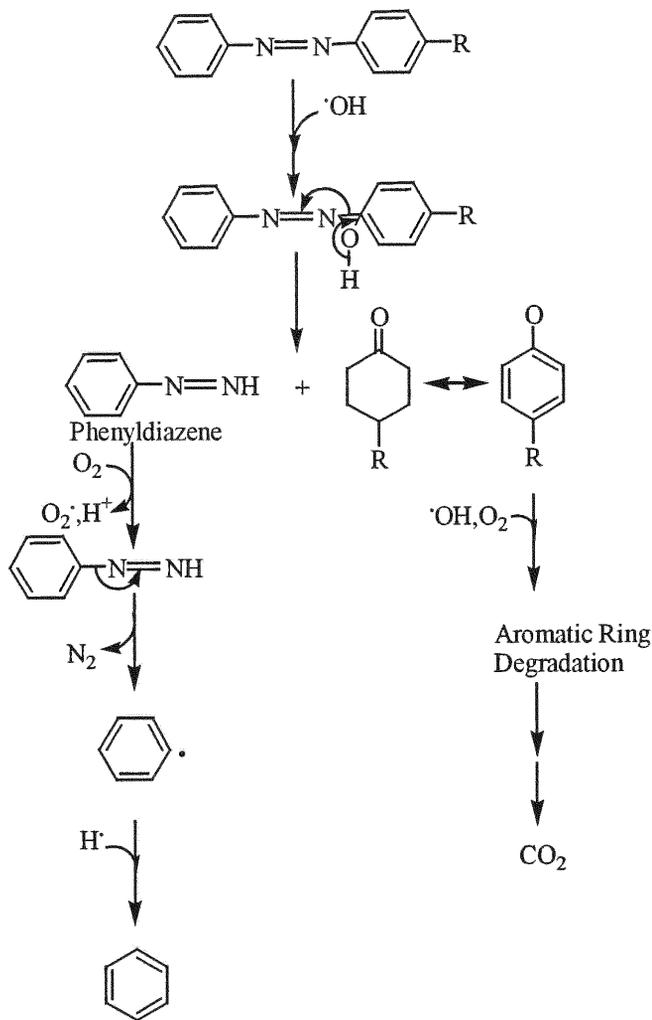


Figure 18. Proposed Mechanism for Benzene generation during Degradation of Azo Dyes (Spadaro et al., 1994)

3.3 Environmental Applications of Fenton's Reagent

Environmental applications in detoxification of hazardous substances require the treated concentration of toxic pollutants to a level of parts per million (ppm) and even parts per billion (ppb). Due to this stringent levels a need of truly elegant chemistry arises. These purity levels which were rarely considered in product synthesis are now possible for wastewater due to Fenton's Reagent.

Fenton's chemistry is a cost-effective and relatively easy way to destroy many toxics (Bigda, 1996). It attacks all reactive substrate concentrations under most adverse conditions. Hydrogen peroxide is used to remove contaminants as cyanide, sulfides, sulfites, chrome and heavy metals by varying batch conditions, with an iron catalyst, the process often oxidizes organics, as well as reducing hexavalent chrome to trivalent precipitable form. Batch reactors give great flexibility and can be programmed to treat many different wastewater's. Commercial Fenton reactors have been used for industrial wastewater treatment during the past 10 to 15 years (Bigda, 1996). An important application illustrating this is removal of phenol, formic acid and other organics from paint stripper rinse water in aerospace industry (Bigda, 1996). Large volumes of rinse water are generated when paint is removed from airline and military aircraft's, which would contain paint flakes, dirt, pigments, solvents, oil and chrome. Phenol levels of over 20,000 ppm in the rinse water have been reduced to less than one ppm using an automated Fenton system (Bigda, 1996). One commercial system has a computer or PLC programmed with 58 sequential commands to control the reactor and produce, for

discharge, purified wastewater which meets all local and EPA regulations. The treatment process can be set for simple neutralization, oxidation of organics, removal of volatile organic compounds (VOCs), reduction of chrome 6 and precipitation of heavy metals.

Fenton's Reagent can be used either as a single process or as one step in combination with other processes for wastewater treatment. Fenton's Reagent is used for treating specialty chemicals, process waters, in refinery and fuel terminals, in engine and metal cleaning, groundwater detoxification and site remediation.

Specialty chemical manufacturing includes manufacture of paint strippers as phenol and formic acid, wood treating chemicals as creosols and copper and plastics and adhesives as phenol formaldehyde. They generate wastewater similar to aerospace industry and contain chelating compounds. Wood preserving plants employ cresols, chlorophenols, arsenic and copper compounds. BTX and phenols often contaminate refinery wastewater streams and tank bottoms at fuel terminals. Plywood, laminates, and composite producers using adhesives can eradicate toxic residues from their effluent.

Process waters can be treated from the industries manufacturing explosives such as TNT and RDX, insecticides, dyes and ink, photochemicals, hazardous waste, pharmaceuticals and other chemicals (Bigda, 1996). Most photo chemicals can be economically treated with catalyzed peroxide. Munitions and demilitarization operations produce pink water containing explosives. TNT, RDX, HMX and others can be oxidized in water using Fenton's Reagent.

Fenton's chemistry has also been experimented to remediate sites and groundwater contaminated with pesticides, chlorinated organics, explosives and a variety of other toxics. Processes have also been cited to treat wastewater generated from soil washing.

Processes using Fenton's Reagent are advantageous where alternative technologies such as biological treatment processes are not effective. Reactions of Fenton's Reagent are faster than the biological processes. In decolorizing dye wastewater many commercial dyes are toxic to microorganisms involved. These types of compounds include high molecular weight PAHs and PCE. Fenton's Reagent has an advantage over UV/ H₂O₂ methods, where colored organic compounds interfere with UV/ H₂O₂ process by UV light absorption and can be successfully degraded by Fenton's Reagent. Fenton's Reagent is a chemical destruction process, thus it destroys the contaminant rather than just transferring them from one phase to another as in the case of physical treatments such as coagulation, adsorption etc. Capital equipment costs for application of Fenton's Reagent can be expected to be very low compared to UV/ H₂O₂ process. Fenton's Reagent has less operation and maintenance cost compared to ozonation process, operating costs depend primarily on reagent consumption.

Fenton's Reagent is most likely to be effective for on-site treatment applications rather than insitu because the reaction would require thorough mixing of the contaminants and the substrates. The optimum pH range for effective treatment by Fenton's Reagent is

in the acidic range of 2 to 4, this implies that a post treatment step is required for the pH adjustment. This treatment technology may not be applicable to alkaline soils and sludges with strong buffering capacities. Proper sludge disposal is required after the treatment. The primary factor contributing to chemical cost is the cost of hydrogen peroxide, it may be important due to this reason to optimize the amount of peroxide required. Fenton's reaction does not oxidize several chemicals which includes acetic acid, acetone, carbon tetrachloride, chloroform, maleic acid, malonic acid, methylene chloride, oxalic acid, n-paraffins, tetrachlorethane, and trichlorethane (Bigda, 1995). Fenton's reaction is highly exothermic, The reaction may be slow to start particularly if the temperature is below 65° F. Since initiation of the process may be sudden, especially if peroxide concentration is high, care must be taken while peroxide is added slowly for temperature to rise above 80° F.

4 OBJECTIVES

In the literature, no research has been conducted on Fenton's degradation of azo dyes comparing three different classes. The optimal dosages for Fe^{2+} , H_2O_2 , and pH are not determined for azo dyes. The effect of a number of azo bonds and auxiliary groups on Fenton's degradation of azo dyes is not documented. Therefore, eleven different azo dyes with three different classes (mono, dis and trisazo dyes) will be studied in this work. The objectives of this part of the Thesis are:

- 1) To establish a stoichiometric relationship among H_2O_2 , Fe^{2+} for the three classes of azo dyes to maximize the degradation efficiency.
- 2) To study the effect of pH an individual class of dyes.
- 3) To study the effect of a number of azo bonds and auxiliary groups on the degradation rate of azo dyes.
- 4) To compare the experimental optimal ratio with the theoretically derived optimal ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ for azo dyes.

5 EXPERIMENTAL

5.1 Materials

H_2O_2 (30%-35%) was obtained from Fisher Scientific Co. Stock solution of Fe^{2+} was prepared with $\text{FeSO}_4(7\text{H}_2\text{O})$ crystals. Monoazo dyes, Acid Blue 92, Acid Orange 8, Acid Red 8, Acid Blue 161, disazo dyes Acid Yellow 38, Acid Red 97, Direct Violet 51 and a trisazo dye Direct Blue 71 were also purchased from Aldrich Chemical Company. All solutions of H_2O_2 , Fe^{2+} and NaOH were prepared with deionized water. The chemical structures of eleven azo dyes are shown below in Figure 19, 20 and 21. The maximum absorption wavelengths of the dye solutions are listed in Table 15.

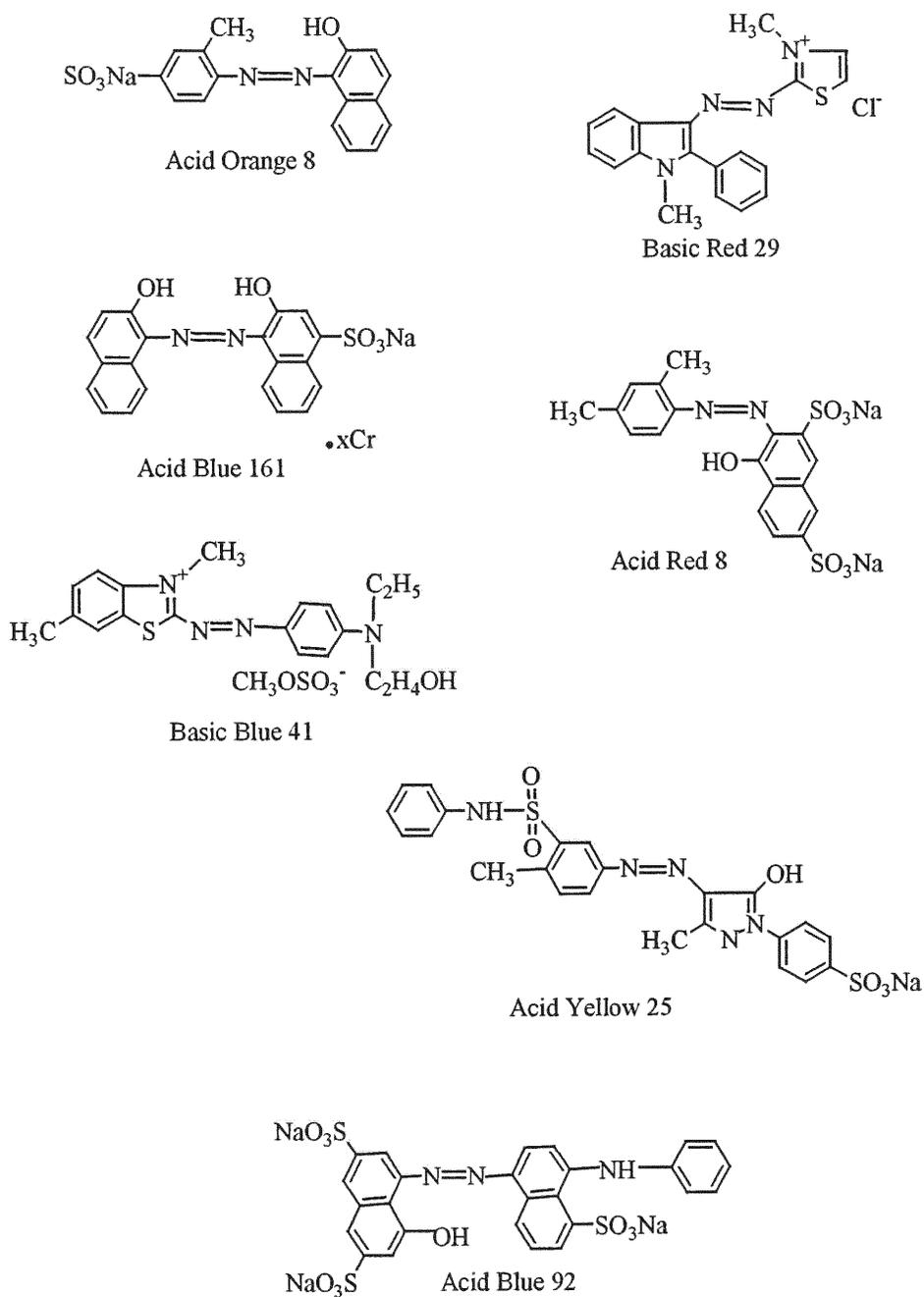


Figure 19. Molecular Structure of Monoazo Dyes (Aldrich Chemical Co.)

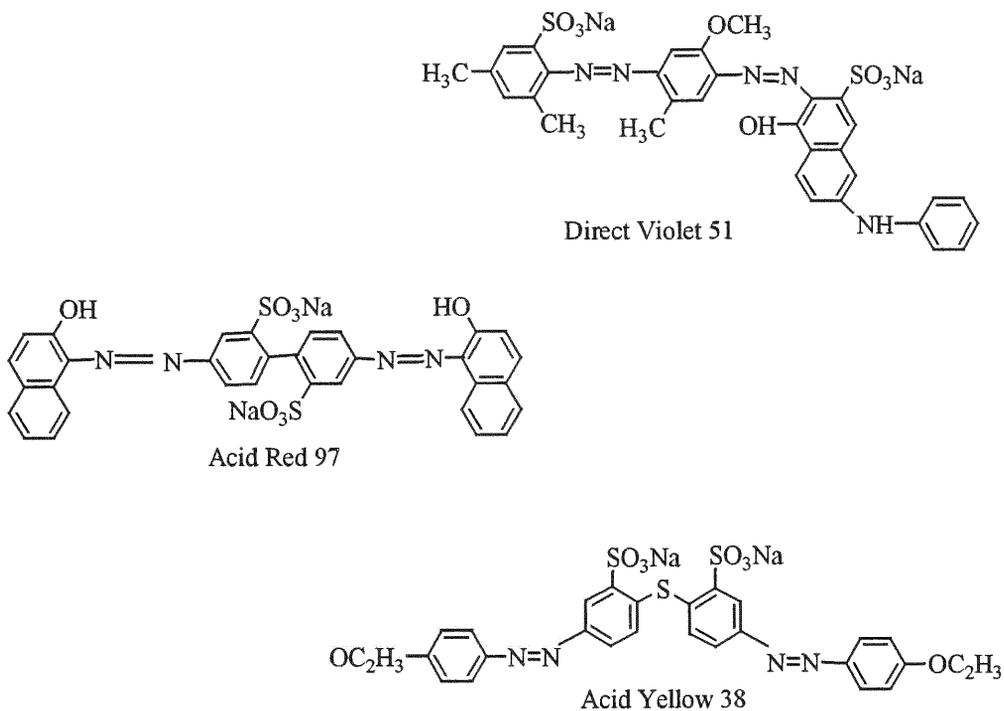


Figure 20. Molecular Structure of Disazo Dyes (Aldrich Chemical Co.)

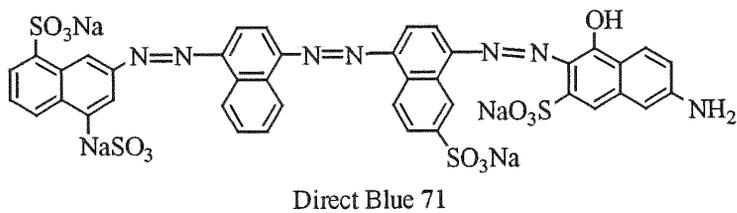


Figure 21. Molecular Structure of Trisazo Dyes (Aldrich Chemical Co.)

Table 15. Maximum Absorption Wavelengths of the Azo Dyes

Dye	Maximum absorption wavelength	Dye	Maximum absorption wavelength
Acid Blue 92	572	Acid Yellow 25	395
Acid Red 8	508	Acid Red 97	496
Acid Blue 161	602	Direct Violet 51	548
Acid Orange 8	490	Acid Yellow 38	374
Direct Blue 71	584		

5.2 Experimental Procedure

Experiments were performed in an open batch system of 50 mL beaker at room temperature of 23 °C. Solutions of the dye were adjusted to the desired pH by adding 1 M H₂SO₄ or 1 M NaOH. A stock solution of the dye with water was prepared and the pH was adjusted as desired. The test procedures are presented as the following groups:

- To assure quality control, duplicates were run to verify the accuracy of two sets of experimental data: [Dye] = 0.1 M, time = 1 min, [Fe²⁺] = 0.001 M for Acid Orange 8
pH = 2, 3, 4
[H₂O₂] = 0.00001 M, 0.0001 M, 0.001 M, 0.01 M, 0.1 M

- The effect of $[H_2O_2]$ on dye: $[Dye] = 0.1 \text{ M}$, $\text{time} = 1 \text{ min}$, $[Fe^{2+}] = 0.001 \text{ M}$

pH = 2, 2.5, 3, 3.5, 4 for Acid Yellow 38 and Acid Orange 8

pH = 3 for all monoazo dyes

pH = 4 for all disazo dyes

pH = 2, 3, and 4 for trisazo dye

$[H_2O_2] = 0.00001 \text{ M}, 0.0001 \text{ M}, 0.001 \text{ M}, 0.01 \text{ M}, 0.1 \text{ M}$
- The effect of $[Fe^{2+}]$ on dye: $[Dye] = 0.1 \text{ M}$, $\text{time} = 1 \text{ min}$, $[H_2O_2] = 0.001 \text{ M}$

pH = 2, 2.5, 3, 3.5, 4 for Acid Yellow 38 and Acid Orange 8

pH = 3 for all monoazo dyes

pH = 4 for all disazo dyes

pH = 2,3,and 4 for trisazo dye,

$[Fe^{2+}] = 0.0005 \text{ M}, 0.001 \text{ M}, 0.005 \text{ M}, 0.01 \text{ M}$,
- The effect of pH: $[Dye] = 0.1 \text{ M}$, Reaction time = 1 min,

$[H_2O_2] = 0.001 \text{ M}$, when $[Fe^{2+}] = 0.0005 \text{ M}, 0.001 \text{ M}, 0.005 \text{ M}, 0.01 \text{ M}$,

$[Fe^{2+}] = 0.001 \text{ M}$, when $[H_2O_2] = 0.00001 \text{ M}, 0.0001 \text{ M}, 0.001 \text{ M}, 0.01 \text{ M}$,

0.1 M

pH = 2, 2.5, 3, 3.5 and 4

A magnetic stirrer ensured a complete mixing condition at 400 rpm. The reaction time was 1 minute, and the equilibrium studies were performed. A control experiment was measured by adding a quantity of water equal to Fenton's Reagent and was measured as a sample. A control for $[H_2O_2]$ in absence of $[Fe^{2+}]$ with dye was measured, and a control for $[Fe^{2+}]$ was measured in absence of $[H_2O_2]$. A drop of 4 N NaOH was used to

terminate the oxidation by raising the pH to 9 in order to prevent the further generation of hydroxyl radicals through Fenton's reaction. For some of the dyes, the addition of NaOH resulted in sludge formation. In these cases a sample was taken and was immediately filtered through a 0.45 μm syringe filter (Acrodisc) and analyzed using a UV-Visible Diode Array Spectrophotometer (HP 8452A). Advanced quantification software is connected with the spectrophotometer, which can show the results by numerical analysis and in graphic forms based on statistical analysis. The color is measured by the absorbance intensity at the maximum absorbance wavelength according to Beer's Law. The calibration curve of each dye was established by the corresponding standard solutions. The number of standards used for calibration was three to four. Least Square method was used to calculate the standard deviation. The standard deviation of calibration ranged from 0.0003 to 0.0007. The correlation coefficient (r^2) was 0.999. One way analysis of a variance was performed on the duplicates to verify the standard deviation of the duplicates on statistical software SPSS. The method used to measure the samples is the same as that of Tang and Chen (1996) for both parts of the thesis.

6 RESULTS AND DISCUSSION

6.1 Quality Control

Several measures were taken to assure quality control. The removal of color was normalized with the initial dye concentration. A control experiment was conducted by adding a quantity of water equal to Fenton's Reagent and was measured as a sample. A

control for H_2O_2 in absence of Fe^{2+} with the dye was measured, and a control for Fe^{2+} was measured in absence of H_2O_2 . Both the controls gave the same concentration as the initial concentration of the dye. The color change was measured immediately after the reaction, in order to assure accuracy.

Two sets of duplicates were carried out. These duplicates were carried out to see if any experimental errors existed, which might be the reason for the lines to fall closely for different pH. The duplicates were also carried out to verify the optimal pH range for monoazo dye Acid Orange 8 and the optimal pH ratio for the color removal. These duplicates were measured at a dye concentration of 1 M, pH levels of 2, 3, and 4 which was the main pH range of interest and at H_2O_2 levels of 0.1 M, 0.01 M, 0.001 M, 0.0001 M, and 0.00001 M for the reaction time of one minute.

From the removal of dye the results were very close for both of the runs. Thus, error bars were not the right choice to determine the statistics of proximity of the points. The data was run through a statistical software SPSS, and a one-way analysis of variance was performed on all the points. Estimated marginal means were calculated, and these are plotted as shown in Figure 22.

The 'tests of between subjects effects' showed very small P-values, which means that the probability of getting such extreme results if no interaction exists is very low. The case summary indicates that at H_2O_2 concentrations of 0.00001 M at all pH values the removal of color is almost equal, it is also the same for H_2O_2 concentration of 0.0001

M at pH 3 and 4, but for higher concentrations, these values are significantly different, and their probability of being same for one concentration at different pH is nil (P-value). The standard deviation was also calculated for the mean and is listed in table 16 along with a case summary.

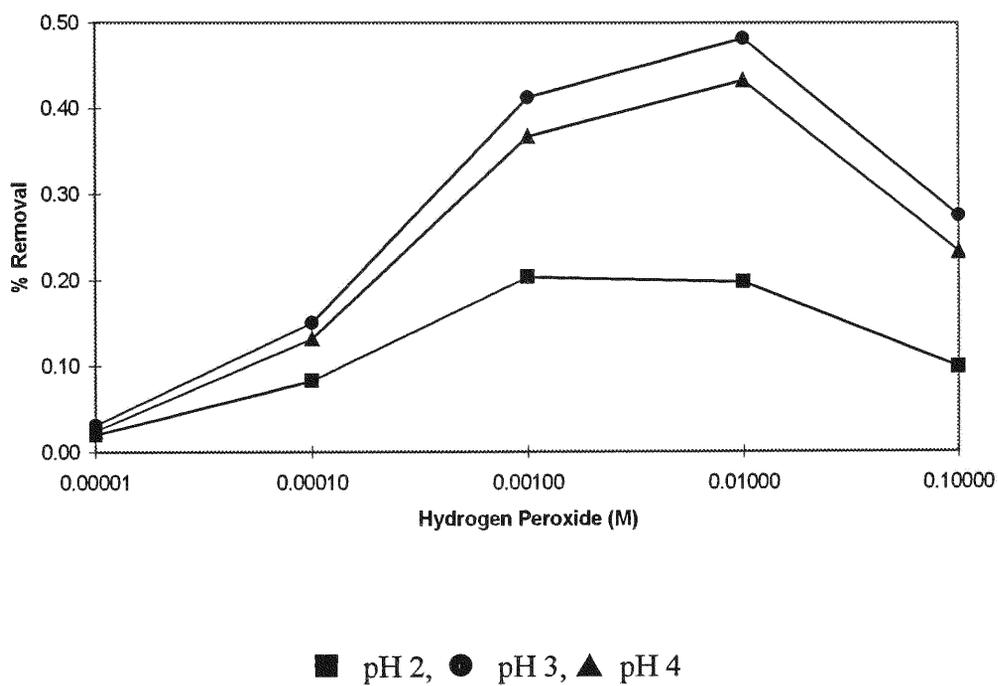
Table 16. Case Summary and Standard Deviation of Duplicates

ID	H ₂ O ₂ (M)	pH	%Rem. 1	%Rem. 2	Mean	Std. Dev.
1	0.00001	2	0.0151	0.0253	0.0202	0.0072
2	0.0001	2	0.0847	0.0798	0.0822	0.0034
3	0.001	2	0.2058	0.2023	0.2040	0.0025
4	0.01	2	0.2220	0.1741	0.1981	0.0339
5	0.1	2	0.1196	0.0775	0.0985	0.0298
6	0.00001	3	0.0266	0.0360	0.0313	0.0662
7	0.0001	3	0.1642	0.1363	0.1503	0.0197
8	0.001	3	0.4200	0.4060	0.4130	0.0099
9	0.01	3	0.4687	0.4953	0.4820	0.0188
10	0.1	3	0.2766	0.2730	0.2748	0.0025
11	0.00001	4	0.0271	0.0213	0.0242	0.0041
12	0.0001	4	0.1457	0.1179	0.1318	0.0196
13	0.001	4	0.3734	0.3617	0.3675	0.0083
14	0.01	4	0.4425	0.4241	0.4333	0.0129
15	0.1	4	0.2411	0.2335	0.2328	0.0054
					Total	0.1526

Figure 22 also demonstrates two major points. First, the optimal pH for the color removal of monoazo dye Acid Orange 8 is 3, and second, the optimal H₂O₂ concentration for color removal in this treatment ranges from 0.001 M to 0.01 M which means that H₂O₂/Fe²⁺ ratio for monoazo dye Acid Orange 8 ranges from 1 to 10 at Fe²⁺ concentration of 0.001 M. The descriptive statistics from the general linear model is

listed in table 17. The total of the mean of different H_2O_2 concentrations was calculated for pH 2, 3 and 4. The total of mean shows that the highest removal is observed at H_2O_2 concentration of 0.01 M, indicating the experimental optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 10. This result agrees well with the theoretical optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 11.

From the mean of the descriptive statistics, the total mean of color removal is highest for H_2O_2 concentration of 0.01 M and the decreasing order is 0.01M, 0.001 M, 0.1 M, 0.0001 M and 0.00001 M. This implies that the optimal ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ in the decreasing order is 10, 1, 100, 0.1 and 0.01. The statistics also imply that pH 3 shows the greatest removal compared to pH 2 and pH 4. Since the standard deviation is very low, it is reasonable to say that the experimental error is nil.



Experimental Conditions: Dye Concentration = 1 M, Fe^{2+} = 0.001 M,

Temperature = 23 °C, Time = 1 min

Figure 22. Estimated Marginal Means of Removal

Table 17. General Linear Model: Descriptive Statistics

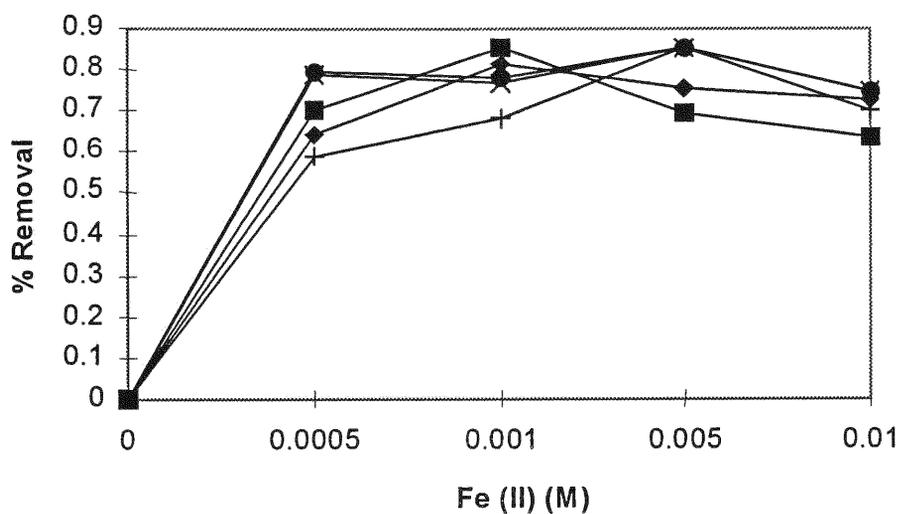
HP	pH	Mean	Std. Deviation	N
0.00001	2	0.02021	0.007234	2
	3	0.03126	0.006628	2
	4	0.02424	0.0040932	2
	Total	0.02524	0.0068998	6
0.0001	2	0.08222	0.003445	2
	3	0.15027	0.019716	2
	4	0.1318	0.096134	2
	Total	0.1214	0.033882	6
0.001	2	0.20408	0.0024977	2
	3	0.41303	0.0099001	2
	4	0.3675	0.0082717	2
	Total	0.3282	0.098456	6
0.01	2	0.19805	0.033934	2
	3	0.481965	0.01879	2
	4	0.43331	0.012962	2
	Total	0.371108	0.13703	6
0.1	2	0.09854	0.0298	2
	3	0.27479	0.0025169	2
	4	0.237277	0.0053723	2
	Total	0.203538	0.084149	6
Total	2	0.120621	0.076097	10
	3	0.27027	0.1746	10
	4	0.23883	0.15792	10
	Total	0.209907	0.152614	30

6.2 Oxidation of Monoazo Dyes

6.2.1 Fe^{2+} and pH Effect on Acid Orange 8

Acid Orange 8 was selected as a representative dye to study the optimal pH for monoazo dyes. The effect of pH with different concentrations of Fe^{2+} for Acid Orange 8 degradation is shown in figure 23. The optimal pH for Fenton's Reagent usually changes for the organic compounds to be oxidized. For example, the optimal pH is 3.5 for chlorinated phenols (Potter and Roth, 1993), 2 to 3 for pentachlorophenol (Watts et al., 1990), 3.5 for 2, 4-dichlorophenol (Tang and Huang, 1997), 3 for chlorobenzene (Sedlak and Andren, 1991), 3.5 for chlorinated aliphatic organic (Tang and Huang, 1996), 4 to 5 for 2, 4-dinitrotoluene (Mohanty and Wei, 1993), 3.5 to 4 for decolorizing dye (Kuo, 1992) and 4 for continuous treatment of a textile wastewater (Lin and Peng, 1995). Since the optimal pH may range from 2 to 4, the pH levels to be studied for each model dye are selected as 2, 2.5, 3, 3.5, and 4.

Figure 23 shows that the percentage removal of Acid Orange 8 increases with increasing Fe^{2+} concentration upto 0.0005M. Above this concentration at pH 2 and 2.5 the percentage removal is 80 - 85 %. At an Fe^{2+} concentration of 0.001 M, the degradation curve at pH 2 and 2.5 are almost the same. At pH 3.5 and 4, the maximum percentage removal is 85.6 % at Fe^{2+} concentration of 0.005 M. Figure 23 suggested that the optimal pH is approximately 3 to 3.5, for most cases and optimal Fe^{2+} is from 0.001 M to 0.005 M.

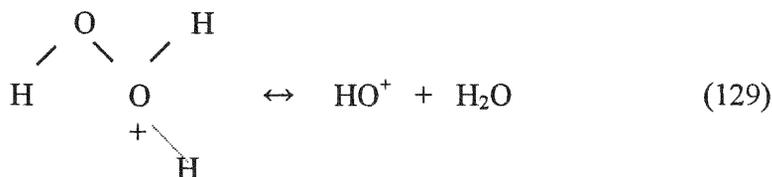


◆ pH 2, ■ pH 2.5, ● pH 3, X pH 3.5, + pH 4

Experimental Conditions: Dye Concentration = 0.1 M, H_2O_2 = 0.001 M,

Temperature = 23 °C

Figure 23. Effect of pH and Fe^{2+} on Degradation of the Monoazo Acid Orange 8



The OH^{\cdot} is strongly electrophilic in nature, which will facilitate electron transfer from Fe^{2+} to H_2O_2 . Therefore, hydroxyl radicals will be more efficiently generated. As pH increases from 3 to 4, the degradation of Acid Orange 8 increases only with an increasing concentration of hydrogen peroxide. For most concentrations of hydrogen peroxide, pH 3 had the maximum degradation. Therefore, pH 3 was selected as the optimal pH to study the effect of H_2O_2 on the other monoazo dyes.

6.2.2 Effect of Fe^{2+} on Monoazo Dyes

The effect of Fe^{2+} on degradation of monoazo dyes at H_2O_2 concentration of 0.001M and pH 3 is shown in figure 25. Figure 25 demonstrates that the monoazo dyes such as Acid Red 8, Acid Blue 161 and Acid Blue 92 have similar degradation patterns at different Fe^{2+} concentrations. For these three dyes the maximum degradation was observed at Fe^{2+} concentration of 0.001 M. This means that the optimal ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ for these dyes is 1, which is the same as Acid Orange 8. Therefore, the optimal ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ for all the monoazo dyes is 1. Apparently, the degradation of dyes is a function of the molecular structure of dyes. In our previous studies, the number of azo bonds contained in an azo dye is also an important factor in determining the

degradation rates by different oxidation processes (Tang et al., 1996; Tang and Chen 1996; Kuo, 1992; and Tang and An, 1995). The degradation rates of monoazo dyes in decreasing order is given by Acid Blue 92, Acid Red 8, Acid Orange 8 and Acid Blue 161 at the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 1.

6.2.4 Effect of H_2O_2 on Monoazo Dyes

Figure 26 shows the percentage degradation of dyes at pH 3. It shows that the degradation of all the monoazo dyes increases with H_2O_2 concentration. However, there is an optimal amount of H_2O_2 required to degrade each dye efficiently. The optimal ratio for Acid Red 8, Acid Blue 92, Acid Blue 161 and Acid Orange 8 ranges from 10, 1-10, 0.1, to 1-10, respectively.

6.3 Oxidation of Disazo Dyes

6.3.1 pH and Fe^{2+} Effect on Acid Yellow 38

Acid Yellow 38, selected as a representative disazo dye, was investigated under the same experimental conditions employed for the monoazo dye, Acid Orange 8. Figure 27 shows the degradation of Acid Yellow 38 at different pH levels as function of Fe^{2+} . These data suggest that the degradation of Acid Yellow 38 at pH 4 is significantly better than that at pH 2. In addition, pH also effects the optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio. For example, the optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio is 0.2 at pH 2, while the optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio is 1 at pH 4. Since disazo dyes contain two azo bonds, complexation between the azo dye and Fe^{2+} should be favorable at higher pH due to less electrical repulsive forces. As a result,

hydroxyl radicals generated through the use of Fenton's Reagent should be more readily available to the dye molecule, for the degradation at a high pH of 4, becomes faster than at low pH of 2.

6.3.2 pH and H₂O₂ Effect on Acid Yellow 38

Figure 28 shows the degradation of Acid Yellow 38 as a function of pH and H₂O₂ dosage. Figure 28 supports the fact that more hydroxyl radicals are generated at pH 4 in oxidizing the disazo dye at pH 4 than at any other pH, because at pH 4 the degradation of Acid Yellow 38 is highest for all the dosage of H₂O₂. This figure also indicates that the degradation of Acid Yellow 38 also increases to a certain level with an increase in H₂O₂ and then either remains steady as in case of pH 3.5 or decreases as in the cases of pH 2 and 2.5. Degradation of the dye increases at pH 3 and 4 with an increase in concentration of H₂O₂. Figures 22 and 23 indicate that pH 4 was optimal pH and was selected for all the other disazo dyes studied.

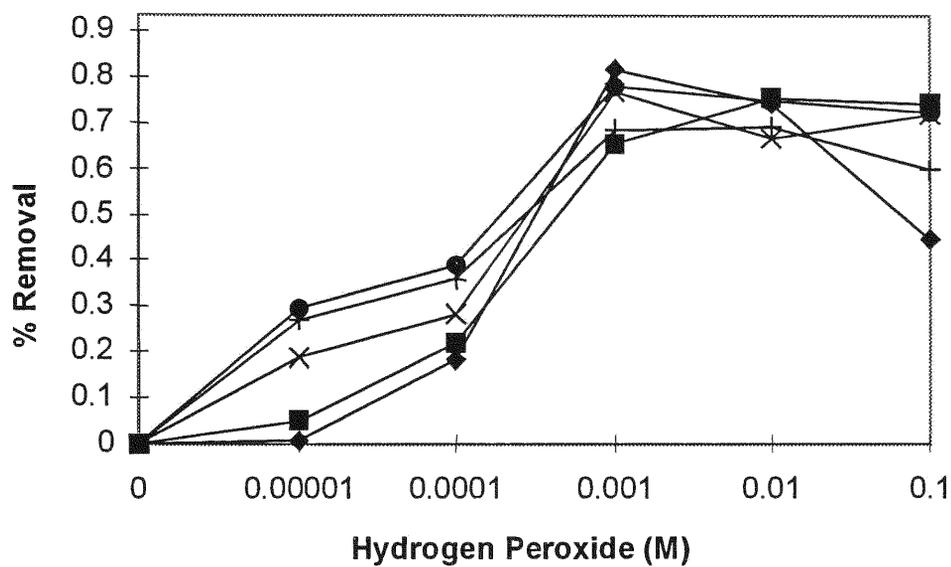
6.3.3 Effect of Fe²⁺ on Disazo Dye

Figure 29 shows the relationship between percentage removal of disazo dyes and Fe²⁺ dosage at the optimal pH 4. The maximum degradation of disazo dye is observed at an Fe²⁺ dosage of 0.001 M. The degradation decreases for Acid Yellow 8 at higher concentrations of ferrous ions whereas degradation increases to about 2% at 0.005 M and then decreases to 26% at 0.001 M after 1 minute for Direct Violet 51. For Acid Red 97,

degradation increases about 1 % each with an increase in concentrations of Fe^{2+} at 0.005 M and 0.001 M. Therefore, the optimal amount of Fe^{2+} is 0.001 M. The decrease in the degradation rate or the steady degradation rate with further increase in Fe^{2+} concentrations can be attributed to the fact that Fe^{2+} can also react with hydroxyl radicals through the reaction given in equation 7.

6.3.4 Effect of H_2O_2 on Disazo Dye

Figure 30 shows the relationship between percentage removal and H_2O_2 concentration for the other disazo dyes. At fixed pH and Fe^{2+} concentrations, the percentage removal of the disazo dyes increases with increasing H_2O_2 . When the H_2O_2 concentration further increases, the degradation increases to about 8% for Acid Yellow 38, as H_2O_2 concentration increases from 0.001 M to 0.1 M. However, degradation is not significantly increased for Direct Violet 51, whereas degradation is decreased for Acid Red 97. This is consistent with equation 9, where a superoxide radical is formed at constant Fe^{2+} and excess of H_2O_2 which competes with the hydroxyl radical, resulting in the lower degradation of the organic substrate. Different dyes have different optimal dosages of H_2O_2 , but an optimal range of dosages occurs for molecules with similar structures. From figure 30, the optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ range for disazo dyes is 1 to 10.

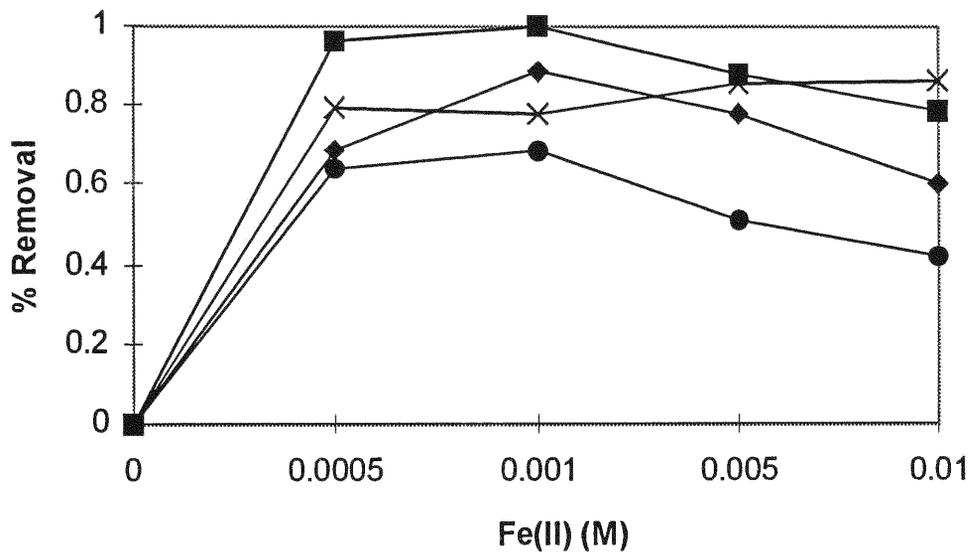


◆ pH 2, ■ pH 2.5, ● pH 3, X pH 3.5, + pH 4

Experimental Conditions: Dye Concentration = 0.1 M, Fe^{2+} = 0.001 M,

Temperature = 23 °C

Figure 24. Effect of pH and H_2O_2 on Degradation of the Monoazo Acid Orange 8

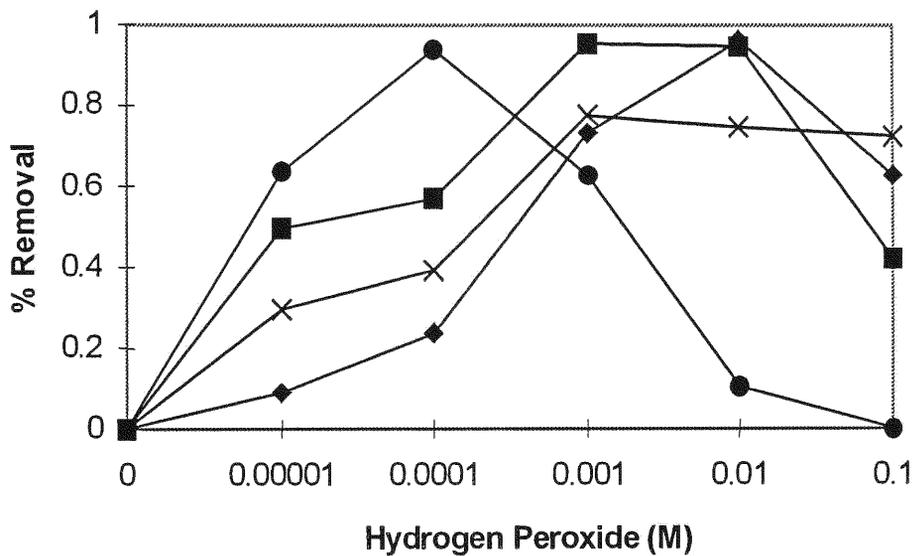


◆ Acid Red 8, ■ Acid Blue 92, ● Acid Blue 161, X Acid Orange 8

Experimental Conditions: Dye Concentration = 0.1 M, pH = 3, H₂O₂ = 0.001 M,

Temperature = 23 °C

Figure 25. Effect of Fe²⁺ on Degradation of the Monoazo Dyes

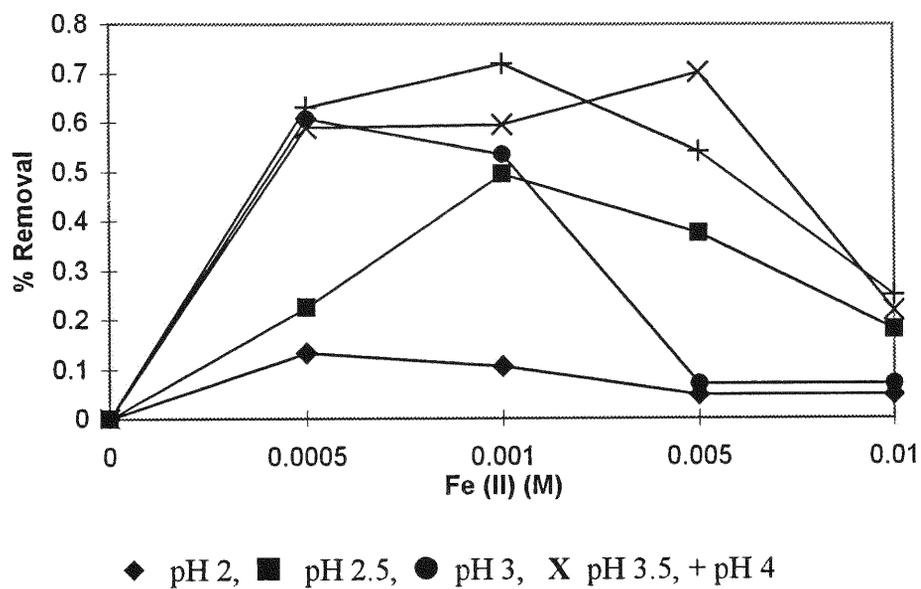


◆ Acid Red 8, ■ Acid Blue 92, ● Acid Blue 161, X Acid Orange 8

Experimental Conditions: Dye Concentration = 0.1 M, pH = 3, Fe^{2+} = 0.001 M,

Temperature = 23 °C

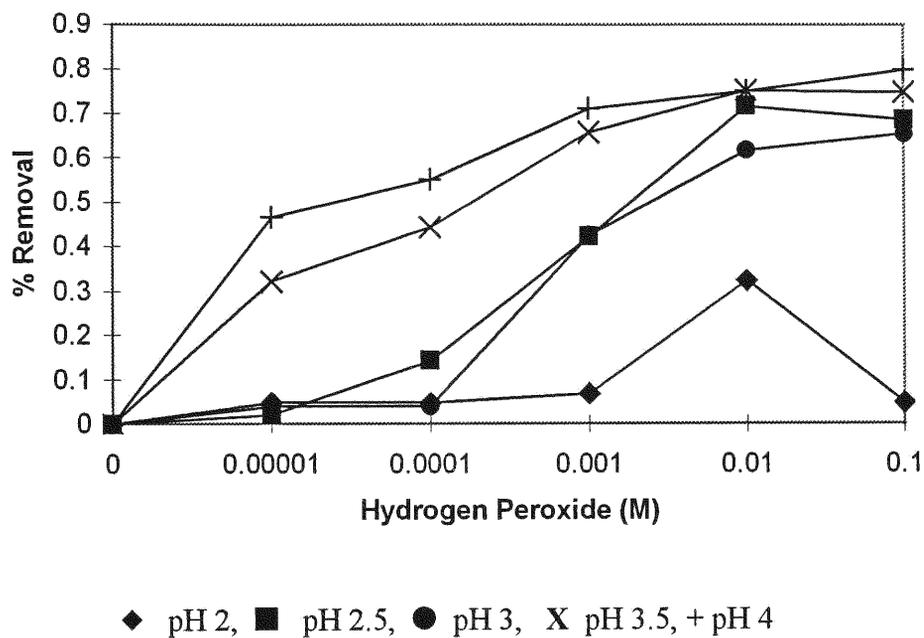
Figure 26. Effect of pH and H_2O_2 on Degradation of the Monoazo Dyes



Experimental Conditions: Dye Concentration = 0.1 M, H₂O₂ = 0.001 M,

Temperature = 23 °C

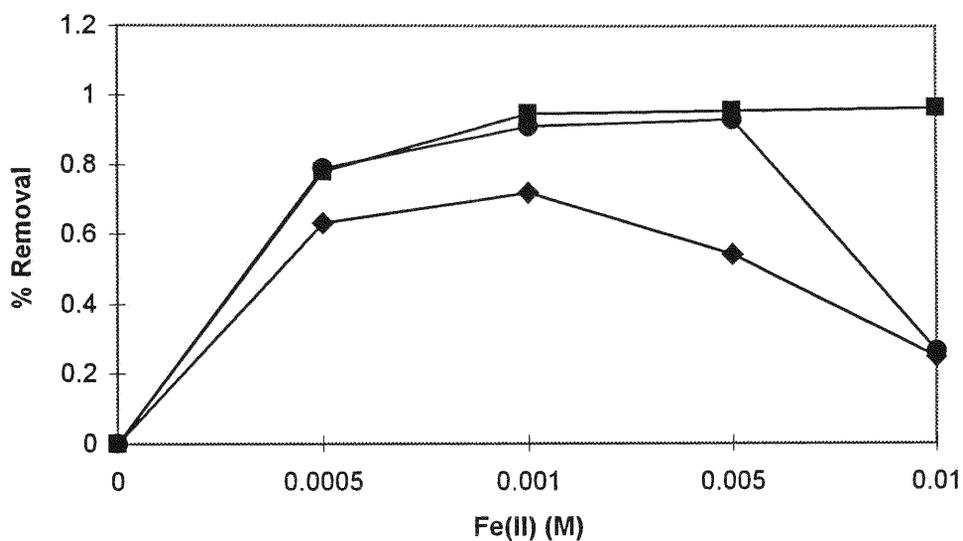
Figure 27. Effect of pH and Fe²⁺ on Degradation of Disazo Dye Acid Yellow 38



Experimental Conditions: Dye Concentration = 0.1 M, Fe^{2+} = 0.001 M,

Temperature = 23 °C

Figure 28. Effect of pH and H_2O_2 on Degradation of Disazo Dye Acid Yellow 38



Acid Yellow 38, ■ Acid Red 97, ● Direct Violet 51

Experimental Conditions: Dye Concentration = 0.1 M, pH = 4, H₂O₂ = 0.001 M,

Temperature = 23 °C

Figure 29. Effect of Fe²⁺ on Degradation of Disazo Dyes

6.4 Oxidation of Trisazo Dye

Degradation of trisazo dye Direct Blue 71 was studied at pH of 2, 3 and 4. At pH 2 the degradation was observed to be similar to that of mono and disazo dyes, but at pH 3 and 4 the dye degraded into a colorless liquid in few seconds. To study this rapid reaction, experiments were carried out by lowering the concentration of Fenton's Reagent. For example, the concentration of Fe^{2+} was lowered from 0.001 M to 0.0001 M to study the effect of H_2O_2 and the concentration of H_2O_2 was lowered from 0.001 M to 0.0001 M to study the effect of Fe^{2+} .

6.4.1 Effect of Fe^{2+} on Direct Blue 71

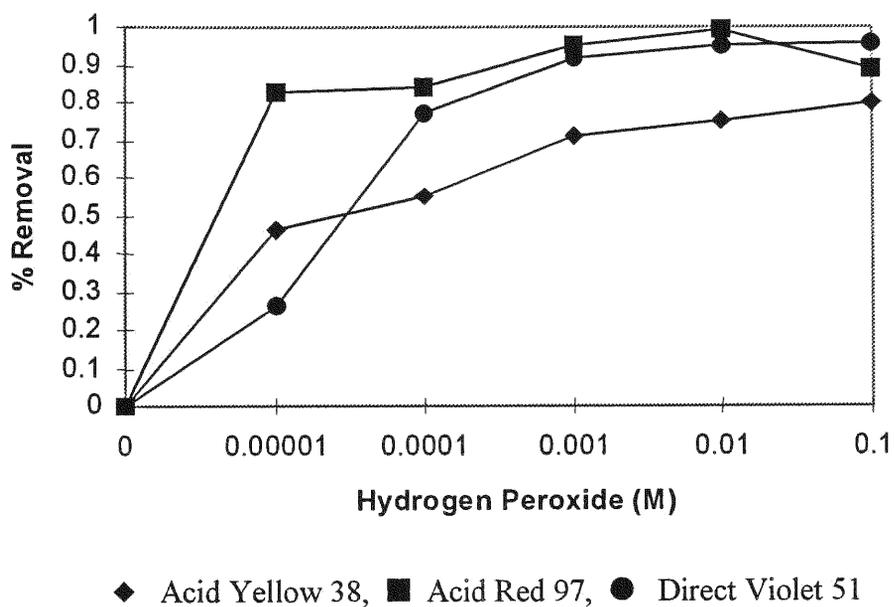
Figure 31 shows the relationship between percentage removal of trisazo dye Direct Blue 71 and Fe^{2+} . The optimal amount of Fe^{2+} required for degradation of Direct Blue 71 is 0.001 M at pH 2, and the optimal ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ is one for Direct Blue 71. Further increase in ferrous ions at a constant amount of hydrogen peroxide results in excess of ferrous ions which will be oxidized to ferric ions by consuming hydroxyl radicals. As a result, the percentage removal of trisazo dye decreases.

6.4.2 Effect of H_2O_2 on Direct Blue 71

Figure 32 relates the degradation of Direct Blue 71 in the presence of different concentrations of H_2O_2 . The figure shows that at pH 2 the degradation of Direct Blue 71

increases linearly with increase in H_2O_2 , till H_2O_2 concentration of 0.001 M, with further increase in concentration, the degradation is same, which has also been observed during the destruction of BTX by Fenton's Reagent (Lou and Lee, 1995). As explained by Harber and Weiss (1934) the oxidation of organic compounds is second order at low H_2O_2 and fixed Fe^{2+} . But with an increase in the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, the reaction approaches zero order kinetics and depends on the competition between hydroxyl radicals and superoxide radicals (Mohanty and Wei, 1993). Thus, at fixed Fe^{2+} and higher H_2O_2 , fewer hydroxyl radicals are available due to the limited Fe^{2+} concentration.

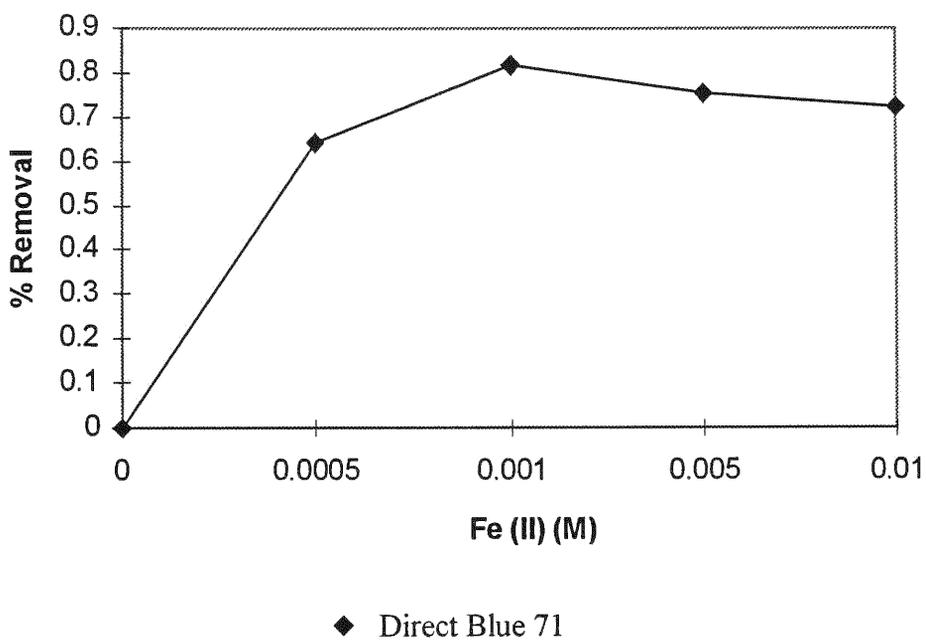
Apparently, the degradation of dyes is a function of the molecular structure of dyes. In our previous studies, the number of azo bonds in an azo dye is also an important factor in determining the degradation rates by different oxidation processes (Tang et al., 1997; Tang and Chen 1996; Kuo, 1992; and Tang and An, 1995). The degradation rates of monoazo dyes in decreasing order is Acid Blue 92, Acid Red 8, Acid Orange 8 and Acid Blue 161 degradation at the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of one.



Experimental Conditions: Dye Concentration = 0.1 M, pH = 4, Fe^{2+} = 0.001 M,

Temperature = 23 °C

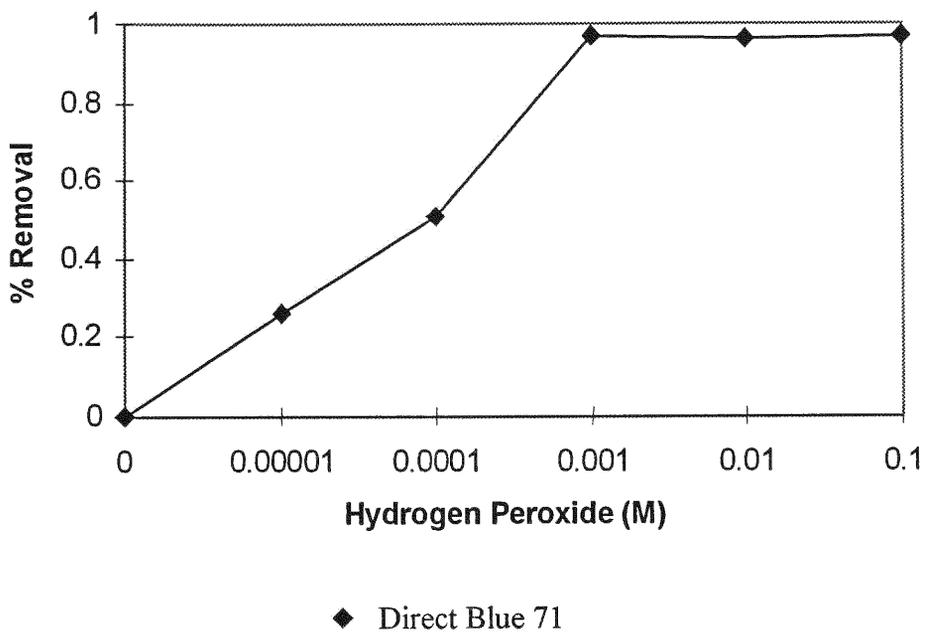
Figure 30. Effect of pH and H_2O_2 on Degradation of Disazo Dyes



Experimental Conditions: Dye Concentration = 0.1 M, pH = 2, H₂O₂ = 0.001 M,

Temperature = 23 °C

Figure 31. Effect of Fe²⁺ on Degradation of Trisazo Dye



Experimental Conditions: Dye Concentration = 0.1 M, pH = 2, Fe^{2+} = 0.001 M,
Temperature = 23 °C

Figure 32. Effect of H_2O_2 on Degradation of Trisazo Dye

6.5 The Optimal Ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$

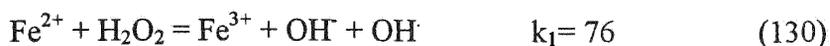
As an excess of H_2O_2 and Fe^{2+} will scavenge hydroxyl radicals, the H_2O_2 to Fe^{2+} ratio has to be maintained at an optimal range for the maximum degradation rate of azo dyes to be achieved. Table 16 summarizes the optimal ratio of H_2O_2 to Fe^{2+} for the degradation of different classes of azo dyes at different pH levels. For each dye at optimal pH, effects of H_2O_2 on dye degradation at a constant Fe^{2+} concentration, and the effect of Fe^{2+} on dye degradation at a constant H_2O_2 concentration have been investigated independently. The range of the optimal ratio of H_2O_2 to Fe^{2+} was obtained. Table 16 suggests that the optimal ratio of monoazo dyes and disazo dyes varies from 1 to 10, and that for trisazo dye is 1 in both cases (color removal at different H_2O_2 concentration when Fe^{2+} concentration is constant and color removal at different Fe^{2+} concentration when H_2O_2 concentration is constant).

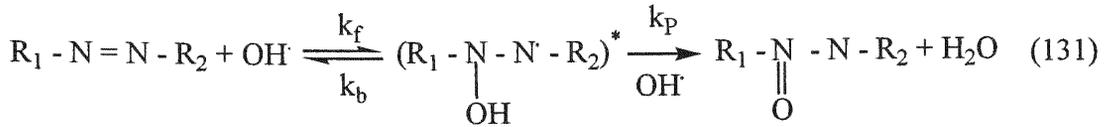
Supporting these findings are extensive reports of the H_2O_2 to Fe^{2+} ratio in the literature for organic compounds. The optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio was reported as 3 to 9 for phenol (Eisenhauer, 1964; and Keating et al., 1978), 0.122 for a textile wastewater (Kuo, 1992), 8.3 for dinitrotoluene (DNT) (Mohanty and Wei, 1993), 1 for atrazine (Arnold et al., 1995), 0.2 for benzene, toluene and xylene (BTX) (Lou and Lee, 1995) and 2 for trihalomethanes (THM) (Tang and Tassos, 1997).

Table 18. Optimal Ratio of H₂O₂ to Fe²⁺ for Degradation of Azo Dyes

Azo Dyes	Optimal over pH range of 2 to 4				
	2	2.5	3	3.5	4
Monoazo	Acid Orange 8		1 to 10		
	Acid Red 8		1 to 10		
	Acid Blue 161		0.1 to 1		
	Acid Blue 92		1 to 10		
Disazo	Acid Yellow 38				1 to 10
	Acid Red 97				1 to 10
	Direct Violet 51				1 to 10
Trisazo	Direct Blue 71	1			

So far, no theoretical treatment has been reported for predicting the optimal ratio of H₂O₂ to Fe²⁺ for azo dyes. This thesis presents the comparison of theoretical and experimental values for azo dyes to resolve this problem for the first time. To theoretically predict the optimal ratio of H₂O₂ to Fe²⁺ the kinetic model reflecting the effect of H₂O₂, Fe²⁺, and organic compounds on the oxidation kinetics developed by Tang and Huang (1997). Briefly, the reaction in equation 1 is the key initiation step in the generation of hydroxyl radicals. Because azo dyes are unsaturated compounds, the first step is the addition of a hydroxyl radical to the double bond of the molecule. After hydroxylation, an activated complex can be assumed as the transition state intermediate. The activated complex will either dissociate to form products such as carbon dioxide and water or return back to the original reactant:





Where: k_f is the rate constant for formation of activated intermediate after the reaction of hydroxyl radicals with the azo dyes [$k = 4.4 \cdot 10^9 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$]. k_b is the rate constant for decomposition of activated intermediate after hydroxyl radicals reaction with the azo dyes and k_p is the rate constant for formation of products by dissociation of the activated intermediate.

In addition to the above reaction in equation, hydroxyl radicals may be terminated through the following reactions at constant pH.

Based upon the above reactions, the kinetic model was developed as follows:

$$r_s = k_{\text{observed}} \left\{ \frac{k_i [H_2O_2][Fe^{2+}]}{k_{i2} [Fe^{2+}] + k_{i3} [H_2O_2]} \right\}^n \quad (s) \quad (132)$$

Where n is the number of hydroxyl radicals needed for the oxidation of one azo dye molecule, r_s is the rate constant of reaction in equation $k_i = 51 \text{ M}^{-1} \text{ s}^{-1}$; $k_{i2} = 3 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{i3} = 2.7 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ are the values for reaction given in equations 1, 7 and 8, on pages 3 and 4, respectively, and

$$k_{\text{observed}} = \frac{k_p k_f}{k_b + k_p}$$

Equation 132 assumes that the oxidation kinetics are pseudo-first order to the concentration of dyes, based on the experimental observation by Watts et al. (1990) when hydroxyl radical concentration is constant.

To obtain the optimal ratio of H_2O_2 to Fe^{2+} , equation 132 can be differentiated with respect to H_2O_2 , and set to zero assuming that H_2O_2 is the optimal concentration defined as $(\text{H}_2\text{O}_2)_{\text{opt}}$. We set:

$$dr_s / d[\text{H}_2\text{O}_2] = 0 \quad (133)$$

The optimal concentration of H_2O_2 can be expressed as follows by solving the above equation.

$$[\text{H}_2\text{O}_2]_{\text{opt.}} = -k_{t2} [\text{Fe}^{2+}]_{\text{opt.}} (s) / 2k_{t3} \quad (134)$$

The optimal concentration of Fe^{2+} expressed as $(\text{Fe}^{2+})_{\text{opt.}}$ can be derived from the same mathematical approach:

$$dr_s / d[\text{Fe}^{2+}] = 0 \quad (135)$$

Then, the optimal concentration of Fe^{2+} is:

$$[\text{Fe}^{2+}]_{\text{opt.}} = -k_{t3} [\text{H}_2\text{O}_2]_{\text{opt.}} (s) / 2k_{t2} \quad (136)$$

Dividing equation 134 by equation 136, derives the optimal ratio of H_2O_2 to Fe^{2+} :

$$\left\{ \frac{[\text{H}_2\text{O}_2]}{[\text{Fe}^{2+}]} \right\}_{\text{opt.}} = \frac{k_{t2}^2}{k_{t3}^2} * \left\{ \frac{[\text{Fe}^{2+}]}{[\text{H}_2\text{O}_2]} \right\}_{\text{opt.}} \quad (137)$$

Therefore, the final form of the optimal ratio between H₂O₂ and Fe²⁺ is:

$$\left\{ \frac{[\text{H}_2\text{O}_2]}{[\text{Fe}^{2+}]} \right\}_{\text{opt.}} = \frac{k_{t2}}{k_{t3}} \quad (138)$$

$$\left\{ \frac{[\text{H}_2\text{O}_2]}{[\text{Fe}^{2+}]} \right\}_{\text{opt.}} = \frac{k_{t2}}{k_{t3}} = \frac{3 \times 10^8}{2.7 \times 10^7} = 11 \quad (139)$$

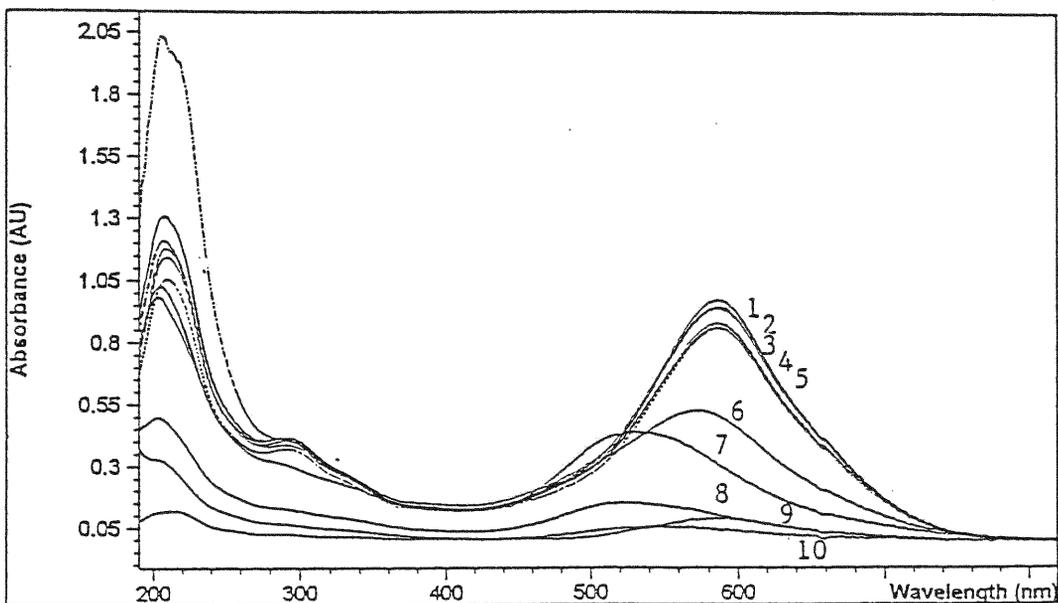
Substituting the numerical values into equation 138, produces an estimate of the theoretical optimal ratio of H₂O₂ to Fe²⁺ as the following:

Experimental values from this study ranging from 1 to 10 suggest that a greater amount of iron salt is required, if degradation was only due to the hydroxyl radical oxidation. Thus, the experimental results suggest that there is another mechanism, contributing to the consumption of Fe²⁺. One possible loss could be that the ferrous ion can serve as ligand for the azo bond and form a complex as follows:



If this complexation with dye molecule occurs, a lesser amount of Fe²⁺ than the initial Fe²⁺ concentration will be available for hydroxyl radical production. Recall from Table 18, that the optimal ratio of H₂O₂ to Fe²⁺ is 1 for trisazo dye. Since trisazo dyes have

three chromophore groups, the lower ratio is probably due to more azo bonds (-N=N-) available to complex with ferrous ions. During the experiments for trisazo dye Direct Blue 71, it was noted that the dye changed the color from blue to purple at pH greater than 2, this supports that complexes are formed. Figure 33 shows the evidence of complexation as the maximum wavelength shifted peaks during varying concentration of Fe^{2+} . The experiments were carried out at pH 4, at an Fe^{2+} concentration of 0.0001 M and different H_2O_2 concentration for curves 1 to 6 and at an H_2O_2 concentration of 0.0001 M and different Fe^{2+} concentration for curves 6 to 10. The change in H_2O_2 concentration did not decrease the color of the dye, but with the change in Fe^{2+} concentration the complexation was observed, since the color of the dye was changed from blue to purple and the peak of wavelength shifted. Greater complexation of Fe^{2+} with dye molecules occurs, as the number of azo bond increases is also consistent with the findings in this thesis.



1-control, 2 - H_2O_2 0.00001 M, 3 - H_2O_2 0.1 M, 4 - H_2O_2 0.0001 M, 5 - H_2O_2 0.01 M, 6 - H_2O_2 0.001 M, 7 - Fe^{2+} 0.001 M, 8 - Fe^{2+} 0.005 M, 9 - Fe^{2+} 0.01 M, 10 - Fe^{2+} 0.005 M

Experimental Conditions: Dye Concentration = 0.1 M, pH = 4, Fe^{2+} = 0.0001 M for

curves 1 to 6, H_2O_2 = 0.0001 M for curves 4, 8, 9 and 10

Temperature = 23 °C

Figure 33. Complexation of Trisazo Dye Direct Blue 71

7 CONCLUSION

Degradation of eight different azo dyes over the range of pH 2 to 4, concentrations of Fe^{2+} from 0.05 M to 0.001 M and concentration of H_2O_2 from 0.1 M to 0.00001 M was studied.

- For monoazo and disazo dyes this optimal ratio ranges from 1 to 10, and for trisazo dyes it is 1.
- The optimal pH for degradation of disazo dye by Fenton's Reagent is pH 4, and for monoazo dye is 3.
- As the number of azo bonds increases, the degree of complexation increases, which requires a greater amount of iron salts for the reaction. In the rapid degradation of Direct Blue 71, a purple colored complex is formed at pH greater than 2.
- The observed optimal ratio of H_2O_2 to Fe^{2+} agreed to a limited degree with the theoretical value of 11, probably because of complexation and variance with the structure of the organics to be destroyed.

8 RECOMMENDATIONS

The recommendations for future investigations in this part is as follows:

Experiments with mixture of dyes: More experiments needs to be carried out, using a mixture of monoazo dyes, disazo dyes and trisazo dyes individually based on this study. The removal efficiency should be studied for this mixture for different dye concentrations and optimal ratio and optimal pH should be determined for this mixture. After individual class evaluation, a mixture of different classes should also be studied to see the optimal color removal conditions.

Intermediates: The formation of toxic intermediates and products is not well understood at this time for the Fenton's Reagent treatment. Color changes observed during the experiments are indicative of the formation of several intermediates during the process. Before these processes can be widely applied, the degradation pathways should be defined and the toxicity investigated.

Selection of Optimal Ratio for Process: The optimal ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was found to lie between 1-10 for most of the dyes. The amount of color removal at these optimal ratios should be correlated with the cost of H_2O_2 , since in certain cases the difference in color removal is not significant for both 1 and 10. In such cases, the selection of optimal ratio should depend on the time for the reaction and the cost of H_2O_2 .

PART II. DEGRADATION OF AZO DYES IN AQUEOUS SOLUTION BY H₂O₂/Fe POWDER

9 INTRODUCTION

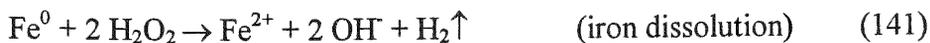
No single unit process is effective to treat textile effluents. Fenton's Reagent seems to be economical and effective treatment only if used in conjunction with flocculation, coagulation and followed by filtration. Nevertheless, Fenton's Reagent produces large amounts of sludge due to the hydrolysis of Fe²⁺ and Fe³⁺. To determine if the additional cost associated with sludge handling can be reduced, Fe powder was used in this study to replace Fe²⁺.

The use of zero-valent iron to reduce chlorinated hydrocarbons was first reported in patent literature by Sweeny and Fischer in 1972. However, Sweeny and Fischer never published in peer reviewed journals; therefore, their work was overlooked by the research community (Gillham et al., 1994). In the late eighties, Glenn Reynolds, a graduate student at the University of Waterloo in Ontario, was researching the corrosion of PVC and iron pipes by water contaminated with organics. Reynolds observed that the organics would disappear from the iron pipes and reported the information to his supervising professor, Robert Gillham. Since the focus of the research project was on the degradation of plastics in pipes, the "discovery" was not given much thought. Several years later, Gillham realized the potential of using the reduction ability of zero-valent iron for practical purposes. He founded EnviroMetal technologies Inc. and holds several patents

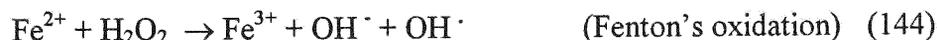
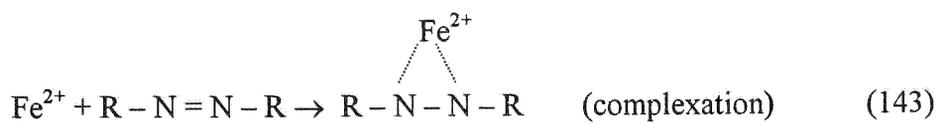
for the application of zero-valent iron degradation of organic compounds (Wilson, 1995). Paul Tratnyek, an assistant professor at the Oregon Graduate Institute, had also made contributions to the zero-valent iron research by the analysis of the reactions and the mechanism behind the reduction process. The use of zero-valent iron as a treatment process is effective, economical, and receiving increasing attention in the industry. In this part, the degradation kinetics of seven monoazo dyes, three disazo dyes and one trisazo dye are investigated and the reaction mechanisms are proposed. The objectives of this component of the study is to investigate the effect of the number of azo bonds, auxiliary functional groups, and pH on degradation kinetics by hydrogen peroxide and zerovalent iron powder.

10 FUNDAMENTAL THEORY

Tang and Chen (1996) first demonstrated that zero valent iron powder (Fe) could be quickly and economically produce the iron salt (Fe^{2+}) required in Fenton's chemistry ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) in presence of H_2O_2 . This process modification has an advantage of reducing the sludge formation over the conventional Fenton's treatment system. The use of metallic iron makes separation of iron easy, and has the dual advantage of adsorbing and oxidizing azo dyes. Four different processes, namely, iron dissolution, dye adsorption, dye reduction, and dye oxidation are very important in removing dye from aqueous solutions (Tang and Chen, 1995). Iron powder reacts with water and dissolves as Fe^{2+} :



When added to this solution, dye molecules RH form complexes with the metal, referred as chemisorption. The metal ions complex with the functional group of the dye molecules, i.e. the ligands, as:



In the presence of organic substrates such as dye molecules RH, hydroxyl radicals HO[·], and ferrous ion (Fe²⁺) at low pH can produce organic free radicals, R[·]:



The organic free radical may then be oxidized by Fe³⁺, reduced by Fe²⁺, or dimerized (Kuo, 1992):



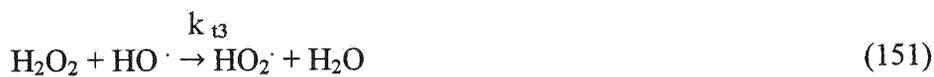
The rate of dye degradation depends on the ratio of H_2O_2 to Fe^{+2} which is also shown in previous work (Kuo, 1992; Lin et al., 1995; Lou et al., 1995; Tang and Chen, 1995; Tang and Chen, 1996). The desired reaction for the production of the hydroxyl radical is:



where k_{11} is $5.3 * 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Competitive reaction is that excessive Fe^{2+} can scavenge hydroxyl radicals:



where k_{12} is $3 * 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In addition, excessive H_2O_2 also consumes hydroxyl radicals as:



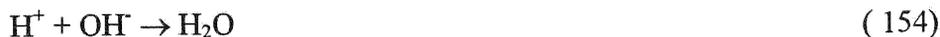
Where k_{13} is $2.7 * 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Given the competitive reactions, it is extremely important that an optimal ratio of H_2O_2 to Fe^{+2} is maintained. If H_2O_2 is in excess super oxide radicals ($\text{HO}_2 \cdot$) are formed which is a weaker oxidant than hydroxyl radical ($\text{HO} \cdot$). The superoxide radical acts as a competitor with the hydroxyl radical during oxidation. As a result the degradation is slower.

11 LITERATURE REVIEW

11.1 Dyes

Advanced oxidation processes have gained considerable attention in decolorizing textile wastewater. However, there was no well documented information in the area of $\text{H}_2\text{O}_2/\text{Fe}^0$ powder before Tang and Chens work (1996). Role of Fe^0 dissolution in the adsorption of reactive red 120 dye by iron powder was investigated in their work (1996).

Reactions were carried out in a well mixed batch reactor. Iron powder dissolution in deionized water with and without H_2O_2 was studied at pH of 2, 2.5, 3, 3.5 and 4. Samples were taken at 0, 0.5, 1.5, 2, until 10 minutes. It showed that Fe^{2+} concentration increased dramatically in the first 2 to 5 minutes. Fe^{2+} concentration increased much faster at lower pH than at higher pH. Fe^0 was described as a oxidation reduction process during which metallic iron powder is oxidized by dissolved oxygen. The reaction was described as follows:



The overall reaction can be summarized as follows



The above reaction in equation implies that acidic environment is necessary to enhance iron dissolution. The experiments showed that the final pH increased from 3 to 5.3. The dissolved Fe^{2+} concentration in first minute was low, indicating iron dissolution a slow process. After one minute the Fe^{2+} concentration increased rapidly. It was also observed that oxidation of Fe^{2+} by dissolved oxygen is a faster process than iron dissolution. At pH greater than 3.5, the ferric ions formed ferric hydroxides or insoluble hydroxide particles, which resulted in the decrease of ferric ion concentration. Iron dissolution constant of 0.1213 mM/s at pH 2 was 30 times greater than 0.0047 mM/s at pH 4. To evaluate iron dissolution in presence of H_2O_2 , studies were carried out at pH 3 and iron powder concentration of 1 g/L. Different H_2O_2 concentrations were used and it was found that the maximum Fe^{2+} concentration occurred at H_2O_2 concentration of 10^{-4} M. The accelerating and inhibitive properties of H_2O_2 in iron corrosion is explained as, when H_2O_2 concentration is low, it can only serve as an electron acceptor from the iron powder surface, therefore it enhances iron dissolution. When the H_2O_2 concentrations exceeded 5×10^{-4} M, the Fe^{2+} dissolved quickly and was oxidized by excess H_2O_2 . High H_2O_2 concentration lead to the passivation by forming $\text{Fe}_{3-x}\text{O}_4$ on the iron powder surface. The total Fe powder dissolution rate decreased when H_2O_2 concentration was greater than 0.001 M.

Dye adsorption is considered one of the important processes during decolorization in this study. The dye studied was reactive red 120, which has several functional groups

containing oxygen and nitrogen atoms, chemisorption was considered as an important part of adsorption process. Since chemisorption is a single layer adsorption, Langmuir adsorption model was used to describe adsorption kinetics. Effect of pH on adsorption of reactive red 120 was studied and it was found that, the lower the pH value, the more the dye adsorbed. Dye adsorption at pH 2 was about five times higher than that at pH 4. It was also proposed that part of the dissolved Fe^{2+} and Fe^{3+} exists in electrical double layer of Fe powder surface, due to which the dye molecule will have more Fe^{2+} and Fe^{3+} ions on the Fe powder surface to complex with. Also, less Fe^{2+} concentration was detected in solution at high pHs of 3.5 and 4 than at pH 2 and 2.5, which means adsorption of Fe^{2+} on Fe powder surface should be relatively low at high pH levels of 3.5 to 4.

The effect of iron powder concentration on dye adsorption was also studied, dye adsorption per unit weight of Fe was not linearly proportional to iron powder concentration. The reason for this was not understood clearly. Adsorption equilibrium studies were performed for 30 minutes. The results from the adsorption equilibrium study obeyed the Langmuir adsorption isotherm. The maximum adsorption capacity was calculated to be 200 mg dye per gram of iron powder.

Since adsorption transfers the contaminant from one phase to another rather than destroying the contaminant, Tang and Chen (1996) also studied with oxidation of this dye. Investigation of pH effect showed that the optimal pH ranged from 3 to 3.5. Lower dye concentrations were found easier to be decolorized during the study of dye concentration effect. The study showed that Fenton's reaction was more important in

decolorization than adsorption. The optimal ratio between H_2O_2 and iron powder was 0.001 M to 1.0 g/ L (1/5.5 to 1/8.7). This ratio may vary with the type of substrate, as it does for Fenton's Reagent, thus it may vary with different types of dyes.

12 OBJECTIVES

Three different classes of mono, dis and tris azo dyes are studied in this thesis. The objective is to generalize the work by Tang and Chen (1996) and to apply it to a single family of dyes (azo dye) with three different classes.

- 1) To investigate the effect of pH on decolorization of five monoazo dyes, three disazo dyes and one trisazo dye by H_2O_2 and Fe^0 powder.
- 2) To investigate the effect on decolorization by H_2O_2 and Fe^0 powder due to the presence of number of azo bonds and the auxiliary groups on azo dyes.
- 3) To investigate the kinetics and mechanism of degradation of the dyes by H_2O_2 and Fe^0 powder.
- 4) To evaluate $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{Fe}^0$ processes by comparing them.

13 EXPERIMENTAL

13.1 Materials

Hydrogen Peroxide (30%-35%) was obtained from Fisher Scientific Co. The iron powder used was a metallic powder less than 10 μm , and purity greater than 99% (Aldrich Chemical Company, Inc.). Monoazo dyes Acid Yellow 25, Acid Blue 92, Basic Red 29, Acid Orange 8, Acid Red 8, Basic Blue 41, Acid Blue 161, disazo dyes Acid Yellow 38, Acid Red 97, Direct Violet 51 and a trisazo dye Direct Blue 71 were also purchased from Aldrich Chemical Company. These dyes are the same as those mentioned in part I of this thesis.

13.2 Experimental Procedure

Experiments were performed in an open batch system of 1000 mL at a room temperature of 23 $^{\circ}\text{C}$. Complete mixing conditions were ensured at 100 rpm. Under complete mixing conditions 10 ml of 0.1 M H_2O_2 and 1 g of Fe powder were added to the system, according to the optimum ratio of H_2O_2 to Fe powder reported by Tang and Chen (1996). The pH of the solution containing iron powder was adjusted. Solutions of the dye were adjusted to the desired pH of 2.5, 3, and 3.5 by adding 1 M H_2SO_4 or 1 M NaOH. A 1 M stock solution of dye was used to make 0.1 M aqueous solutions. A sample was taken as soon as the dye was added. Hydrogen peroxide was added to the reactor at the beginning of the experiment. A sample was taken to determine how much

dye was adsorbed on iron powder initially before oxidation began. Samples were withdrawn at 0, 0.5, 1, 2, 5, 10, 20, 30 and 60 min using a 10 mL syringe. A drop of 4 N NaOH was used to terminate the oxidation by raising the pH to 9 to prevent further generation of hydroxyl radicals through Fenton's reaction. The samples were then filtered through a 0.45 μm syringe filter from Acrodisc and were analyzed using a UV-Visible Diode Array Spectrophotometer (HP 8452A). Advanced quantification software is connected with the spectrophotometer, which can show the results, by numerical analysis and graphic forms based on statistical analysis. The color is measured by the absorbance intensity at the maximum absorbance wavelength according to the Beer's law, the calibration curve for each dye was established by the corresponding standard solutions. The calibration curve was established in the same way as mentioned in part I of the thesis. Controls were measured for each dye without Fe powder and H_2O_2 . The removal of dye color was normalized with the initial concentration. The kinetics of the degradation was studied for 60 minutes for all the dyes. Two monoazo dyes were basic dyes, and were suspected to precipitate in basic conditions, therefore no Reagents were added and the precipitation kinetics for Basic Blue 41 and Basic Red 29 were studied at pH levels of 9, 10, 11, and 12.

14 RESULTS AND DISCUSSION

14.1 Effect of pH on Degradation of Monoazo Dyes

The pH effect on the oxidation kinetics of five different monoazo dyes is shown in figures 34, 35, and 36. The maximum degradation of the dye appears to occur at pH 2.5 or less for all the monoazo dyes. As pH increased from 2.5 to 3.5, the degradation decreased. To quantitatively evaluate the decolorization kinetics, during the first 10 minutes, the reaction is described using the first order kinetics:

$$dC_{\text{dye}} / dt = - kC_{\text{dye}} \quad (156)$$

where C_{dye} is the concentration of dye (mM) and k is the first order degradation constant (1/min). Table 19 shows the first order constants for different monoazo dyes at pH 2.5, 3, and 3.5, and an initial concentration of 0.1 mM.

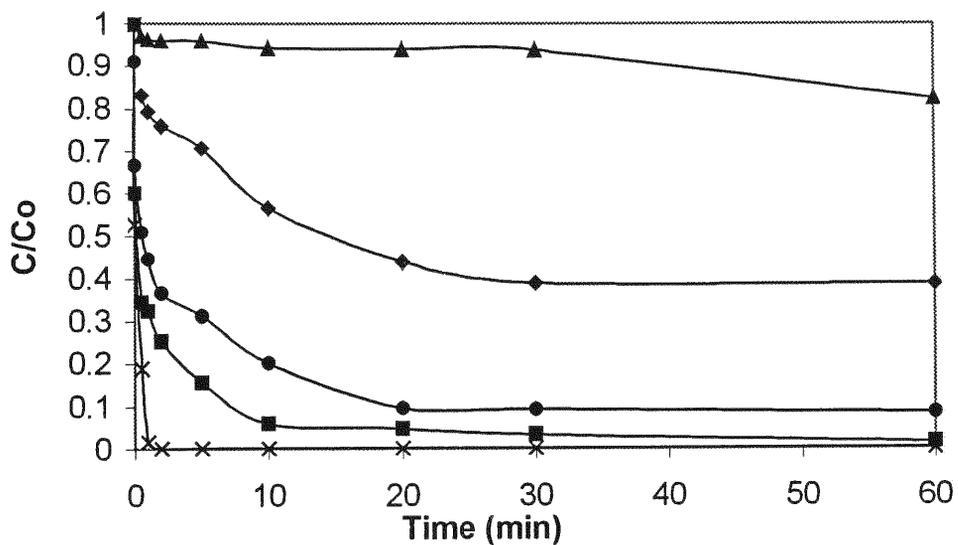
Table 19. First Order Rate Constants of Different Monoazo Dyes

Monoazo dyes	pH 2.5		pH 3		pH 3.5	
	k(1/min)	r ²	k(1/min)	r ²	k(1/min)	r ²
Acid Yellow 25	0.1754	0.977	0.5711	0.999	0.0072	0.9111
Acid Red 8	0.5295	0.9694	0.4351	0.916	0.0319	0.9185
Acid Blue 161	0.589	0.9775	0.4337	0.9486	0.0078	0.9491
Acid Orange 8	0.0088	0.9863	0.012	0.9877	0.0191	0.9997
Acid Blue 92	*	*	0.3742	0.9527	0.1732	0.9637

* The first-order oxidation rate constant cannot be determined due to rapid decolorization.

At pH 2.5 the degradation rates of monoazo dyes in the decreasing order is given by Acid Blue 161 > Acid Red 8 > Acid Yellow 25 > Acid Orange 8 > Acid Blue 92. Acid Blue 161 also has significant adsorption followed by oxidation. Degradation of Acid Red 8 is similar to Acid Blue 161. Thus, at pH 2.5 Acid Blue 92, Acid Blue 161, and Acid Red 8 are easily adsorbed due to naphthalene ring. Acid Blue 92 is adsorbed at a very fast rate. Acid Yellow 25 is moderately degraded and Acid Orange 8 is the least degraded dye.

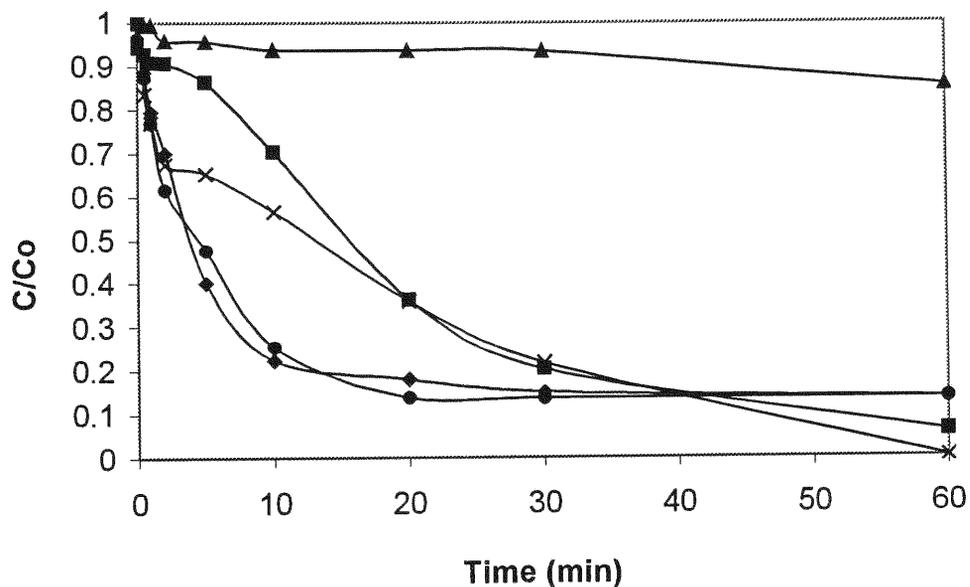
Fe^{+2} is a transition metal ion present in a hydrated form that forms a wide variety of ligands with electron donors such as N and O in the dye molecule. Since, the molecular structure has lesser functional groups, than that of Acid Red 8 and Acid Blue 161, Acid Orange 8 has lesser ligands to complex with Fe^{2+} . This may be one of the reasons for the low degradation rate of Acid Orange 8.



■ Acid Red 8, ◆ Acid Yellow 25, ▲ Acid Orange 8, ✕ Acid Blue 92, ● Acid
 Blue 161

Experimental Conditions: Dye Concentration = 0.1 M, Iron Powder = 1 g/L, H_2O_2 =
 0.001 M, Temperature = 23 °C

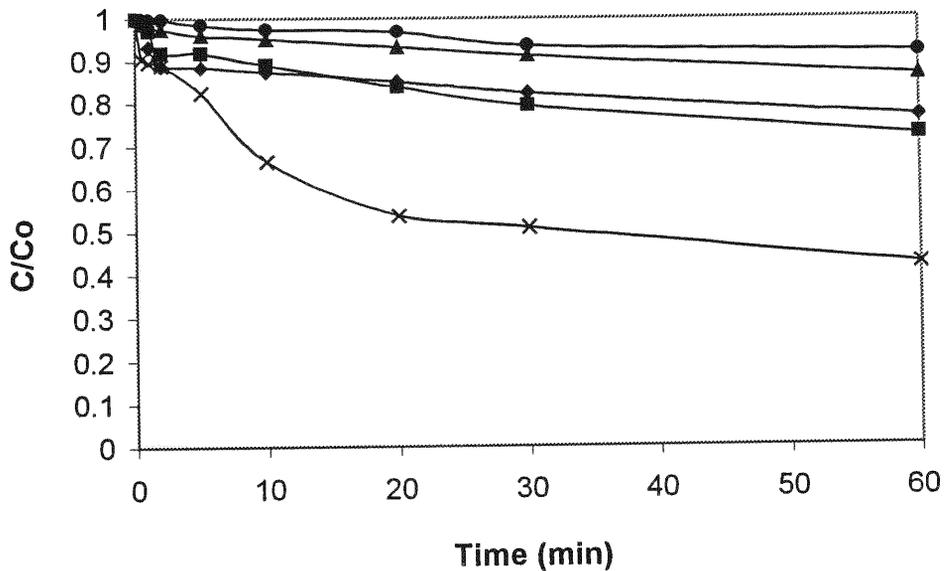
Figure 34: Degradation of Monoazo Dyes at pH 2.5



■ Acid Red 8, ◆ Acid Yellow 25, ▲ Acid Orange 8, ✕ Acid Blue 92, ● Acid
 Blue 161

Experimental Conditions: Dye Concentration = 0.1 M, Iron Powder = 1 g/L, H_2O_2 =
 0.001 M, Temperature = 23 °C

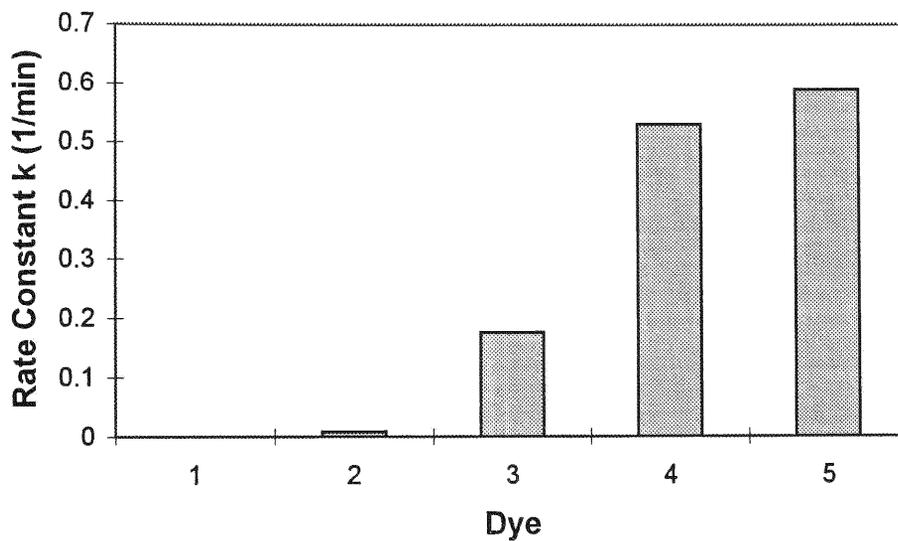
Figure 35. Degradation of Monoazo Dyes at pH 3



■ Acid Red 8, ◆ Acid Yellow 25, ▲ Acid Orange 8, ✕ Acid Blue 92, ● Acid
 Blue 161

Experimental Conditions: Dye Concentration = 0.1 M, Iron Powder = 1 g/L, H_2O_2 =
 0.001 M, Temperature = 23 °C

Figure 36. Degradation of Monoazo Dyes at pH 3.5



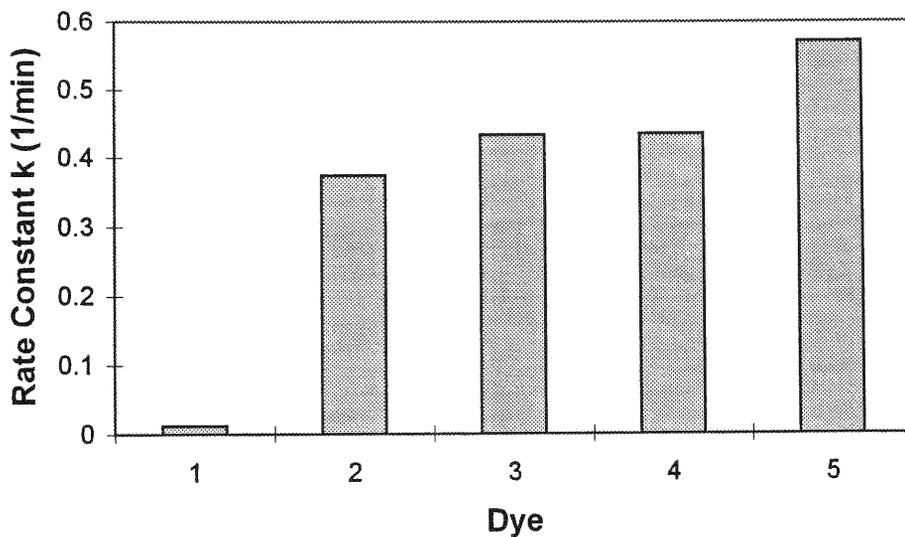
1-Acid Blue 92, 2-Acid Orange 8, 3-Acid Yellow 25, 4-Acid Red 8, 5-Acid Blue 161

Experimental Conditions: Dye Concentration = 0.1 M, Iron Powder = 1 g/L, H_2O_2 = 0.001 M, Temperature = 23 °C

Figure 37. First-order Rate Constants of Different Monoazo Dyes at pH 2.5

Figure 37 shows the degradation kinetics of monoazo dyes at pH 3. Acid Blue 161 and Acid Blue 92 have similar molecular structures with two conjugate naphthalene rings and thus are relatively easy to oxidize due to the π electron density, which is higher than Acid Red 8 containing one naphthalene ring. Acid Orange 8 is the most difficult dye to oxidize. One possible reason is that Acid Orange 8 only contains one naphthalene ring. Therefore, the π electron density may be much less than monoazo dyes containing two naphthalene rings.

Significant reduction of degradation rate constants was observed at pH 3.5. For most of the monoazo dyes except Acid Blue 92, the rate constants decreased one order of magnitude from an average rate constant of 0.45 1/min to an average rate constant of 0.02 1/min. Interestingly, the order of degradation reversed compared with pH 2.5. At pH 3.5, Acid Blue 92 and Acid Red 8 were degraded fastest, while these dyes are the slowest to be degraded at pH 2.5. The number of sulfonic functional group plays an important role. Negatively charged, if it is not associated with H^+ , a sulfonic group will be present in negative ionic form as pH increases from 2.5 to 3.5. As a result, the aromatic ring will have denser electronic cloud, which allows the dye to degrade more readily by a hydroxyl radical at pH 3.5, than at pH 2.5, because the elementary iron surface is positive at low pH of 2.5 to 3.5, due to excessive number of protons in the solution.

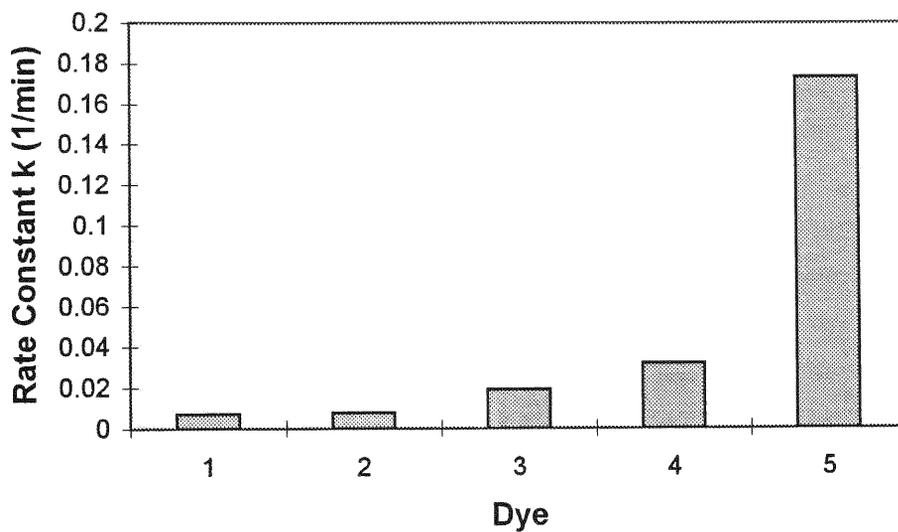


1-Acid Orange 8, 2-Acid Blue 92, 3-Acid Blue 161, 4-Acid Red 8, 5-Acid Yellow 25

Experimental Conditions: Concentration = 0.1 M, Iron Powder = 1 g/L, H_2O_2 = 0.001 M,

Temperature = 23 °C

Figure 38. First-order Rate Constants of Different Monoazo Dyes at pH 3



1-Acid Yellow 25, 2-Acid Blue 161, 3-Acid Orange 8, 4-Acid Red 8, 5-Acid Blue 92

Experimental Conditions: Dye Concentration = 0.1 M, Iron Powder = 1 g/L,

H_2O_2 = 0.001 M, Temperature = 23 °C

Figure 39. First-order Rate Constants of Different Monoazo Dyes at pH 3.5

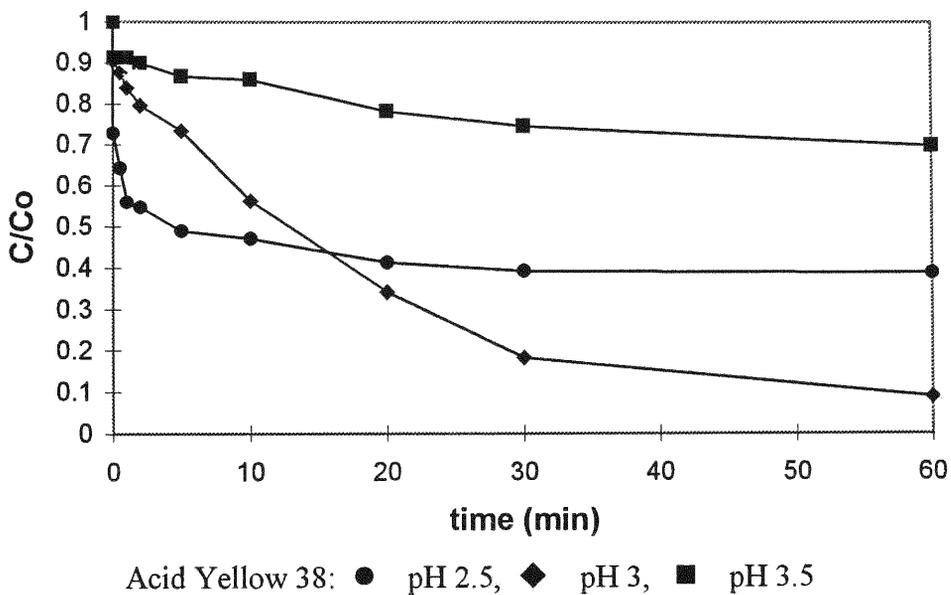
4.2 Effect of pH on Degradation of Disazo Dyes

Three disazo dyes Acid Red 97, Acid Yellow 38, and Direct Violet 51 were studied. At pH 3, the oxidation rate of Acid Yellow 38 was higher compared to Direct Violet 51, but Direct Violet 51 was highly adsorbed at this pH. Almost 95% was decolorized in 2 minutes reducing oxidation. Whereas for Acid Yellow 38 the adsorption was relatively less than the oxidation. At pH 2.5, Acid Yellow 38 is more adsorbed and less oxidized than at pH 3. Direct Violet 51 is only slightly decolorized and no oxidation is observed at pH 2.5, this shows that at pH 2.5 oxidation is not a controlling mechanism for the degradation of disazo dyes. While at pH 3.5 significant amount of Direct Violet 51 is decolorized and oxidation is dominant, which is also observed for Acid Yellow 38. The oxidation kinetic data of figure 40 and 41 are used to derive the first order rate constants listed in table 20.

Table 20. First Order Rate Constants of Different Disazo Dyes

Disazo	pH 2.5		pH 3		pH 3.5	
	k(1/min)	r ²	k(1/min)	r ²	K(1/min)	r ²
Acid Yellow 38	0.0814	0.9814	0.3808	0.9704	0.0231	0.9001
Direct Violet 51	*	0.9973	0.0058	0.91	0.0833	0.9706
Acid Red 97	*	*	*	*	*	*

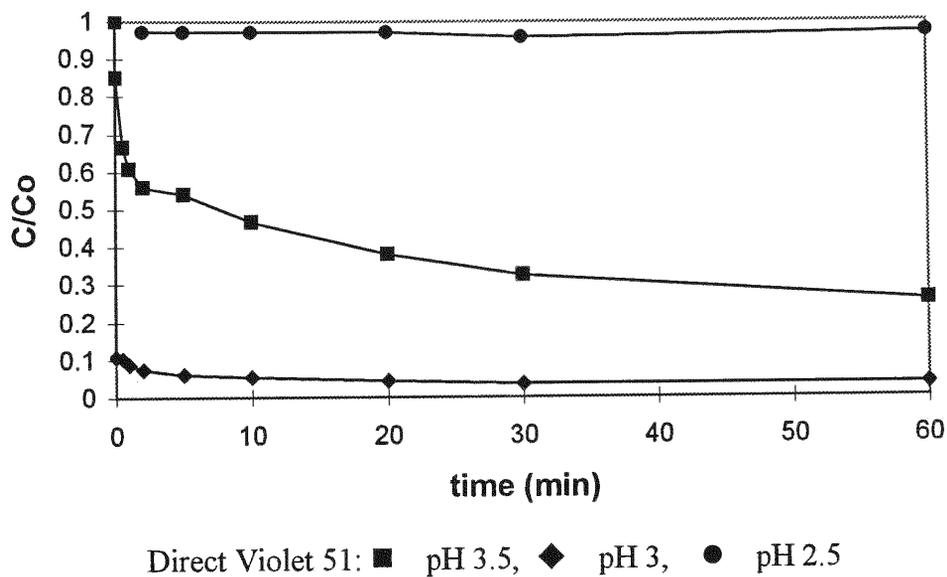
- The first-order oxidation rate constant is zero.



Experimental Conditions: Concentration = 0.1 M, Iron Powder = 1 g/L, H₂O₂ = 0.001 M,

Temperature = 23 °C

Figure 40. pH Effect on Degradation of Acid Yellow 38



Experimental Conditions: Concentration = 0.1 M, Iron Powder = 1 g/L, H_2O_2 = 0.001 M,

Temperature = 23 °C

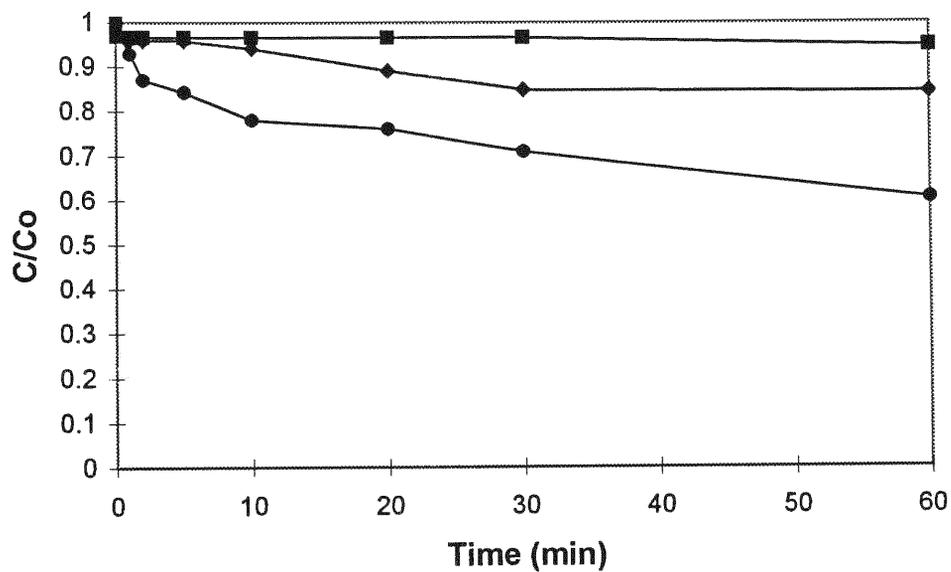
Figure 41. pH Effect on Degradation of Direct violet 51.

14.3 Effect of pH on Degradation of Trisazo Dye

The pH effect on the degradation of a trisazo dye Direct Blue 71 in figure 42 for a pH of 2.5, 3, and 3.5 is similar to the effect for monoazo dyes. At pH 2.5 the maximum degradation of Direct Blue 71 was observed. During the first ten minutes, the degradation for Direct Blue was faster at pH 2.5 than at pH 3 and 3.5. After ten minutes the degradation pattern at all three pH were similar. Since iron dissolution is faster at lower pH, more dissolved iron (Fe^{2+}) is available for Fenton's oxidation at pH 2.5.

Figure 42 also shows that, oxidation of a trisazo dye Direct Blue 71 is highest at pH 2.5. This is also due to higher iron dissolution at low pH in first 10 minutes and availability of Fe^{2+} for Fenton's oxidation of trisazo dye due to iron dissolution. From the kinetic data the degradation kinetic rate constants are 0.057 1/min ($R^2 = 0.9975$) and 0.0359 ($R^2 = 0.9211$) at pH 2.5 and 3, respectively.

For most of the dyes, which have been studied, it can be concluded that oxidation rates were high at a lower pH. At pH 3.5, in most cases like Direct Blue 71, if the iron dissolution is less than the simultaneous oxidation is also less. Thus, it could be seen that the dissolved iron at different pH plays an important role in the dye degradation through Fenton's mechanism. Degradation is rapid in the first ten minutes of the reaction time.



Direct Blue 51: ■ pH 3.5, ◆ pH 3, ● pH 2.5

Experimental Conditions: Concentration = 0.1 M, Iron Powder = 1 g/L, H₂O₂ = 0.001 M,

Temperature = 23 °C

Figure 42. pH Effect on Degradation of Direct Blue 51.

More Fe^{+2} than that required by the optimum ratio will not enhance oxidation as no hydrogen peroxide is available to generate additional hydroxyl radicals. Thus at a lower pH, all hydrogen peroxide reacts with Fe^{2+} to generate hydroxyl radical which enhances the degradation rate of the dye.

14.4 Effect of Molecular Structure

The number of azo bonds and the type of auxiliary group attached to the dyes has a significant effect on the rate of degradation (Kuo, 1992; Tang et al., 1996; Tang and Chen, 1995; 1996). Based on the removal kinetics of several dyes, chemisorption is an important mechanism. Chemisorption depends on the type of auxiliary group attached to the dye molecule. As discussed before Acid Orange 8 has a much lower degradation rate at all pH. One of the explanations may be that this molecule has the least number of functional groups compared to the other dyes. Since similar rates of degradation of Acid Orange 8 is observed at different values of pH, chemisorption may be the major initial rate controlling mechanism. By contrast Acid Blue 92 is adsorbed instantaneously and is almost completely degraded at lower pH values within 2 minutes, even though the dye has a very similar structure to Acid Blue 161. It is the same case with Direct Blue 51.

One possible explanation for this is that both of these dyes contain one amide group, which is very easily adsorbed on metal. The rate of oxidation also depends on the molecular structure of dyes, this has been observed previously (Tang et al., 1997) and is verified in this study with Acid Red 8 and Acid Blue 161 at pH 3. Under this condition

the degradation rate of Acid Red 8 is faster than Acid Blue 161. Acid Red 8 has only one naphthalene ring while Acid Blue 161 has two conjugate naphthalene rings, which introduces a steric constraint. It supports that at pH 3, oxidation is also a controlling mechanism. For disazo dyes, Acid Yellow 38 is less difficult to degrade than Direct Blue 71, possibly because Acid Yellow 38 has a thiol group which is difficult to degrade. The rate of oxidation is influenced by the number of azo bonds attached to the dye molecule. As seen from the rate constants at pH 3.5, degradation rates of azo dye decrease as the number of azo bond increases. For example, the degradation rates decrease in the order of monoazo dye Acid Blue 92 > disazo dye Direct Violet 51 > trisazo dye Direct Blue 71.

14.5 Precipitation of Basic Monoazo Dyes

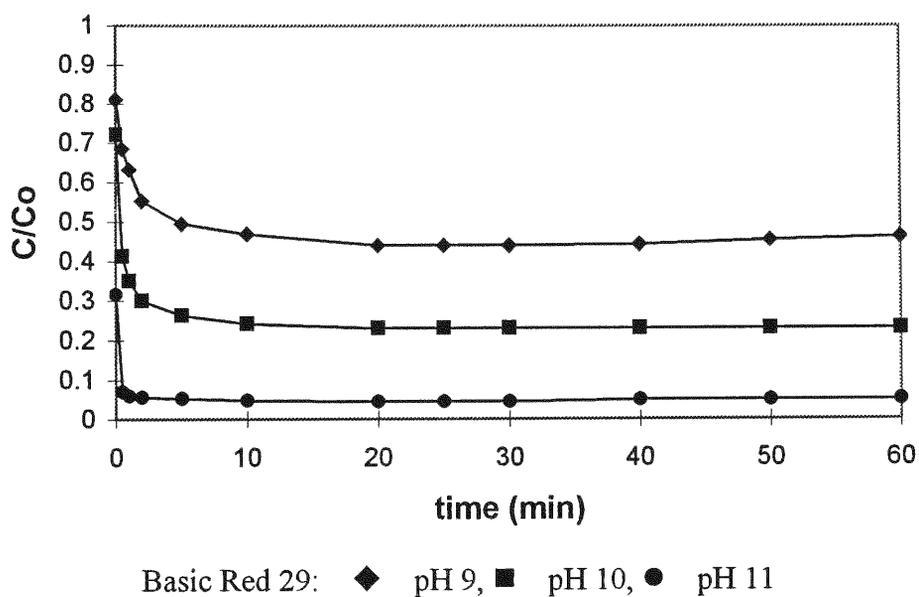
Basic dyes precipitate in basic solutions because of a positive charge on the molecule. When a base is added, the positive charge of the dye reacts with the hydroxide ions of the base and neutralizes the positive dye. Figure 43 shows the pH effect on the precipitation kinetics of Basic Red 29. In these studies, almost all the dye particles are precipitated at the bottom of the reactor within 10 minutes. As the pH increases, more dye particles settle which is clearly shown in figure 43. At pH 9 almost 55% of the dye is removed, at pH 10 more than 75 % of the dye is precipitated and at pH 10, 95 % removal of the dye is observed. At pH 11 and 12 the precipitation of Basic Red is completed in seconds and is hardly possible to measure. The rate of precipitation of Basic Red 29 is greater than the rate of precipitation of Basic Blue 42. Figure 43 presents the precipitation kinetics of Basic Blue 41.

Table 21. First Order Rate Constants for Precipitation of Basic Monoazo Dyes

Monoazo dyes	pH 9		pH 10		pH 11		pH 12	
	K (1/min)	r ²						
Basic Blue 41	0.0309	0.9431	0.0793	0.9372	0.3512	0.91	0.8247	0.977
Basic Red 29	0.2501	0.9613	0.7223	0.9081	0.1415	0.8162	*	*

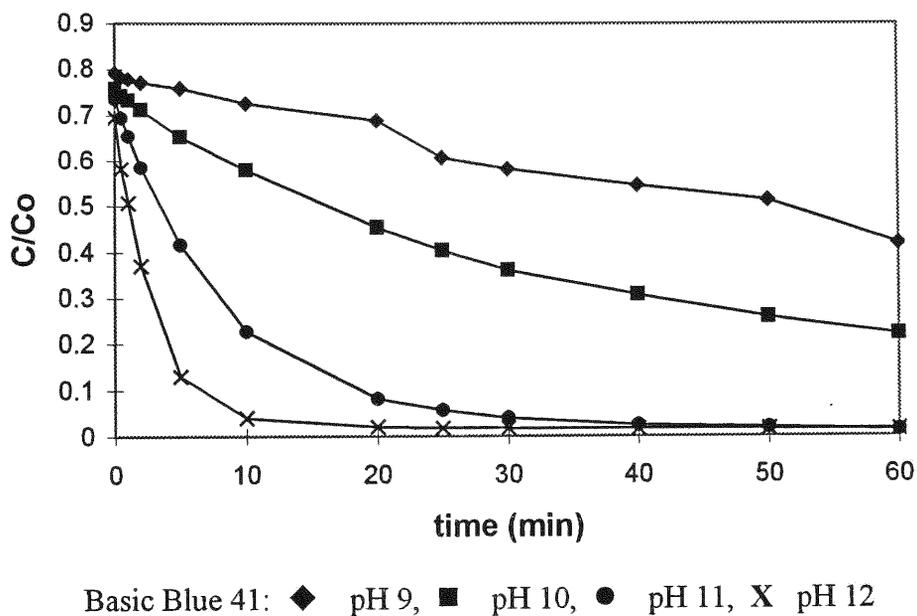
- Decolorization is rapid to calculate the first-order oxidation rate constant.

Figure 44 compares the precipitation kinetics of Basic Red 29 at pH 9 and pH 10. At higher pH of 11 and 12 the dye molecules degraded instantly within half a minute and it was hardly possible to calculate the rate constants. At pH 10 the precipitation rate of Basic Red 29 is greater than that at pH 9. This is because the positive charge of the basic dye is attacked by more hydroxide ions at pH 10 compared to pH 9 and same is true for pH 11 and pH 12 where the precipitation increases.



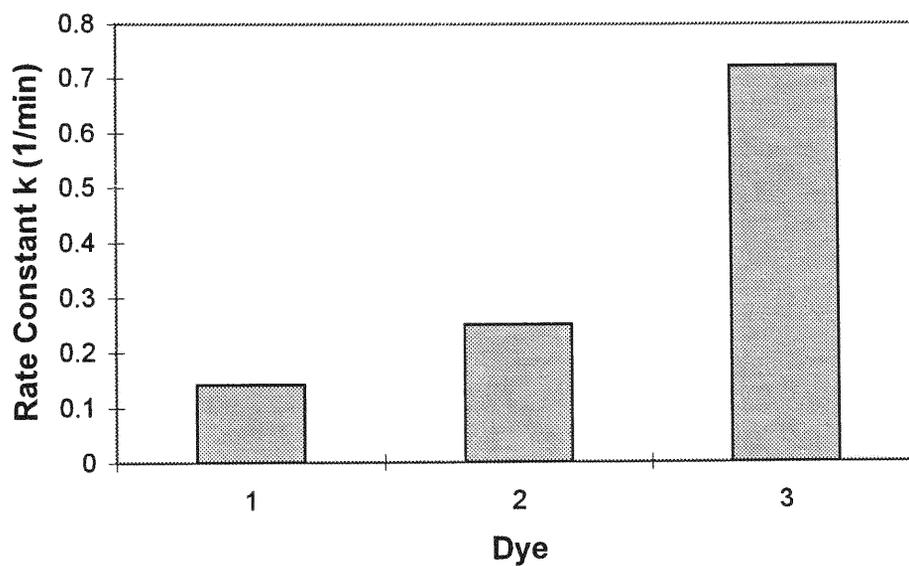
Experimental Conditions: Concentration = 0.1 M, Temperature = 23 °C

Figure 43. Precipitation of Basic Red 29 under Basic Environment



Experimental Conditions: Concentration = 0.1 M, Temp = 23 °C

Figure 44. Precipitation of Basic Blue 41 in Basic Environment.



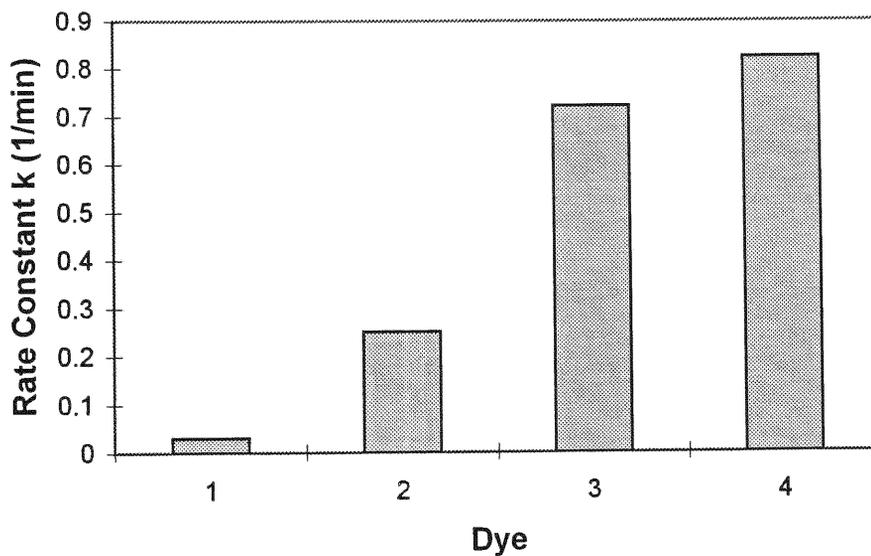
1- pH 9, 2- pH 10, 3- pH 11

Experimental Conditions: Concentration = 0.1 M, Temp = 23 °C

Figure 45. Precipitation of Basic Red 29 in Basic Solutions

Figure 46 compares the precipitation rate constants of the Basic Blue 41 at pH 9, 10, 11 and 12. The rate of precipitation reaction increases with increasing pH. This shows that as the pH increases more hydroxide ions are available to react with positive charge of the dye thus destroying the dye molecule. At pH 12 almost 98 % of the dye is degraded in 20 minutes. At pH 11 almost same amount of degradation of the dye is seen after 50 minutes as seen for pH 12 at 50 minutes which means that the increase in the pH beyond pH 11 increases the rate of precipitation but the degradation efficiency is the same after 50 min.

It can be concluded from table 5 that at pH 9 and 10 the precipitation rate of Basic Red 8 is greater than Basic Blue 41. The reason for this is that Basic Red 29 has a positive charge on a smaller molecule, which is linked with chromophore. Since chromophore is responsible for the color, the color quickly disappeared once it had been destroyed. For Basic Blue 41, the positive charge lies on a larger molecule attached to the azo bond (chromophore). Thus, when these two basic dyes are neutralized by hydroxide ions, the larger dye of Basic Blue 41 will be neutralized slower than Basic Red 29. Since the color was removed so quickly it was not necessary to carry out the oxidation reaction.



1- pH 9, 2-pH10, 3- pH 11, 4- pH 12

Experimental Conditions: Concentration = 0.1 M, Temp = 23 °C

Figure 46. Precipitation of Basic Blue 41 in Basic Solutions

15 CONCLUSIONS

- At lower pH the dye degradation is faster in first 10 minutes, the pH range was found to be 2.5-3. While at higher pH dye degradation was slower in first ten minutes and the pH range was 3-3.5.
- The decolorization kinetics for mono azo dye is of pseudo first order.
- The rate of decolorization depends on the number of azo bonds present in the dye molecule and on the type of auxiliary group present in the dye molecule. Oxidation takes place at the chromophore structure, thus similar dye molecules have similar rate of degradation.
- In H_2O_2 and Fe powder system, adsorption as well as oxidation of dye takes place simultaneously, thus offering a dual advantage in removal. Due to the continuous dissolution of Fe powder and dye adsorption on Fe powder, $\text{H}_2\text{O}_2/\text{Fe}$ powder may be better than $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system at lower pH.

16 RECOMMENDATIONS

Good research not only advances the understanding of processes but also raises more questions when properly pursued. In this investigation, the following additional suggestions are the most important for future work:

Mechanisms: The mechanism is not well understood in the Fe powder/ H_2O_2 system for all these dyes, research is needed to study each of these azo dyes and their

behavior in different systems. These systems include study of adsorption of azo dyes in the presence of iron powder, amount of Fe^{2+} and Fe^{3+} present in the solution. This would in turn indicate the available Fe^{2+} for Fenton's reaction and Fe^{2+} and Fe^{3+} available for chemisorption for each dye.

Chemisorption and Oxidation: In order to understand chemisorption, all the dyes should be studied only with iron powder. This will indicate how much dye is adsorbed at different pH levels. The oxidation of trisazo dye at a high concentration and pH of 4 indicated complexation in Fenton's treatment. Such condition for all the other dyes might also be possible at higher concentrations or in different experimental conditions. An advantage of the dual mechanism of chemisorption and oxidation should be taken while designing the treatment unit to enhance the rapid color removal. Thus, different experimental conditions need to be studied for all the azo dyes.

Optimal Condition Studies: A study needs to be performed for the Fe powder/ H_2O_2 system to determine the optimal pH, H_2O_2 and iron powder for each dye. These studies can be performed once the amount of Fe^{2+} and Fe^{3+} present in the solution is determined.

Surface Analysis: Several different types of powdered iron are available commercially with which the degradation of all the dyes should be investigated. Since, surface area is a major factor in Fe powder dissolution and dye adsorption, a specific surface area of iron powder should be determined.

Intermediates: The formation of toxic intermediates and products is not clearly understood at this time for the Fe powder/H₂O₂ system. Color changes observed during the experiments are indicative of the formation of several intermediates during the process. Before these processes can be widely applied, the degradation pathways should be defined and the toxicity investigated.

OVERALL CONCLUSIONS

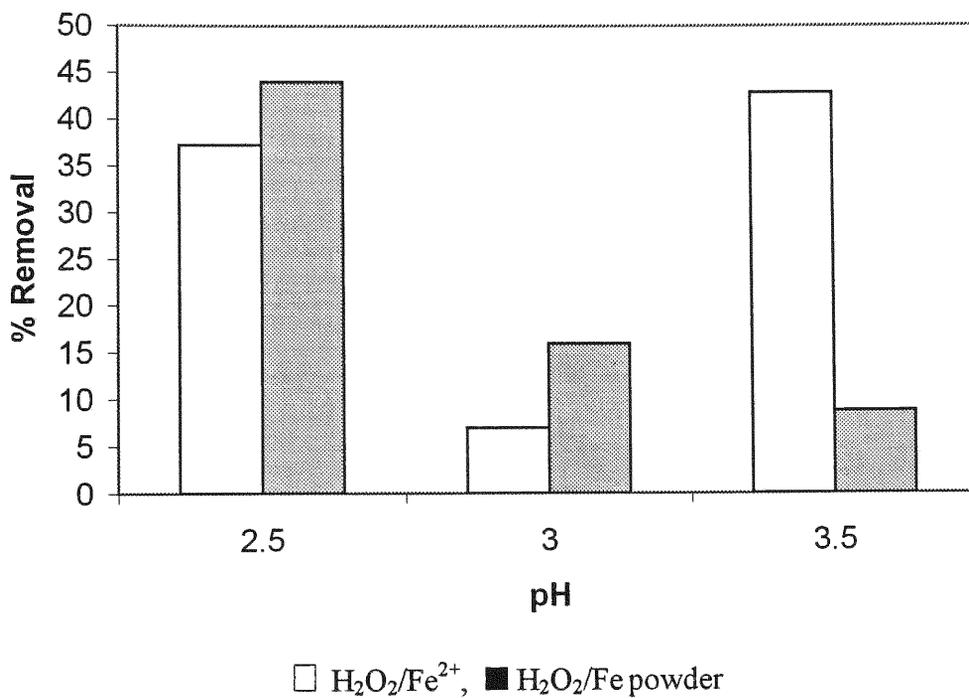
Fenton's Reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) was discovered in 1891 by H. J. H. Fenton. The reaction mechanism was studied 50 years after the discovery and a universal mechanism was accepted in 1971. In the late eighties, Fenton's Reagent was studied to treat contaminants in the environment. Zero valent iron powders potential as a reducing agent to treat contaminants in environment was discovered in late eighties. Tang and Chen (1995) discovered zero valent irons' oxidation potential in the presence of H_2O_2 ($\text{H}_2\text{O}_2/\text{Fe}$). The reaction mechanism for $\text{H}_2\text{O}_2/\text{Fe}$ consists of adsorption besides Fenton's oxidation, the extent of which is still not clear.

This thesis addressed the degradation of eleven azo dyes at 0.1 M concentration by $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{Fe}$ powder processes. Among the eleven azo dyes Basic Blue 41 and Basic Red 29 (monoazo) were not degraded because they completely precipitated in alkaline solutions; thus, oxidation was necessary by either of the two studied processes. ANOVA analysis were conducted to support any different observations among the variables on removal by the process in the study.

Kinetics

The reaction kinetics for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was already studied (Lou and Lee, 1995) and was found to be pseudo first order reaction. The reaction kinetics for $\text{Fe}/\text{H}_2\text{O}_2$ system was not studied before. The second part of the thesis shows that the reaction kinetics for

$\text{Fe}/\text{H}_2\text{O}_2$ is also pseudo first order for the first ten minutes of decolorization for the azo dyes. The decolorization for the azo dyes was almost complete in the first minute of the reaction time for the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ treatment system. Whereas the decolorization for the $\text{Fe}/\text{H}_2\text{O}_2$ treatment system took nearly 60 minutes for most of the dyes, the maximum decolorization was achieved within first ten minutes. Both the treatment systems used H_2O_2 concentration of 0.001 M for all the dyes. The initial concentration of all the dyes was 0.1 M. In order to compare both processes, Acid Yellow 38 was selected as a model dye. For $\text{H}_2\text{O}_2/\text{Fe}$ powder system, the amount of Fe^{2+} present in deionized water at different pH with respect to time is known (Chen, 1995). Thus, the amount of Fe^{2+} present in the $\text{H}_2\text{O}_2/\text{Fe}$ powder system at 1 minute and at pH 2.5 was 0.005 M, pH 3 and pH 3.5 was 0.0005 M. These values are an approximation and represent the maximum possible amount of Fe^{2+} , which can be present. These molar concentrations of Fe^{2+} for same pH and time were used for the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system to see the amount of removal by Fenton's treatment. The percentage removal was then compared as shown in the figure 47. Figure 47 shows that the removal of color is high for the $\text{H}_2\text{O}_2/\text{Fe}$ powder system at a lower pH and it decreases as pH level increases.



Experimental Conditions: Acid Yellow 38 Concentration = 0.1 M, H₂O₂ = 0.001 M,

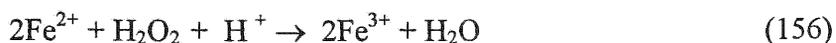
Time = 1 min, Fe²⁺ = 0.005 M at pH 2.5 and 0.0005 M at pH 3 and 3.5,

Temperature = 23 °C

**Figure 47. Comparisons of H₂O₂/Fe²⁺ and H₂O₂/Fe powder for Disazo
Acid Yellow 38**

Mechanisms

Reaction mechanism for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, is the Fenton's reaction. This mechanism is common for both systems.



This equation shows that an acidic environment is required in order to produce a maximum amount of hydroxyl radicals (Tang and Huang, 1996). In the presence of organic substrates such as dye molecules RH, hydroxyl radicals, and ferrous ion at low pH can produce organic free radicals R \cdot ;



The organic free radical may then be oxidized by Fe^{3+} , reduced by Fe^{2+} , or dimerized (Kuo, 1992), according to the following reactions:



Another competitive reaction is that excessive Fe^{2+} can scavenge hydroxyl radicals through the following reaction:



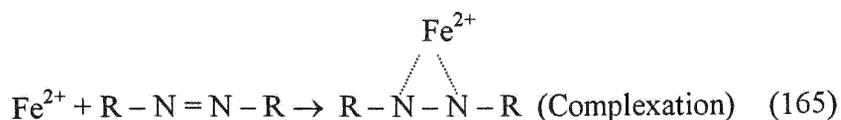
Where k_{12} has a value of $3 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$, in addition to this, excessive H_2O_2 also consumes hydroxyl radicals as shown by:



In addition to oxidation, the $\text{Fe}/\text{H}_2\text{O}_2$ system offers an advantage of adsorption and complexation (chemisorption).



When H_2O_2 and Fe^{2+} is added to the aqueous solution containing azo dyes, the dye molecules form a complex with the metal, which is referred to as chemisorption where metal ions form complex with the functional group of the dye molecules, i.e. ligands.



Thus, the Fe/H₂O₂ system offers a dual advantage of adsorption along with oxidation, compared to Fe²⁺/H₂O₂ system, which is only oxidation.

Moreover, Fe²⁺/H₂O₂ has all the iron in dissolved form and thus a large amount of Fe²⁺ reacts with the hydroxyl ions to form sludge, which has to be removed by coagulation and flocculation followed by filtration. For Fe/H₂O₂, some of the iron is available for adsorption or chemisorption, whereas rest of it is dissolved in form of Fe²⁺ and oxidized by Fenton's oxidation. This will result in a lesser amount of sludge to be handled. Thus, in order to select the process, the reaction time as well as the amount of sludge produced should be considered.

OVERALL RECOMMENDATIONS

In order to enhance the comparative efforts of this study for the two processes, it is recommended that future experiments should be conducted using the same experimental approaches for both of the processes. In order to improve statistical analysis, future studies should consider additional replicates of individual tests and complete experiments. The other recommendations are the same as those for individual parts.

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APPENDIX A

Table A. 1. Rate Constants of Compounds from Literature Review

Substrate	Co mg/L	pH	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Rate Constant	Order of reaction	Reference
2,4,6-TCP	50	4	20	16.69	5.52	4.03	pseudo-first order	Lou, 1995
2,4-DCP	50	4	20	16.69	5.52	4.03	pseudo-first order	Lou, 1995
2-CP	50	4	20	16.69	5.52	2.91	pseudo-first order	Lou, 1995
Benzene	5 x 10 ⁻⁴	3.5	n/a	2 x 10 ⁻⁴	5 x 10 ⁻³	8.2*10 ⁹	pseudo-first order	Tang, 1996
Bromoform	5 x 10 ⁻⁴	3.5	n/a	2 x 10 ⁻⁴	5 x 10 ⁻³	7.2*10 ⁹	pseudo-first order	Tang, 1996
Bromoform	5 x 10 ⁻⁴	3.5	n/a	2 x 10 ⁻⁴	5 x 10 ⁻³	6.3*10 ⁹	pseudo-first order	Tang, 1996
Bromoform	40.2x 10 ⁻³	3.5	n/a	214.55	688.6	0.00667	pseudo-first order	Tang, 1997
Bromoform	40.2x 10 ⁻³	3.5	n/a	214.55	688.6	0.0132	pseudo-first order	Tang, 1997
Bromoform	40.2x 10 ⁻³	3.5	n/a	214.55	688.6	0.0174	pseudo-first order	Tang, 1997
Bromoform	80.4x 10 ⁻³	3.5	n/a	107.27	344.3	0.00831	pseudo-first order	Tang, 1997
Bromoform	80.4x 10 ⁻³	3.5	n/a	107.27	344.3	0.0141	pseudo-first order	Tang, 1997
Bromoform	80.4x 10 ⁻³	3.5	n/a	107.27	344.3	0.0184	pseudo-first order	Tang, 1997
Bromoform	200x 10 ⁻³	3.5	n/a	42.88	137.6	0.00989	pseudo-first order	Tang, 1997
Bromoform	200x 10 ⁻³	3.5	n/a	42.88	137.6	0.0175	pseudo-first order	Tang, 1997
Bromoform	200x 10 ⁻³	3.5	n/a	42.88	137.6	0.0222	pseudo-first order	Tang, 1997
Dibromochloromethane	40.2x 10 ⁻³	3.5	n/a	41.781889	688.6	0.00472	pseudo-first order	Tang, 1997
Dibromochloromethane	40.2x 10 ⁻³	3.5	n/a	41.781889	688.6	0.00891	pseudo-first order	Tang, 1997
Dibromochloromethane	40.2x 10 ⁻³	3.5	n/a	41.781889	688.6	0.0133	pseudo-first order	Tang, 1997
Dibromochloromethane	40.2x 10 ⁻³	3.5	n/a	20.8899708	344.3	0.00529	pseudo-first order	Tang, 1997
Dibromochloromethane	40.2x 10 ⁻³	3.5	n/a	20.8899708	344.3	0.00945	pseudo-first order	Tang, 1997
Dibromochloromethane	40.2x 10 ⁻³	3.5	n/a	20.8899708	344.3	0.0135	pseudo-first order	Tang, 1997
Dibromochloromethane	200x 10 ⁻³	3.5	n/a	8.3503554	137.6	0.00627	pseudo-first order	Tang, 1997
Dibromochloromethane	200x 10 ⁻³	3.5	n/a	8.3503554	137.6	0.0113	pseudo-first order	Tang, 1997
Dibromochloromethane	200x 10 ⁻³	3.5	n/a	8.3503554	137.6	0.0167	pseudo-first order	Tang, 1997
Dibromochloromethane	40.2x 10 ⁻³	3.5	n/a	4.1781889	688.6	0.00245	pseudo-first order	Tang, 1997

Table A. 1. Rate Constants of Compounds from Literature Review (Continued)

Substrate	Co mg/L	pH	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Rate Constant	Order of reaction	Reference
Dichlorobromomethane	40.2x 10 ⁻³	3.5	n/a	4.1781889	688.6	0.00332	pseudo-first order	Tang, 1997
Dichlorobromomethane	40.2x 10 ⁻³	3.5	n/a	4.1781889	688.6	0.00411	pseudo-first order	Tang, 1997
Dichlorobromomethane	80.4x 10 ⁻³	3.5	n/a	2.08899708	344.3	0.00251	pseudo-first order	Tang, 1997
Dichlorobromomethane	80.4x 10 ⁻³	3.5	n/a	0.83505355	137.6	0.00311	pseudo-first order	Tang, 1997
HMSA	80.4x 10 ⁻³	3.5	n/a	0.83505355	137.6	0.00668	pseudo-first order	Tang, 1997
HMSA	200x 10 ⁻³	3.5	n/a	0.83505355	137.6	0.00835	pseudo-first order	Tang, 1997
Toluene	200x 10 ⁻³	2	25	10 ⁻⁴ M	.1 M	3.3-2.7*10 ⁻⁶ s ⁻¹	first order	Martin, 1989
Xylene	200x 10 ⁻³	3	25	.001 M	.1 M	10 ⁻⁴ s ⁻¹	first order	Martin, 1989

Table A. 2. Half-Life Kinetics of Compounds from Literature Review

Substrate	Co mg/L	pH	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Time min	Half-life t1/2 min	HClO ₄ M	Reference
Atrazine	33.82	3	n/a	3.63	3.712	371.2	114	1.015	Arnold et al., 1995
2,4,5-trichlorophenol	0.005	n/a	25	0.1666	16.66	100	36	0.015	Barbeni et al., 1987
2,4,5-trichlorophenol	0.005	n/a	25	0.1666	16.66	100	12	0.005	Barbeni et al., 1987
2-Chlorophenol	0.005	n/a	25	0.1666	16.66	100	125	0.015	Barbeni et al., 1987
2-Chlorophenol	0.005	n/a	25	0.1666	16.66	100	14.5	0.005	Barbeni et al., 1987
3,4-dichlorophenol	0.005	n/a	25	0.1666	16.66	100	16	0.015	Barbeni et al., 1987
3,4-dichlorophenol	0.005	n/a	25	0.1666	16.66	100	6.3	0.005	Barbeni et al., 1987
3-Chlorophenol	0.005	n/a	25	0.1666	16.66	100	34	0.015	Barbeni et al., 1987
3-Chlorophenol	0.005	n/a	25	0.1666	16.66	100	6.5	0.005	Barbeni et al., 1987
4-Chlorophenol	0.005	n/a	25	0.1666	16.66	100	180	0.015	Barbeni et al., 1987
4-Chlorophenol	0.005	n/a	25	0.1666	16.66	100	12.5	0.005	Barbeni et al., 1987
2-dinitrophenol	100 mM	5	n/a	0.35 mM	18 (mol/mol sub)	n/a	13	n/a	Lipczynska, 1991
Azo dye AYL	40	3	25 (dark)	13.9 (FeSO ₄)	34	60	97.5	n/a	Ngo, 1995
Azo dye AYL	40	3	45 (dark)	13.9 (FeSO ₄)	17	17	97.5	n/a	Ngo, 1995

Table A. 2. Half-Life Kinetics of Compounds from Literature Review (Continued)

Substrate	C ₀ mg/L	pH	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Time min	Half-life t1/2 min	HClO ₄ M	Reference
Azo dye AYL	40	3	25(sunlight)	13.9 (FeSO ₄)	17	25	97	n/a	Ngo, 1995
Azo dye AYL	40	3	25 (dark)	13.9 (FeSO ₄)	17	80	95	n/a	Ngo, 1995
Azo dye AYL	40	3	30 (dark)	13.9 (FeSO ₄)	17	60	95	n/a	Ngo, 1995
Azo dye AYL	40	3	25(sunlight)	13.9 (FeSO ₄)	10	45	93	n/a	Ngo, 1995
nitrobenzene	100 mM	5.9	n/a	0.35 mM	18 (mol/mol sub)	n/a	360	n/a	Lipczynska, 1991
nitrophenol	100 mM	4.5	n/a	0.35 mM	18 (mol/mol sub)	n/a	60	n/a	Lipczynska, 1991
nitrophenol	100 mM	5.25	n/a	0.35 mM	18 (mol/mol sub)	n/a	23	n/a	Lipczynska, 1991

Table A. 3. Percentage Removal Kinetics according to Compounds

Substrate	C ₀ mg/L	pH initial	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Time min	% Removal	Reference
2,3-dichlorophenol	5 mM	3.5	22-25	0.018	2.6	25	88	Potter, 1993
2,4-D	0.1mM	2.8	28	10	100	960	100	Pignatello, et al., 1992
2,4-D	0.1mM	2	21	2.5	2.5	2	88	Pignatello, et al., 1992
2,4-D	0.1mM	4.5	21	2.5	2.5	2	86	Pignatello, et al., 1992
2,4-D	0.1mM	6	21	2.5	2.5	2	85	Pignatello, et al., 1992
2,4-D	0.1mM	1	21	2.5	2.5	2	79	Pignatello, et al., 1992
2,4-D	0.1mM	1	21	2.5	2.5	2	79	Pignatello, et al., 1992
2,4-D	0.1mM	3	21	2.5	2.5	2	76	Pignatello, et al., 1992
2,4-dichlorophenol	5 mM	3.5	22-25	0.018	2.3	240	70-75	Potter, 1993
2,5-dichlorophenol	5 mM	3.5	22-25	0.018	2.3	180	86	Potter, 1993
2,6-dichlorophenol	5 mM	3.5	22-25	0.018	2.3	240	70-75	Potter, 1993
3,5-dichlorophenol	5 mM	3.5	22-25	0.018	2.3	240	70-75	Potter, 1993
Acid Dye	300	3	50	500 (FeSO ₄)	875	30	99 (COD)	Kuo, 1992
Acid Dye	300	3	50	8000 (FeSO ₄)	875	30	97(Color)	Kuo, 1992
Acid Dye	300	3	50	8000 (FeSO ₄)	875	30	90 (COD)	Kuo, 1992
Acid Dye	300	3	50	500 (FeSO ₄)	875	30	83 (COD)	Kuo, 1992

Table A. 3. Percentage Removal Kinetics according to Compounds (Continued)

Substrate	C ₀ mg/L	pH initial	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Time min	% Removal	Reference
Atrazine	33.82	9	n/a	19.93	19.93	1440	37	Arnold, S. M. 1995
AYL	40	3	25 (dark)	13.9 (FeSO ₄)	34	60	97.5	Ngo, 1995
AYL	40	3	45 (dark)	1.9 (FeSO ₄)	17	17	97.5	Ngo, 1995
AYL	40	3	25(sunlight)	13.9 (FeSO ₄)	34	20	97.5	Ngo, 1995
AYL	40	3	25 (dark)	13.9 (FeSO ₄)	578	27	97	Ngo, 1995
AYL	40	3	35 (dark)	13.9 (FeSO ₄)	17	40	97	Ngo, 1995
AYL	40	3	25(sunlight)	13.9 (FeSO ₄)	17	25	97	Ngo, 1995
AYL	40	3	25 (dark)	13.9 (FeSO ₄)	17	80	95	Ngo, 1995
AYL	40	3	30 (dark)	13.9 (FeSO ₄)	17	60	95	Ngo, 1995
AYL	40	3	25(sunlight)	13.9 (FeSO ₄)	10	45	93	Ngo, 1995
Basic dye	300	3	50	500 (FeSO ₄)	292	30	99 (COD)	Kuo, 1992
Basic dye	300	3	50	8000 (FeSO ₄)	292	30	97(Color)	Kuo, 1992
Basic dye	300	3	50	8000 (FeSO ₄)	292	30	90 (COD)	Kuo, 1992
Basic dye	300	3	50	500 (FeSO ₄)	292	30	82 (COD)	Kuo, 1992
Benzene	50	4	20	16.69	5.52	60	80	Lou, J. C. 1995
Benzene	50	4	20	0	5.52	60	20	Lou, J. C. 1995
Bromoform	295*10 ⁻³	3.5	n/a	159.48	318.96	20	85	Tang, 1997
Bromoform	98.3*10 ⁻³	3.5	n/a	486.8	486.8	3	83	Tang, 1997
Bromoform	98.3*10 ⁻³	3.5	n/a	486.8	973.6	20	78	Tang, 1997
Bromoform	49.2*10 ⁻³	3.5	n/a	973.5	1947	20	66	Tang, 1997
Bromoform	295*10 ⁻³	3.5	n/a	159.48	3189.6	2	33	Tang, 1997
Bromoform	98.3*10 ⁻³	3.5	n/a	486.8	9736	2	31	Tang, 1997
Bromoform	49.2*10 ⁻³	3.5	n/a	973.5	19470	2	30	Tang, 1997
Bromoform	98.3*10 ⁻³	3.5	n/a	486.8	97360	3	25	Tang, 1997
Direct dye	300	3	50	83 (FeSO ₄)	292	30	98(COD)	Kuo, 1992
Direct dye	300	3	50	8000 (FeSO ₄)	292	30	97(Color)	Kuo, 1992
Direct dye	300	3	50	83 (FeSO ₄)	292	30	96(COD)	Kuo, 1992
Direct dye	300	3	50	8000 (FeSO ₄)	292	30	90 (COD)	Kuo, 1992
Disperse dye	300	3	50	8000 (FeSO ₄)	292	5	97(Color)	Kuo, 1992

Table A. 3. Percentage Removal Kinetics according to Compounds (Continued)

Substrate	Co mg/L	pH initial	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Time min	% Removal	Reference
Monochlorophenol	5 mM	3.5	22-25	0.018	4.1	40	97	Potter, 1993
Monochlorophenol	5.04 mM	3.5	23	0.0355	12.89	20	97	Potter, 1993
Monochlorophenol	5.69 mM	3.5	23	0.0053	11.6	140	90	Potter, 1993
Monochlorophenol	5.43 mM	3.5	23	0.0083	11.97	25	90	Potter, 1993
Monochlorophenol	5.88 mM	3.5	23	0.0153	11.05	23	90	Potter, 1993
Monochlorophenol	5.43 mM	3.5	24	0.00424	12.21	230	80	Potter, 1993
Monochlorophenol	5 mM	3.5	22-25	0.018	2.1	5	70	Potter, 1993
p-chlorophenol	5 mM	3.5	22-25	0.018	2.3	65	94	Potter, 1993
p-chlorophenol	5 mM	3.5	22-25	0.018	2.3	5	72	Potter, 1993
p-chlorophenol	5 mM	3.5	22-25	0.018	2.3	15	72	Potter, 1993
Phenol & Formaldehyde	5000	n/a	n/a	n/a		30-60	100	Degussa Corp., Kuo, 1992
Reactive dye	300	3	50	250 (FeSO ₄)	584	30	98(COD)	Kuo, 1992
Reactive dye	300	3	50	8000 (FeSO ₄)	584	30	97(Color)	Kuo, 1992
Reactive dye	300	3	50	8000 (FeSO ₄)	584	30	90 (COD)	Kuo, 1992
Reactive dye	300	3	50	250 (FeSO ₄)	584	30	86(COD)	Kuo, 1992
Starch	30,000(BOD)	n/a	n/a	5 (FeSO ₄)	50	30	91 (BOD)	Burbank, 1975
Toluene	50	4	20	16.69	5.52	60	80	Lou, J. C. 1995
Toluene	50	4	20	0	5.52	60	20	Lou, J. C. 1995
Xylene	50	4	20	16.69	5.52	60	90-94	Lou, J. C. 1995
Xylene	50	4	20	0	5.52	60	20	Lou, J. C. 1995

Table A. 4. Kinetics of Final Concentration of the Compounds from Literature Review

Substrate	Co mg/L	pH initial	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Time min	Ct mg/L	Reference
2,3-Dichlorophenol	20	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
2,4-Dichlorophenol	20	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
2,5-Dichlorophenol	20	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
2-Chlorobenzoate	200	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
2-Chlorophenol	500	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
3-Chlorobenzoate	100	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
3-Chlorophenol	500	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
4-Chlorobenzoate	50	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
4-Chlorophenol	500	3	60	.02% FeCl ₂	0.30%	60	ND (mM)	Koyama et al., 1994
PCB	0.1	2	25	800 M	200 M	20	1 (mM)	Sedlak 1991
PCB	0.1	3	25	800 M	200 M	20	1 (mM)	Sedlak 1991
PCB	0.1	4	25	800 M	200 M	20	1 (mM)	Sedlak 1991
PCB	0.1	7	25	800 M	200 M	20	1 (mM)	Sedlak 1991
p-Chlorobiphenyl	10	3	60	.02% FeCl ₂	0.30%	60	10.6 (mM)	Koyama et al., 1994
Phenol	50	3	10	0.1	9	2	33.6	Eisenhauer, 1964
Phenol	50	3	10	0.1	9	5	27.8	Eisenhauer, 1965
Phenol	50	3	10	0.1	9	15	8.5	Eisenhauer, 1966
Phenol	50	3	10	0.25	9	2	21.2	Eisenhauer, 1967
Phenol	50	3	10	0.25	9	5	11.6	Eisenhauer, 1968
Phenol	50	3	10	0.25	9	15	0	Eisenhauer, 1969
Phenol	50	3	10	0.5	9	2	3	Eisenhauer, 1970
Phenol	50	3	10	0.5	9	5	0	Eisenhauer, 1971
Phenol	50	3	10	0.5	9	15	0	Eisenhauer, 1972
Phenol	50	3	10	1	9	2	0	Eisenhauer, 1973
Phenol	50	3	10	1	9	5	0	Eisenhauer, 1974
Phenol	50	3	10	1	9	15	0	Eisenhauer, 1975
Phenol	50	3	10	1	3	2	2	Eisenhauer, 1976
Phenol	50	3	10	1	3	5	0	Eisenhauer, 1977

Table A. 4. Kinetics of Final Concentration of the Compounds from Literature Review (Continued)

Substrate	C ₀ mg/L	pH initial	Temp oC	Fe ²⁺ mol/mol sub	H ₂ O ₂ mol/mol subs	Time min	Ct mg/L	Reference
Phenol	50	3	10	1	1	2	16	Eisenhauer, 1982
Phenol	50	3	10	1	1	5	14.2	Eisenhauer, 1983
Phenol	50	3	10	1	1	15	13.6	Eisenhauer, 1984
Phenol	50	3	10	1	0.5	2	16	Eisenhauer, 1985
Phenol	50	3	10	1	0.5	5	16	Eisenhauer, 1986
Phenol	50	3	10	1	0.5	15	16	Eisenhauer, 1987

APPENDIX B

Experimental Data of Part I.

Table B.1. Degradation of Acid Orange 8, $H_2O_2 = 0.001$ M, Time = 1 min

H_2O_2 (M)	pH = 2	pH = 3	pH = 4
	t=1 min	t=1 min	t=1 min
Co	0.821	0.8428	0.08292
0	0	0	0
0.00001	0.8086	0.8204	0.8067
0.0001	0.7515	0.7044	0.7084
0.001	0.652	0.4888	0.5196
0.01	0.6387	0.4478	0.4623
0.1	0.7228	0.6097	0.6293

Table B.2. Degradation of Acid Orange 8, Duplicate of Table B.1, $H_2O_2 = 0.001$ M, Time = 1 min

H_2O_2 (M)	pH = 2	pH = 3	pH = 4
	t=1 min	t=1 min	t=1 min
Co	0.0821	0.08428	0.08292
0	0	0	0
0.00001	0.08002	0.08125	0.08115
0.0001	0.07555	0.07279	0.07314
0.001	0.06549	0.05006	0.05293
0.01	0.06781	0.04254	0.04775
0.1	0.07574	0.06127	0.06356

Table B.3. Degradation of Acid Orange 8, $H_2O_2 = 0.001$ M, Time = 1 min

Fe^{2+} (M)	Concentration of Dye at pH = 2	Concentration of Dye at pH = 2.5	Concentration of Dye at pH = 3	Concentration of Dye at pH = 3.5	Concentration of Dye at pH = 4
0	0.084	0.084	0.084	0.084	0.084
0.0005	0.030114	0.025074	0.017413	0.018094	0.034532
0.001	0.005565	0.003588	0.003807	0.004252	0.010947
0.005	0.001349	0.001088	0.000548	0.000612	0.001576
0.01	0.00037	0.0004	7.4E-05	0.000153	0.000467

Table B.4. Degradation of Acid Orange 8, Fe²⁺ = 0.001 M, Time = 1 min

H ₂ O ₂ (M)	Concentration of Dye at pH = 2	Concentration of Dye at pH = 2.5	Concentration of Dye at pH = 3	Concentration of Dye at pH = 3.5	Concentration of Dye at pH = 4
0	0.0805	0.084	0.0805	0.0805	0.0805
0.00001	0.079856	0.079716	0.056865	0.065229	0.058749
0.0001	0.065242	0.065705	0.03454	0.046574	0.037658
0.001	0.012057	0.029047	0.00755	0.010945	0.011938
0.01	0.003111	0.02074	0.001885	0.003623	0.003653
0.1	0.001726	0.021731	0.000522	0.001025	0.001465

Table B.5. Degradation of Monoazo Dyes, H₂O₂ = 0.001 M, Time = 1 min

Fe ²⁺ (M)	Acid Red 8 (M)	Acid Blue 92 (M)	Acid Blue 161 (M)	Acid Orange8 (M)
0	0.08695	0.11135	0.1035	0.084
0.0005	0.02733	0.00462	0.03716	0.017413
0.001	0.01002	0.00033	0.03262	0.003807
0.005	0.01914	0.01396	0.05052	0.000548
0.01	0.0347	0.02419	0.05982	7.4E-05

Table B.6. Degradation of Monoazo Dyes, Fe²⁺ = 0.001 M, Time = 1 min

H ₂ O ₂ (M)	Acid Red 8 (M)	Acid Blue 92 (M)	Acid Blue 161 (M)	Acid Orange8 (M)
0	0.08695	0.11135	0.1035	0.084
0.00001	0.07915	0.055953	0.037664	0.059338
0.0001	0.06637	0.0242	0.002207	0.036042
0.001	0.02322	0.001028	0.000824	0.007879
0.01	0.0035	5.42E-05	0.000737	0.001967
0.1	0.03217	3.15E-05	0.000737	0.000545

Table B.7. Degradation of Acid Yellow 38, H₂O₂ = 0.001 M, Time = 1 min

Fe ²⁺ (M)	Concentration of Dye at pH = 2	Concentration of Dye at pH = 2.5	Concentration of Dye at pH = 3	Concentration of Dye at pH = 3.5	Concentration of Dye at pH = 4
0	0.1	0.14	0.077	0.1238	0.1286
0.0005	0.1	0.1085	0.0302	0.0499	0.0474
0.001	0.091	0.0707	0.0358	0.0364	0.0358
0.005	0.094	0.0879	0.0716	0.0707	0.0589
0.01	0.1	0.1148	0.102	0.0967	0.0966

Table B.8. Degradation of Acid Yellow 38, $\text{Fe}^{2+} = 0.001 \text{ M}$, Time = 1 min

H_2O_2 (M)	Concentration of Dye at pH = 2	Concentration of Dye at pH = 2.5	Concentration of Dye at pH = 3	Concentration of Dye at pH = 3.5	Concentration of Dye at pH = 4
0	0.1	0.14	0.077	0.1238	0.1286
0.00001	0.1	0.13	0.074	0.0507	0.0688
0.0001	0.1	0.12	0.0739	0.0695	0.0577
0.001	0.0979	0.0809	0.0443	0.0423	0.037
0.01	0.0709	0.0395	0.0294	0.0305	0.032
0.1	0.1	0.044	0.0265	0.0311	0.0259

Table B.9. Degradation of Disazo Dyes at pH 4, $\text{H}_2\text{O}_2 = 0.001 \text{ M}$, Time = 1 min

Fe^{2+} (M)	Direct Violet 51 (M)	Acid Red 97 (M)	Acid Yellow 38 (M)
0	0.1048	0.1111	0.1286
0.0005	0.0221	0.0244	0.0474
0.001	0.0093	0.0059	0.0358
0.005	0.0071	0.0048	0.0589
0.01	0.0081	0.0038	0.0966

Table B.10. Degradation of Disazo Dyes at pH 4, $\text{Fe}^{2+} = 0.001 \text{ M}$, Time = 1 min

H_2O_2 (M)	Direct Violet 51 (M)	Acid Red 97 (M)	Acid Yellow 38 (M)
0	0.1048	0.1111	0.1286
0.00001	0.0771	0.0188	0.0688
0.0001	0.024	0.018	0.0577
0.001	0.0088	0.0052	0.037
0.01	0.0048	0.0011	0.032
0.1	0.0042	0.0123	0.0259

Experimental Data of Part II.

Table B.11. Degradation of Monoazo Dyes at pH 2.5

Time	Acid Red 8 (M)	Acid Yellow 25 (M)	Acid Orange 8 (M)	Acid Blue 92 (M)	Acid Blue 161 (M)
0	.1	0.112	0.1195	0.05264	0.09109
0	.05	0.1198	0.116	0.01894	0.06655
1	.03238	0.08889	0.1151	0.00173	0.04454
2	.02521	0.0884	0.1148	0.0001	0.03654
5	.01557	0.0792	0.114	0.0001	0.03121
10	.006	0.025	0.1128	0.0001	0.02022
20	.0047	0.02	0.1124	0.0001	0.00961
30	.0033	0.0168	0.1121	0.0001	0.00938
60	.0015	0.0153	0.00985	0.0001	0.00851

Table B.12. Degradation of Monoazo Dyes at pH 3

Time	Acid Red 8 (M)	Acid Yellow 25 (M)	Acid Orange 8 (M)	Acid Blue 92 (M)	Acid Blue 161 (M)
0	0.1228	0.102	0.1263	0.12963	0.08375
0	0.1157	0.0978	0.1256	0.10834	0.08029
1	0.1116	0.09124	0.1255	0.09978	0.07277
2	0.1113	0.09059	0.1211	0.08728	0.064063
5	0.1108	0.090288	0.1209	0.08461	0.05122
10	0.0862	0.08929	0.1185	0.07321	0.03955
20	0.0328	0.08692	0.1183	0.04654	0.01142
30	0.0275	0.084177	0.1182	0.02827	0.01129
60	0.0073	0.0784	0.108	0.0001	0.01128

Table B.13. Degradation of Monoazo Dyes at pH 3.5

Time	Acid Red 8 (M)	Acid Yellow 25 (M)	Acid Orange 8 (M)	Acid Blue 92 (M)	Acid Blue 161 (M)
0	0.12	0.0995	0.1295	0.07264	0.09084
0	0.1198	0.0919	0.128	0.06578	0.09062
1	0.1164	0.08012	0.1271	0.06515	0.09058
2	0.1103	0.0801	0.1263	0.6466	0.09053
5	0.1103	0.07042	0.1245	0.599	0.08956
10	0.107	0.0564	0.1233	0.4824	0.08858
20	0.1008	0.0438	0.1209	0.3901	0.08808
30	0.0953	0.03881	0.1183	0.3705	0.085
60	0.087	0.3864	0.1122	0.3072	0.0836

Table B.14. Degradation of Disazo Acid Yellow 38

Time	pH 2.5	pH 3	pH 3.5
0	0.1259	0.1211	0.1432
0	0.0917	0.1097	0.1307
1	0.0705	0.1017	0.1306
2	0.0689	0.0964	0.1288
5	0.0615	0.08896	0.1242
10	0.0593	0.0682	0.123
20	0.052	0.04154	0.112
30	0.0496	0.0222	0.1069
60	0.049	0.01076	0.1

Table B.15. Degradation of Disazo Direct Violet 51

Time	pH 2.5	pH 3	pH 3.5
0	0.0991	0.1	0.0956
0	0.09638	0.1084	0.0813
1	0.09638	0.0871	0.0582
2	0.09638	0.0736	0.0534
5	0.09638	0.0607	0.0516
10	0.09638	0.0533	0.0446
20	0.09638	0.0444	0.0363
30	0.09638	0.0347	0.031
60	0.09638	0.034	0.0247

Table B.16. Degradation of Disazo Dye Acid Red 97

Time	pH 2.5
0	0.11
0	0.11
1	0.10814
2	0.10467
5	0.10467
10	0.10467
20	0.10467
30	0.1029
60	0.10237

Table B.17. Degradation of Trisazo Direct Blue 71

Time	pH 2.5	pH 3	pH 3.5
0	0.1098	0.119	0.0991
0	0.1064	0.119	0.099
1	0.106	0.114	0.0929
2	0.106	0.114	0.087
5	0.106	0.114	0.084
10	0.106	0.112	0.0781
20	0.106	0.106	0.076
30	0.106	0.101	0.0709
60	0.104	0.1005	0.0605

Table B.18. Comparison of Degradation of Acid Yellow 38 by Both Processes

pH	% Removal by H_2O_2/Fe^{2+}		% Removal by H_2O_2/Fe powder	
	C_i	C_t	C_i	C_t
2.5	0.14	0.0879	0.1259	0.0705
3	0.077	0.0302	0.1211	0.1017
3.5	0.1238	0.0499	0.1432	0.1306