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Advanced Oxidation Process of Sulfolane in Wastewater Using Fenton Reagent

by

Nurul'Ain binti Ahmad Basri

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2009

Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NURUL'AIN BT AHMAD BASRI

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Nurul'Ain bt. Ahmad Basri

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ABSTRACT

Toxicity from industrial wastewater remains a problem even after conventional activated sludge treatment process, because of the persistence of some toxicant compounds. Among chemical processes, the advanced oxidation process (AOP) has been used to reduce the organic load or toxicity of different wastewaters. AOPs are based on the generation of hydroxyl free radicals, which have a high electrochemical oxidant potential. The generation of hydroxyl radicals involves the combination of classical oxidants, such as H_2O_2 or O_3 with UV radiation or a catalyst. The formed radicals react with organic materials breaking them down gradually in a stepwise process. The generation of hydroxyl radicals can be achieved by a variety of reactions, such as ozone/UV, hydrogen peroxide/UV, Fenton Oxidation, photo-Fenton, or titanium dioxide/hydrogen peroxide/solar radiation. The advantage of AOPs is that they effectively destroy the organic compounds, converting them mainly to carbon dioxide and water. Sulfolane is widely used as an industrial solvent to purify natural gas where large amounts of waste contains Sulfolane to be disposed off to wastewater during the downtimes is produced. The present study is to investigate the effects of H_2O_2 concentration, Iron concentration, pH and temperature of the treatment of wastewater containing abundant Sulfolane by Advanced Oxidation Process (AOP) using Fenton reagent. This process consists of Ferrous salts combined with hydrogen peroxide under acidic conditions. The test series conducted consists of test series A: H_2O_2: Fe^{2+} = 1:1 (1 mole of H_2O_2 to 1 mole of Fe^{2+}), test series B: H_2O_2: Fe^{2+} = 1:2 (1 mole of H_2O_2 to 2 mole of Fe^{2+}), test series C: H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+}), test series D: The effect of pH for pH 2, 3, 4-5, 7-8 and test series E: the effect of temperature for 27°C, 40°C and 60°C. Advanced Oxidation Process using Fenton reagent is effective at enhancing the biodegradability of wastewater. This reaction allows the generation of hydroxyl radicals as shown in reaction (1):

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

CHAPTER 1
INTRODUCTION

1.1 Background of Study

In industrial wastewater treatment, reduction or removal of organic and inorganic compound concentrations is essential. Generation of wastewater in industrial processes is sometimes unavoidable and in most cases a process to reduce the organic load and other contaminants must be employed before water discharge. Among chemical processes, the advanced oxidation process (AOP) has been used to reduce the organic load or toxicity of different wastewaters.

Advanced Oxidation Processes, refers to a set of chemical treatment procedures designed to remove organic and inorganic materials in waste water by oxidation. Contaminants are oxidized by four different reagents: ozone, hydrogen peroxide, oxygen, and air, in precise, pre-programmed dosages, sequences, and combinations. These procedures may also be combined with UV irradiation and specific catalysts. This results in the development of hydroxyl radicals. A well known example of AOP is the use of Fenton's reagent.

The AOP procedure is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in waste water. The contaminant materials are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts, in example they undergo mineralization. A goal of the waste water treatment by means of AOP procedures is the reduction of the chemical contaminants and the toxicity to such an extent that the cleaned waste water may be reintroduced into receiving streams or, at least, into a conventional sewage treatment.

AOP Advantages:

- remarkable cut down in ozone demand
- no harmful residuals or by-products
- total solution for non-biodegradable contaminants and COD/BOD reduction in water
- optimal combination of ozone, UV and H_2O_2 available depending on water quality and requirements before discharge

In this work, Fenton reagent is used as a chemical process for wastewater treatment. Fenton's reagent has proven to be an economically feasible and effective oxidant to destruct an extensive of hazardous wastes. (Nora San Sebastian Martinez, 2003).

1.2 Problem Statement

Sulfolane is a clear, colorless liquid commonly used in the chemical industry as an extractive distillation solvent or reaction solvent. Sulfolane is an aprotic organosulfur compound, and it is readily soluble in water. Sulfolane is widely used as an industrial solvent to purify natural gas which is called Sulfinol Process. The sulfinol process purifies natural gas by removing H_2S, CO_2, COS and mercaptans from natural gas with a mixture of alkanolamine (DIPA) and sulfolane. Large amounts of waste contains Sulfolane to be disposed off during the downtimes is produced. It might be difficult to treat the waste water using the available biological treatment packages due to its high chemical oxygen demand (COD) level. Hence, must revert to chemical treatments such as Fenton's reagent before discharge into the common drainage system. High COD in effluent will result in removal of oxygen from natural water thus reduces its ability to sustain aquatic life and against the environmental laws and regulations. In this work, Fenton reagent is used as a chemical process for wastewater treatment. But is Fenton's reagent is more economically feasible and effective oxidant to destruct an extensive of hazardous wastes.

1.3 Objective and Scope of Study

The objective of this study is to investigate advanced oxidation process (AOP) of Sulfolane using Fenton Reagent in wastewater. Biological treatment could not treat any solution with high COD level, thus we need to decrease the COD level. In order to achieve this objective, a few tasks and research need to be carried out by collecting all technical details regarding AOP and Fenton reagents by studying the fundamental behavioral of the reagent and Sulfolane. To oxidize Sulfolane using Fenton's Reagent, (solution of hydrogen peroxide and iron catalyst) the following scopes need to take into consideration:

- Effect of iron (Fe^{2+}) concentration in the Fenton process
- Effect of hydrogen peroxide concentration in Fenton process
- Effect of pH in Fenton process
- Effect of temperature in Fenton process

1.4 Relevancy

The sulfinol process purifies natural gas by removing H_2S, CO_2, COS and mercaptans from natural gas with a mixture of alkanolamine (DIPA) and sulfolane. Large amounts of waste to be disposed off during the downtimes are produced. It might be difficult to treat the waste water using the available biological treatment packages due to its high chemical oxygen demand (COD) level. Biological treatment could not treat any solution with high COD level. Revert to chemical treatments such as Advanced Oxidation Process using Fenton's reagent before discharged into the common drainage system.

1.5 Feasibility

Methods in understanding can be done in UTP (literature research, experiments). The project was proven feasible to be implemented in terms of timeliness, apparatus and chemicals. The experiments done in this study could be completed within two semesters of a study year. All apparatus and chemicals can be obtained from the chemical laboratories.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Introduction: The use of hydrogen peroxyde

Hydrogen peroxide (H_2O_2) is a strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established. Numerous applications of H_2O_2 in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, cyanides, and chlorine, are known.

H_2O_2 is also useful in the treatment of the gaseous sulphur oxides and nitrogen oxides being converted to the corresponding acids. Other related uses include the bleaching of pulp and paper and organic synthesis. H_2O_2 has applications in the surface treatment industry involving cleaning, decorating, protecting and etching of metals (L'air Liquide).

By dissociation into oxygen and water H_2O_2 can also supply oxygen to micro organisms in biological treatment facilities and in the bioremediation of contaminated sites. It can be used as a disinfecting agent in the control of undesirable biofilm growth. Since the oxygen concentration is generally rate limiting during the in situ biodegradation of organic contaminants, several applications using injection of H_2O_2 into the subsurface have been successfully attempted to enhance the biodegradation activity. H_2O_2 can be decomposed into water and oxygen by enzymatic and nonenzymatic routes. (Calabrese and Kostecki)

Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides), because of low rates of reaction at reasonable H_2O_2 concentrations. Transition metal salts (e.g. iron salts), ozone and UV-light can activate H_2O_2 to form hydroxyl radicals which are strong oxidants:

- ozone and hydrogen peroxide

  $O_3+H_2O_2 \rightarrow OH^{\bullet}+O_2+HO_2^{\bullet}$

- iron salts and hydrogen peroxide

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

- UV-light and hydrogen peroxide

  $H_2O_2[+UV] \rightarrow 2OH^{\bullet}$

The oxidation processes utilizing activation of H_2O_2 by iron salts, referred to as Fenton's reagent, are discussed in this study.

In general, oxidation processes which are based on the generation of radical intermediates are termed advanced oxidation techniques. Hydroxyl radicals are stronger oxidants than ozone and H_2O_2. Hydroxyl radicals non-specifically oxidize target compounds at high reaction rates.

2.2 Fenton's Reagent

Many metals have special oxygen transfer properties which improve the utility of hydrogen peroxide. By far, the most common of these is iron which, when used in the prescribed manner, results in the generation of highly reactive hydroxyl radicals (. OH). The reactivity of this system was first observed in 1894 by its inventor H.J.H. Fenton, but its utility was not recognized until the 1930's once the mechanisms were identified. Today, Fenton's Reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (phenols, formaldehyde, and complex wastes derived from dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals). The process may be applied to wastewaters, sludges, or contaminated soils, with the effects being:

- Organic pollutant destruction
- Toxicity reduction
- Biodegradability improvement
- BOD / COD removal
- Odor and color removal

The primary benefits of the Fenton reagent are its ability to convert a broad range of pollutants to harmless or biodegradable products, its benign nature (residual reagents do not pose an environmental threat), and the relatively low cost of the reagents. Among AOPs, the Fenton's reagent has been efficiently used as a chemical process for wastewater treatment and pre-treatment. The Fenton's system consists of Ferrous salts combined with hydrogen peroxide under acidic conditions. This reaction allows the generation of hydroxyl radicals as shown in reaction (1):

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

Fe^{3+} produced can react with H_2O_2 and hydroperoxyl radical in the so-called Fenton-like reaction, which leads to regenerating Fe^{2+} (reactions (2) and (3)). Fe^{2+} regeneration is also possible by reacting with organic radical intermediates (reaction (4)):

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

$Fe^{3+} + HO_2 \longrightarrow Fe^{2+} + O_2 + H^{+}$ (3)

$Fe^{3+} + R^{\bullet} \longrightarrow Fe^{2+} + R^{+}$ (4)

The Fenton's reaction has a short reaction time among AOPs; therefore, Fenton's reagent is used when high COD removal is required. A wide variety of Fenton's reagent applications have been reported, such as treatment of textile in wastewater, treatment of 1-amino-8-naphtol-3,6-disulfonic acid manufacturing wastewater, improvement on dewatering of activated sludge, etc.

In this work, the Fenton's reagent is used in Advanced Oxidation Process of Sulfolane to remove COD from an industrial wastewater characterized by its high value of COD in the wastewater. (Nora San Sebastian Martinez, 2003)

2.2.1 Effect of H_2O_2 Concentration

As the H_2O_2 dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, whereupon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity.

2.2.2 Effect of Iron Concentration

In the absence of iron, there is no evidence of hydroxyl radical formation when, for example, H_2O_2 is added to a phenolic wastewater (i.e., no reduction in the level of phenol occurs). As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes inefficient. This feature (an optimal dose range for iron catalyst) is characteristic of Fenton's Reagent, although the definition of the range varies between wastewaters.

2.2.3 Effect of pH on Fenton's Reagent

Fenton oxidation is known highly pH dependant process, since pH plays an important role in the mechanism of $^{\cdot}OH$ production in the Fenton's reaction. At high pH (pH>4), the generation of $^{\cdot}OH$ gets slower because of the formation of the ferric hydroxyl complexes and the complexes would further form $Fe(OH)_4$,when,the pH value is higher than 9.0. At very low pH values (<2.0), the reaction is slowed down, due to the formation of complex species $[Fe(H_20)_6]^{2+,}$ which reacts more slowly with peroxide compared to that of $[Fe(OH)(H_2O)_5]^{2+.}$ In addition, the peroxide gets solvated in the presence of high concentrations of H^+ ion, to form stable oxonium ion$[H_3O_2]^+$. An oxonium ion makes peroxide electrophilic to enhance its stability and presumably reduces substantially the reactivity with Fe^{2+} ion. The usual optimum working pH when using this system is in the range 3-5. However neutral pH has also been found to be the most appropriate to oxidize some chemicals like polynuclear, aromatic hydrocarbons, nitrobenzenes, amines etc (Beltran et al.1998). Broadly speaking, it is assumed that the poor conversions is achieved at neutral pH are related to reduction in stability of both Fe^{2+} and H_2O_2 when increasing pH from acidic conditions. Moreover at neutral pH ferrous iron is readily oxidized by atmospheric and ferric ion precipitates preventing the regeneration of Fe $^{2+}$. However other factors may affect the influence of pH, specially the presence of organic and inorganic species able to stabilize or promote by complexation the auto-oxidation of ferrous ion (Yamazaki and Piette, 1991).

2.2.4 Effect of Temperature

The rate of reaction with Fenton's Reagent is affected by temperature. This is one reason why most declarations rate constants include a temperature at which that constant is valid. Perhaps the most straightforward relationship between temperature and rate constants was suggested by Svante Arrhenius in 1889. Estimates of E_A can be made using experimental values of rate constants determined at different temperatures. This is called Arrhenius equation;

$\mathbf{k = A \cdot e^{-EA/RT}}$ where; E_A = activation energy

A = pre-exponentyial factor

T = temperature (°K)

R = gas constant (8.314 J/mol)

As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between 20^0C to 40 ^{0}C. Moderating the temperature is important not only for economic reasons, but for safety reasons as well. (Bishop & Walling, 1996)

2.3 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals. COD measurements are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution.

Chemical oxygen demand is related to biochemical oxygen demand (BOD), another standard test for assaying the oxygen-demanding strength of waste waters. However, biochemical oxygen demand only measures the amount of oxygen consumed by microbial oxidation and is most relevant to waters rich in organic matter. It is important to understand that COD and BOD do not necessarily measure the same types of oxygen consumption. For example, COD does not measure the oxygen-consuming potential associated with certain dissolved organic compounds such as acetate. However, acetate can be metabolized by microorganisms and would therefore be detected in an assay of BOD. In contrast, the oxygen-consuming potential of cellulose is not measured during a short-term BOD assay, but it is measured during a COD test.

2.4 Sulfolane

Sulfolane $C_4H_8O_2S$ (also tetramethylene sulfone, systematic name: 2,3,4,5-tetrahydrothiophene-1,1-dioxide) is a clear, colorless liquid commonly used in the chemical industry as an extractive distillation solvent or reaction solvent. Sulfolane is classified as a sulfone, a group of organosulfur compounds containing a sulfonyl functional group. The sulfonyl group is a sulfur atom doubly bonded to two oxygen atoms. The sulfur-oxygen double bond is highly polar, allowing for its high solubility in water, while the four carbon ring provides non-polar stability. These properties allow it to be miscible in both water and hydrocarbons, resulting in its widespread use as a solvent for purifying hydrocarbon mixtures. Sulfolane is widely used as an industrial solvent, especially in the extraction of aromatic hydrocarbons from hydrocarbon mixtures and to purify natural gas.

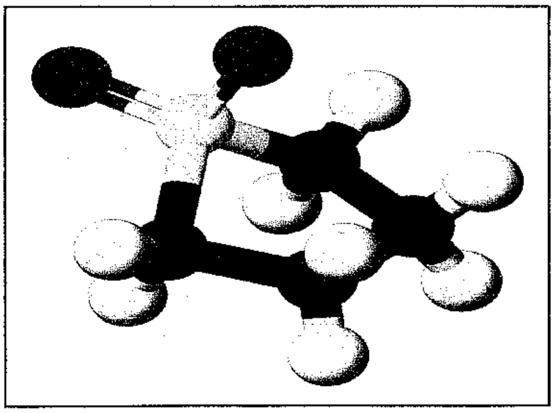

Figure 2.1: Sulfolane

Shortly after the sulfinol process was implemented, sulfolane was found to be highly effective in separating high purity aromatic compounds from hydrocarbon mixtures using liquid-liquid extraction. This process is still widely used today in refineries and the petrochemical industry. Because sulfolane is the most efficient industrial solvent for purifying aromatics, they operate at the lowest solvent-to-feed ratio, making sulfolane units highly cost effective. In addition, it is selective in a range that complements distilliation; where sulfolane can't separate two compounds, distillation easily can and vice versa, keeping sulfolane units useful for a wide range of compounds with minimal additional cost. While sulfolane is highly stable and can therefore be reused many times, it does eventually break down into acidic byproducts. A number of measures have been developed to remove these byproducts, allowing the sulfolane to be reused and increase the lifetime of a given supply. Some methods that have been developed to regenerate spent sulfolane include vacuum and steam distillation, back extraction, adsorption, and anion-cation exchange resin columns

2.5 Biodegradation

The biodegradation of sulfolane has been investigated in an activated sludge system, in wastewater treatment, in laboratory microcosm studies using contaminated aquifer sediments, and as part of a natural attenuation study in natural wetlands. Most studies have demonstrated that sulfolane is readily biodegradable in nutrient-enriched aerobic microcosms from a variety of sulfolane-contaminated environmental samples. (Chou and Swatloski 1983).

The stoichiometry of the complete oxidation of sulfolane was given by Greene *et al.* (1999) as:

$$\mathbf{C_4H_8O_2S + 6.5O_2 \rightarrow 4CO_2 + 3H_2O + 2H^+ + SO4^{2-}}$$

Thus, the release of H_2SO_4, a strong acid, caused the observed drop in pH that resulted in termination of the microbial activity in the study. (Chou and Swatloski, 1983)

A number of recent studies have investigated sulfolane biodegradation using nutrient-amended and unamended microcosms, under aerobic and anaerobic conditions, and at temperatures ranging from 8 to 28°C. Microcosm studies were conducted using water with sediments and soils from sulfolane contaminated aquifers. Sulfolane concentrations reported in these microcosm studies reflect chemical analysis of the supernatant liquid in mg·L^{-1}. Sediments/aquifer materials ranged from sandstone, to till and sand, to wetland sediments. (Fedorak and Coy, 1996)

Biodegradability enhancement

Although some contaminants can easily be biodegraded by aerobic microorganisms it still seems worthwhile to investigate the effects of Fenton's reagent pre-treatment on the biodegradability of this type of wastewater. Figure 2.1 shows the COD removal efficiencies with three different treatments. (Xiao Jun Wang, Yan Song, Jun, Sheng Mai, 2008)

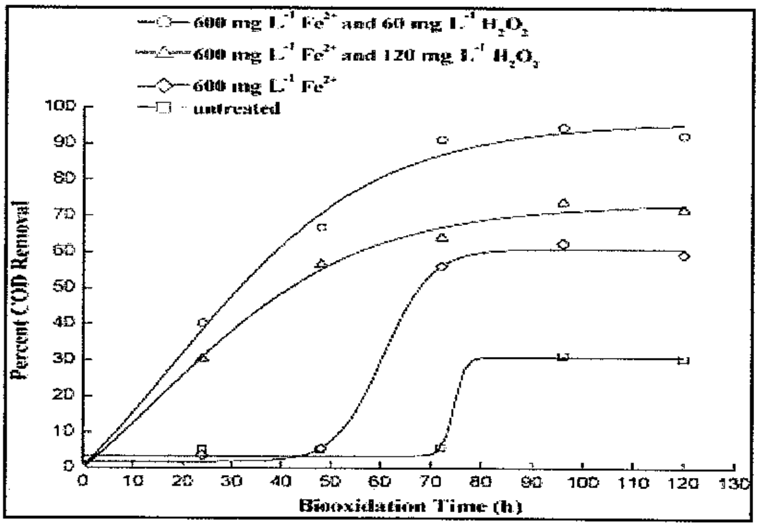

Figure 2.2: Biodegradation plot for the untreated and pretreated wastewater.

. CHAPTER 3

METHODOLOGY

3.1 Research

Many important references were obtained from the journal that been published by websites. The journals described on wastewaters, advanced oxidation process, Fenton system and a lot more. After collecting journals, interpretations of the journal contents need to carry out in favor of to select the useful information. The key milestone of this project is shown in APPENDIX B.

3.2 Project Activities

3.2.1 Preparing 200mg/L COD of Sulfolane

1. 1 liter volumetric flask is prepared.
2. Set the micropipette at 0.0916ml sulfolane to be used and pipette out sulfolane into the 1 liter volumetric flask and add distilled water into the flask till the mark. Shake thoroughly.
3. The amount of sulfolane to be used in preparing 200mg/L COD of sulfolane is calculated using stoichiometric oxidation reaction of sulfolane.

Calculation:

Balancing the equation:

$C_4H_8O_2S + 6.5O_2 \longrightarrow 4CO_2 + 3H_2O + 2H^+ + SO_4^{2-}$

Molar Mass of $C_4H_8O_2S$: 120.17 g/mol

Molar mass of O_2: 32 g/mol

$6.5\ O_2: 6.5(32) = 208$ g/mol

200 COD (mg/L) = (208/120.12) x Sulfolane (mg/L)

Sulfolane (mg/L) = 200 mg/L x (120.12/208)

= 115.5 mg/L

Density of Sulfolane = 1.261 g/cm^3 = 1261 mg/cm^3

Mass = density x volume

115.5 mg = 1261 mg x volume

Volume = 115.5/1261

= 0.0916 ml of Sulfolane

3.2.2 Reacting Sulfolane with Fenton's Reagent

1. 8 vials with 2ml of NaOH in each vial are prepared.
2. 500 ml of Sulfolane solution is prepared and poured into the reactor.

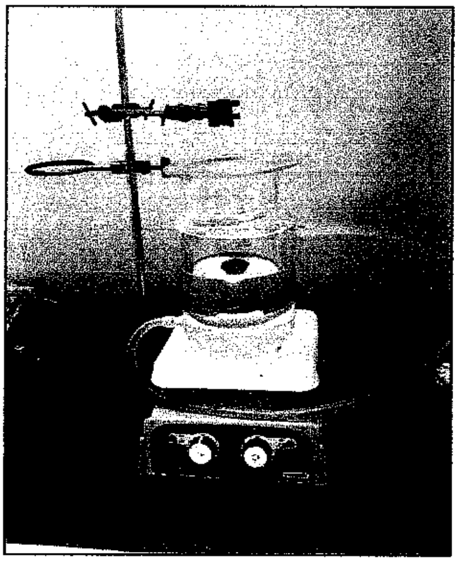

Figure 3.1: 1000mg/L of Sulfolane in jacketed flask

Figure 3.2: Reacting Sulfolane with Fenton Reagent

3. $FeSO_4$ powder of 34.5 g weight is added into the reactor and take note the value of pH.
4. H_2O_2 solution is added. The pH of the solution must be within the fixed pH range of 3 to 4. The pH is adjusted by adding H_2SO_4 or NaOH.
5. 2ml of samples are withdrawn for every 0, 1, 2, 4, 6, 8, 10, 30 minutes into the vial. The sample taken will be dissolved with 2ml NaOH in vial to stop further reaction.
6. Put the sample into the hot bath for 20 minutes to remove excess H_2O_2.

7. Filter out the solution leaving the precipitate behind and pour the filtrate into a new vial.
8. COD reading of each solution in each vial at different timing is taken and a table is formed for the reading.
9. Continue the experiment while changing :

- The concentration of $FeSO_4$ while keeping the concentration of H_2O_2 constant

- The pH value of solution.
- The temperature of solution

Calculation

Theoretical amount of H_2O_2;

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{o}OH + OH^{-}$

1 mole $H_2O_2 \longrightarrow$ 1 mole ^{o}OH

For 200 mg/L COD of Sulfolane;

Molar Mass;

(200/8) mMole g H_2O_2 = 25 mMole

Molar Mass of H_2O_2: 34 g/mole

0.025 mole x 34 g/mole = 4.25 g H_2O_2 (is 30% of H_2O_2 to be used)

= 4.25 x (100/30)

= 2.83 g of H_2O x (1/1.261 g/cm^3)

= 2.25 cm^3 of H_2O_2

(For 1 liter solution of 200mg/L COD)

$FeSO_4.7H_2O \longrightarrow$ 25 mMole = 0.025 Mole

Molar mass of $FeSO_4$: 278 g/mole

(0.025/50) mole x 278 g/mole = 0.139 g of $FeSO_4$

(For 1 liter solution of 1000mg/L COD)

3.2.3 Checking COD level using COD tester (scanning spectrometer)

1. Two vials are prepared.
2. A blank COD vial and another with 2ml of Sulfolane solution are prepared.
3. Heat up the digester (COD thermo reactor) to 150^{0}C.
4. Put the vials into the COD thermo reactor and let it heat up for 2 hours.

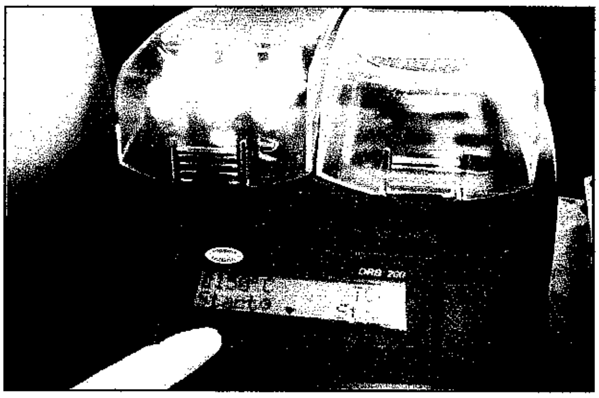

Figure 3.3: COD thermoreactor

5. Cool down for approximately 30 minutes before put into the COD tester (scanning spectrometer).
6. Take the COD reading from the panel.

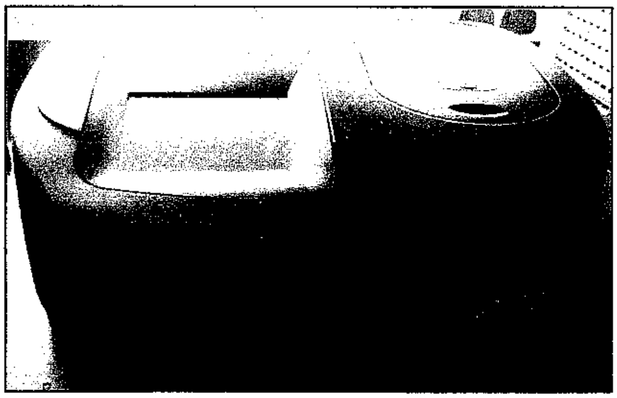

Figure 3.4: Scanning spectrometer

3.3 Tools and Equipments Required

1. Lab apparatus and measuring equipments
2. Magnetic stirrer hot plate
3. Scanning spectrometer
4. COD thermo reactor
5. Ion chromatograph

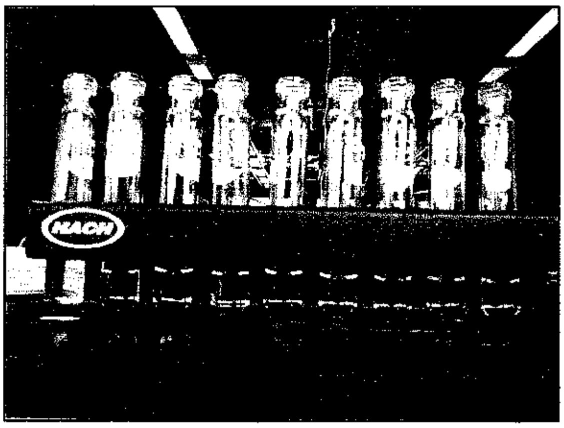

Figure 3.5: Vials with 2ml of NaOH are prepared

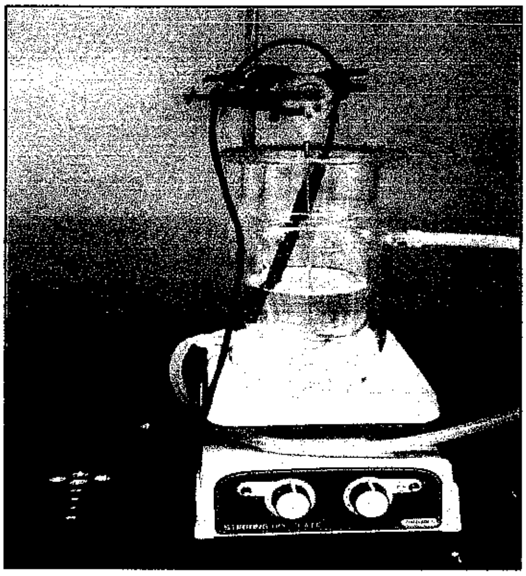

Figure 3.6: Jacketed flask, Magnetic stirrer plate and Ion chromatograph

Figure 3.7: Filtered out solution leaving the precipitate behind

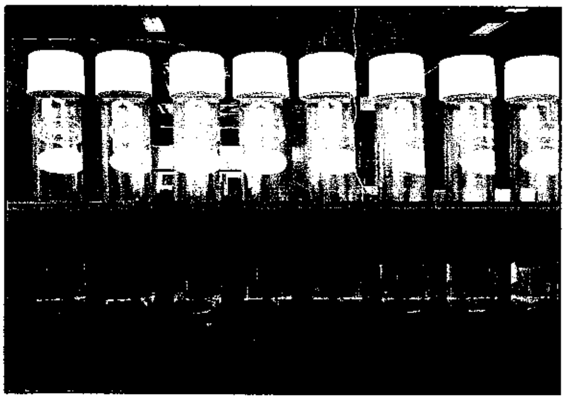

Figure 3.8: COD solution of Sulfolane after 2 hours in thermoreactor

CHAPTER 4

RESULT AND DISCUSSION

4.1 Results

Effect of H_2O_2 and Fe^{2+} concentration

Test series A: H_2O_2: Fe^{2+} = 1:1 (1 mole of H_2O_2 to 1 mole of Fe^{2+})

1st Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	3.03	150	0
1.00	27.8	3.00	152	-1.33333
2.00	27.7	2.98	149	0.666667
4.00	27.5	2.98	145	3.333333
6.00	27.5	2.97	150	0
8.00	27.3	2.97	143	4.666667
10.00	27.4	2.95	140	6.666667
30.00	27.5	2.95	140	6.666667

Table 4.1: Result for test series A: 1st run

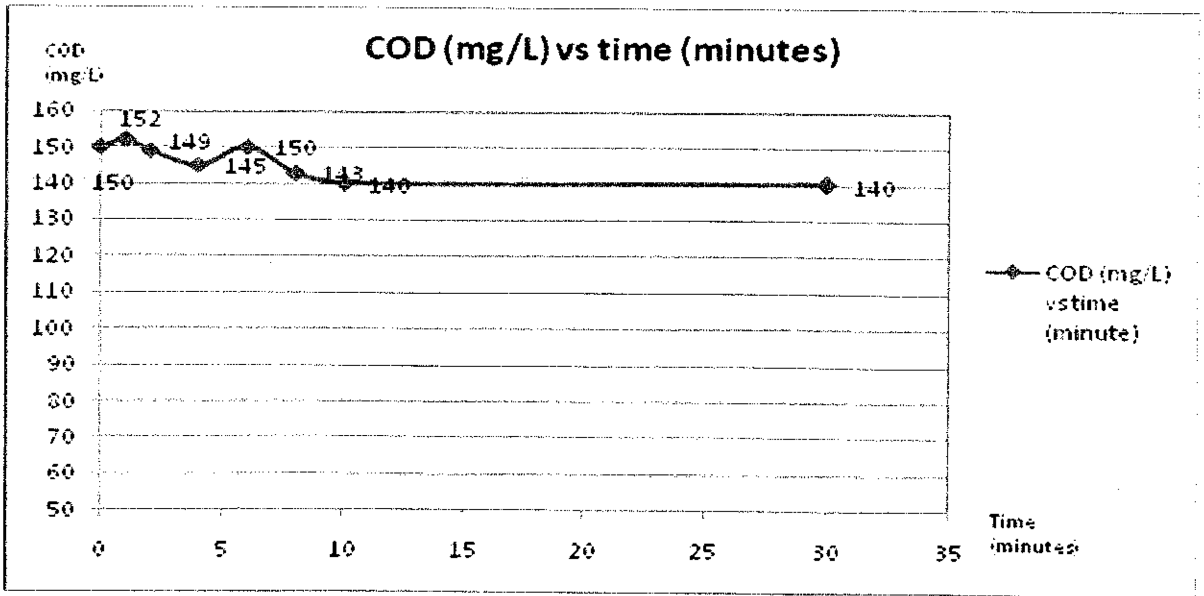

Figure 4.1: Graph of COD versus time for Test series A: 1st run

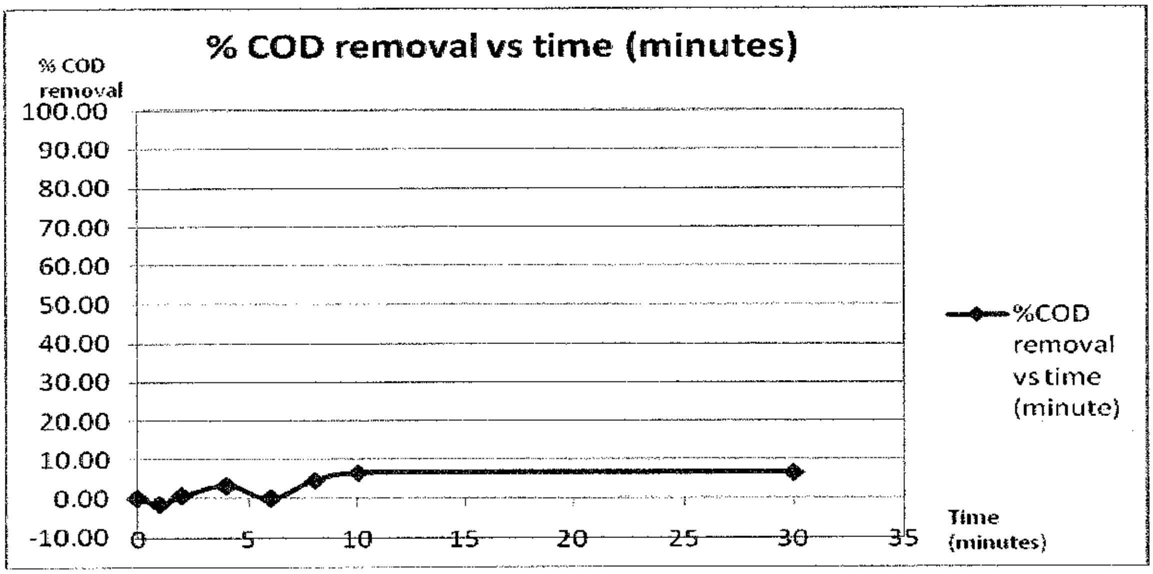

Figure 4.2: Graph of %COD removal versus time for Test series A: 1st run

In **test series A** for 1st run the dosage ratio of H_2O_2: Fe^{2+} is same which is 1:1 based on the calculation of stoichiometric equation. It was observed that the reaction of Sulfolane with Fenton reagent is dependent upon the dosages of H_2O_2 and Fe^{2+}. At pH 3, the Sulfolane COD was reduced by 0.67% after 2 minutes of reaction time. At the end of 30 minutes reaction time the COD was reduced by 6.67%. The pH of the mixture also decreased from initial value of 3.03 to final value of 2.95.

Test series A: H_2O_2: Fe^{2+} = 1:1 (1 mole of H_2O_2 to 1 mole of Fe^{2+})

2nd Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	3.00	156	0
1.00	27.7	3.00	155	0.641026
2.00	27.7	2.99	150	3.846154
4.00	27.5	2.98	149	4.487179
6.00	27.4	2.97	144	7.692308
8.00	27.3	2.97	144	7.692308
10.00	27.4	2.94	143	8.333333
30.00	27.0	2.94	140	10.25641

Table 4.2: Result for test series A: 2nd run

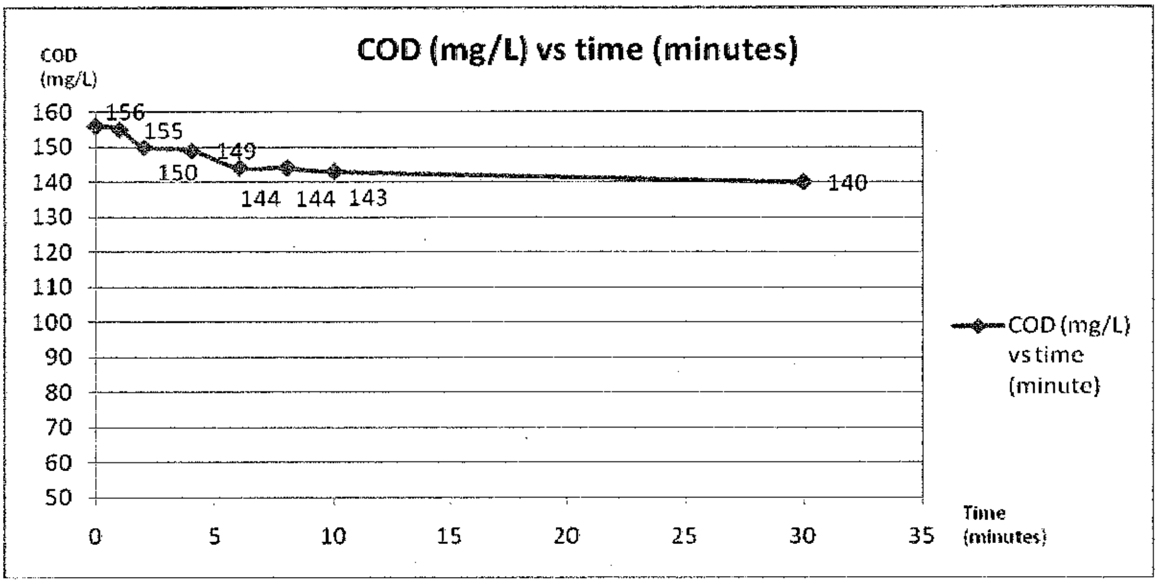

Figure 4.3: Graph of COD versus time for Test series A: 2nd run

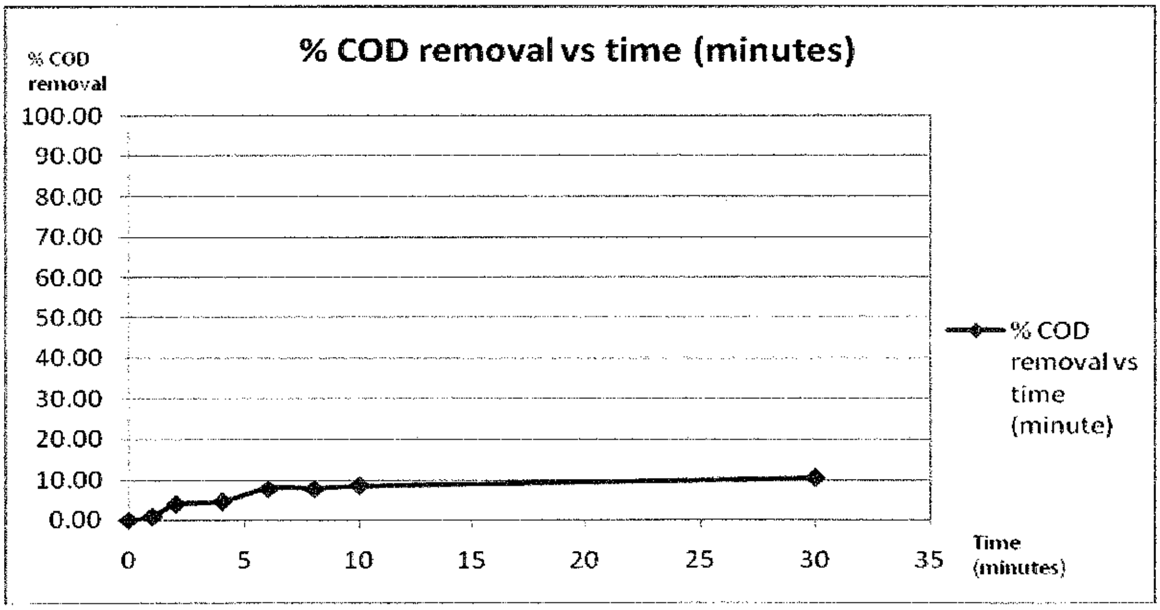

Figure 4.4: Graph of %COD removal versus time for Test series A: 2nd run

In test series A for the 2nd run, it was observed that the reaction of Sulfolane with Fenton reagent is dependent upon the dosages of H_2O_2 and Fe $^{2+}$. At pH 3, the Sulfolane COD was reduced by 3.85% after 2 minutes of reaction time. At the end of 30 minutes reaction time the COD was reduced by 10.26%. The pH of the mixture also decreased from initial value of 3.00 to final value of 2.94.

Test series B: H_2O_2: Fe^{2+} = 1:2 (1 mole of H_2O_2 to 2 mole of Fe^{2+})

1st Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	3.03	135	0
1.00	27.8	3.00	139	-2.96296
2.00	27.7	2.98	139	-2.96296
4.00	27.5	2.98	134	0.740741
6.00	27.5	2.97	130	3.703704
8.00	27.3	2.97	129	4.444444
10.00	27.4	2.95	129	4.444444
30.00	27.5	2.95	120	11.11111

Table 4.3: Result for test series B: 1st run

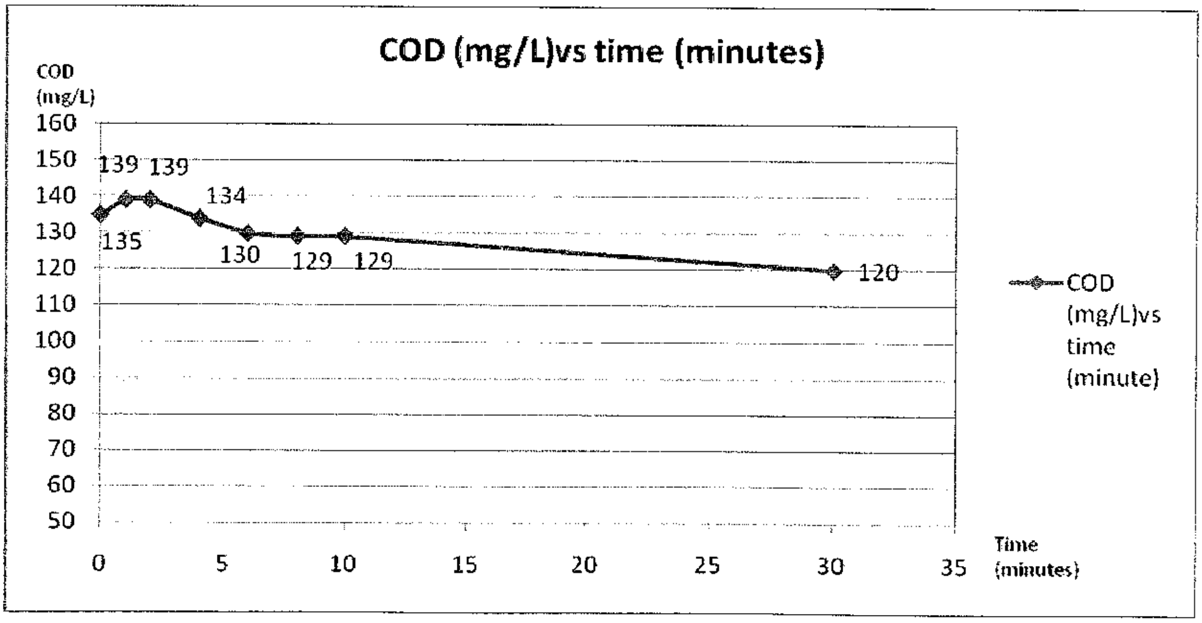

Figure 4.5: Graph of COD versus time for Test series B: 1st run

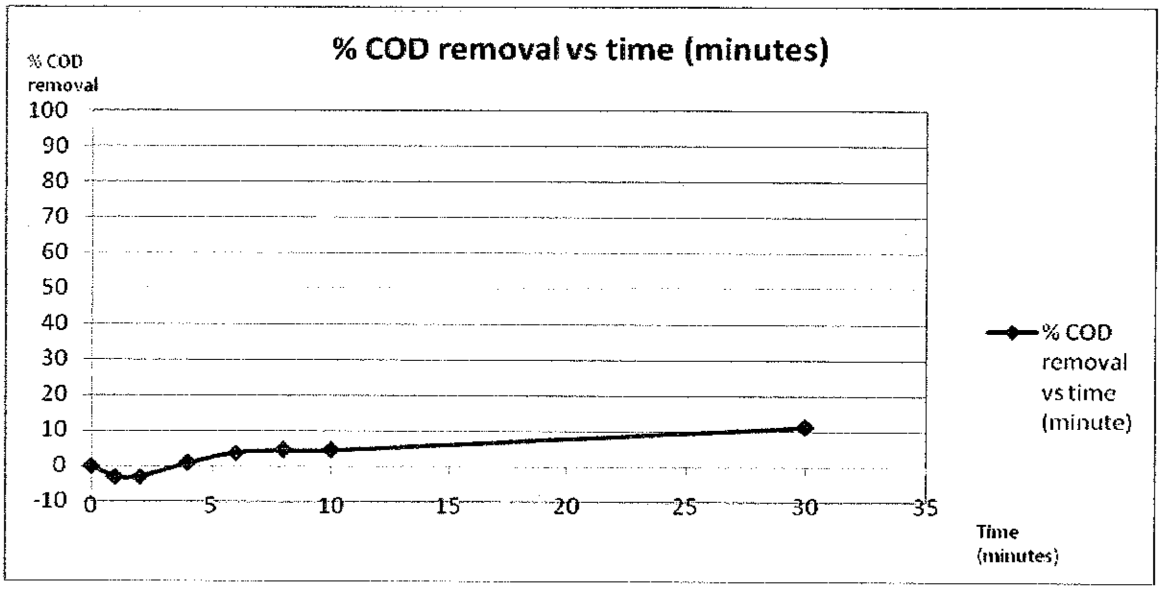

Figure 4.6: Graph of %COD removal versus time for Test series B: 1st run

In test series B for 1st run, it was observed that the reaction of Sulfolane with Fenton reagent is dependent upon the dosages of H_2O_2 and Fe^{2+}. At pH 2.98, the Sulfolane COD was reduced by 0.74% after 4 minutes of reaction time. At the end of 30 minutes reaction time the COD was reduced by 11.11%. The pH of the mixture also decreased from initial value of 3.03 to final value of 2.95.

Test series B: H_2O_2: Fe^{2+} = 1:2 (1 mole of H_2O_2 to 2 mole of Fe^{2+})

2nd Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	3.01	156	0
1.00	27.9	3.00	145	7.051282
2.00	27.9	3.02	139	10.89744
4.00	27.7	3.01	138	11.53846
6.00	27.5	3.00	135	13.46154
8.00	27.3	2.99	130	16.66667
10.00	27.4	2.97	129	17.30769
30.00	27.3	2.95	129	17.30769

Table 4.4: Result for test series B: 2nd run

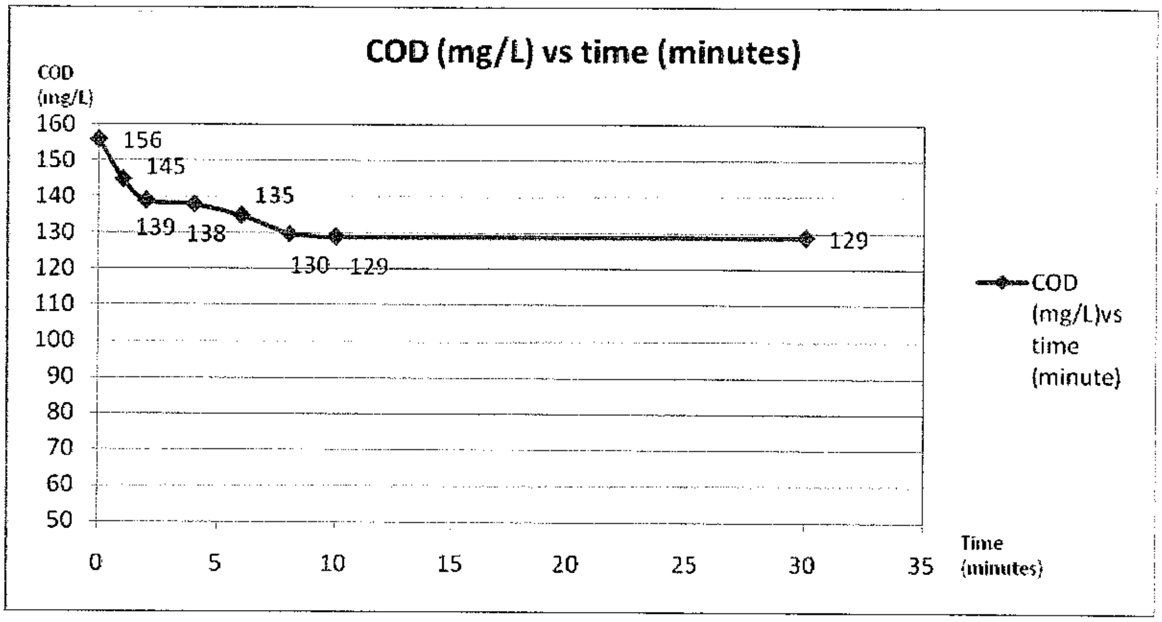

Figure 4.7: Graph of COD versus time for Test series B: 2nd run

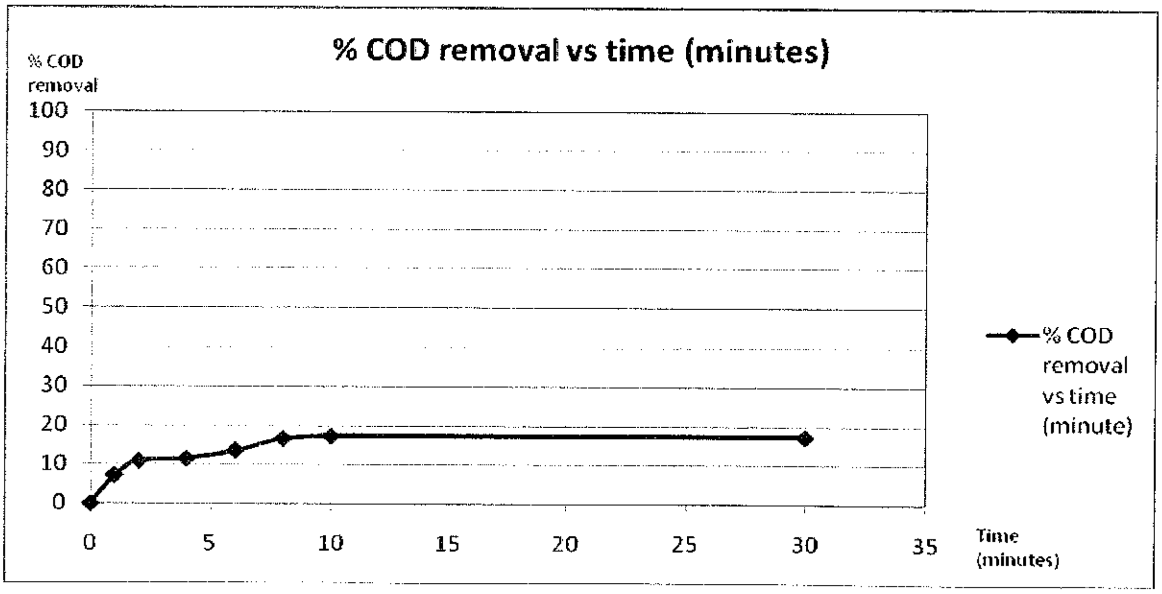

Figure 4.8: %COD removal versus time for Test series B: 2nd run

In test series B for the 2nd run, it was observed that the reaction of Sulfolane with Fenton reagent is dependent upon the dosages of H_2O_2 and Fe $^{2+}$. At pH 3.02, the Sulfolane COD was reduced by 10.90% after 2 minutes of reaction time. At the end of 30 minutes reaction time the COD was reduced by 17.31%. The pH of the mixture also decreased from initial value of 3.01 to final value of 2.95.

Test series C: H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+})

1st Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	3.00	156	0
1.00	27.9	3.00	133	14.74359
2.00	27.8	3.01	130	16.66667
4.00	27.7	3.02	125	19.87179
6.00	27.6	3.00	120	23.07692
8.00	27.6	3.00	110	29.48718
10.00	27.5	3.00	80	48.71795
30.00	27.5	3.00	75	51.92308

Table 4.5: Result for test series C: 1st run

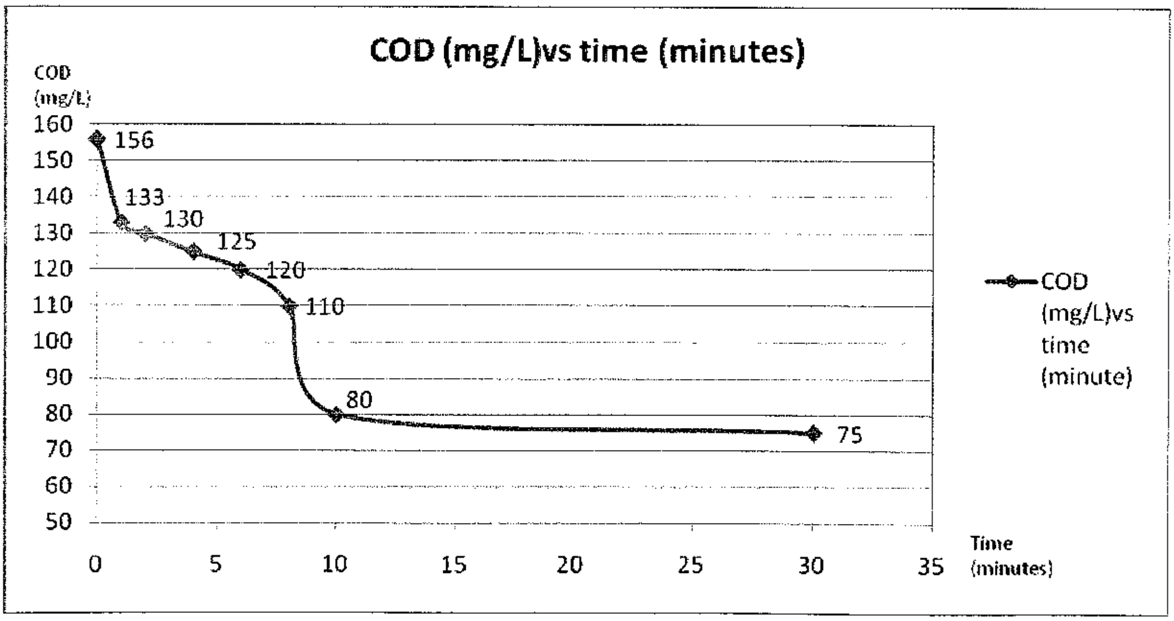

Figure 4.9: Graph of COD versus time for Test series C: 1st run

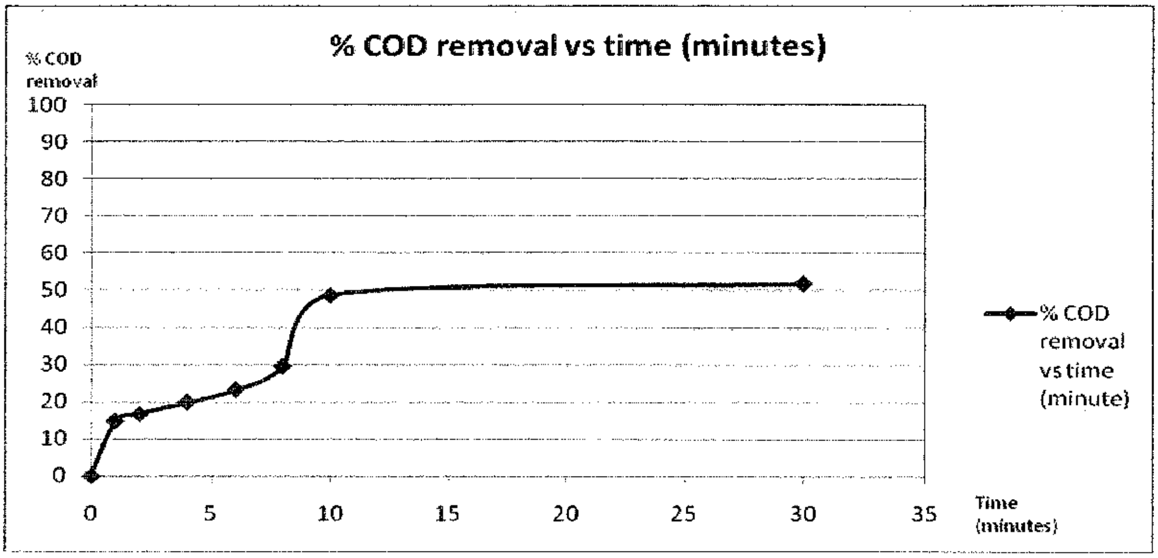

Figure 4.10: %COD removal versus time for Test series C: 1st run

In test series C for 1st run, it was observed that the reaction of Sulfolane with Fenton reagent is dependent upon the dosages of H_2O_2 and Fe^{2+}. At pH 3.00, the Sulfolane COD was reduced by 16.67% after 1 minute of reaction time. At the end of 30 minutes reaction time the COD was reduced by 51.92%. The pH of the mixture is fixed from initial value of 3.00. In this test series the pH is fixed at range of 3.00 to 3.5 by putting few drops of NaOH into the mixture in jacketed flask.

Test series C: H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+})

2nd Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	3.00	156	0
1.00	27.9	3.00	130	16.66667
2.00	27.8	3.01	125	19.87179
4.00	27.7	3.02	115	26.28205
6.00	27.5	3.00	102	34.61538
8.00	27.5	3.00	87	44.23077
10.00	27.5	3.00	69	55.76923
30.00	27.5	3.00	65	58.33333

Table 4.6: Result for test series C: 2nd run

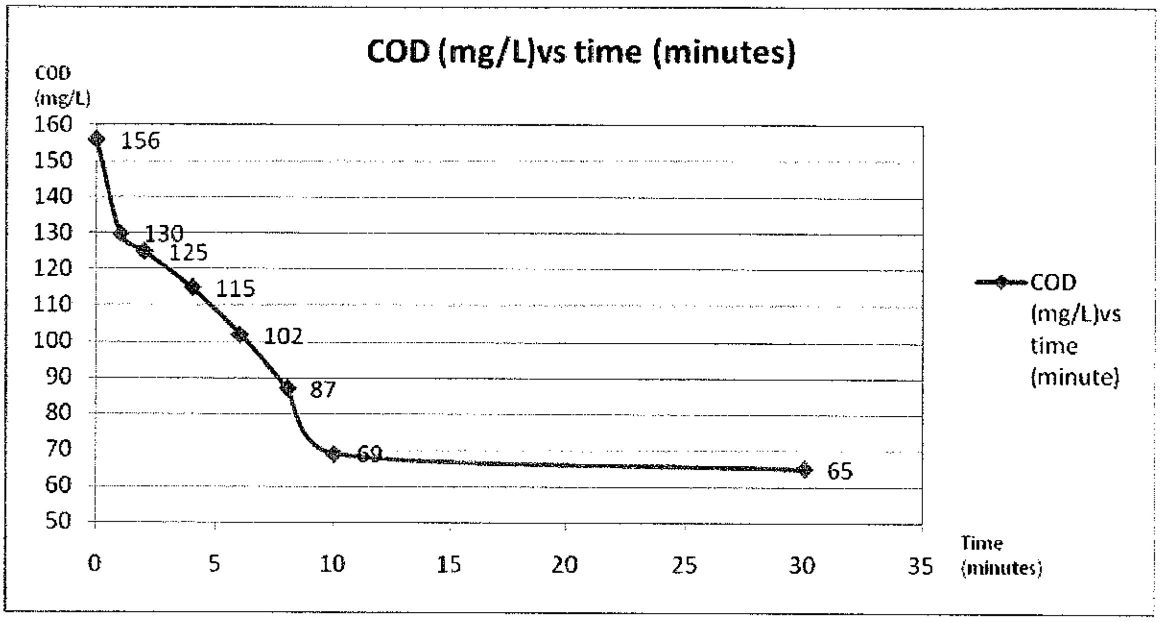

Figure 4.11: Graph of COD versus time for test series C: 2nd Run

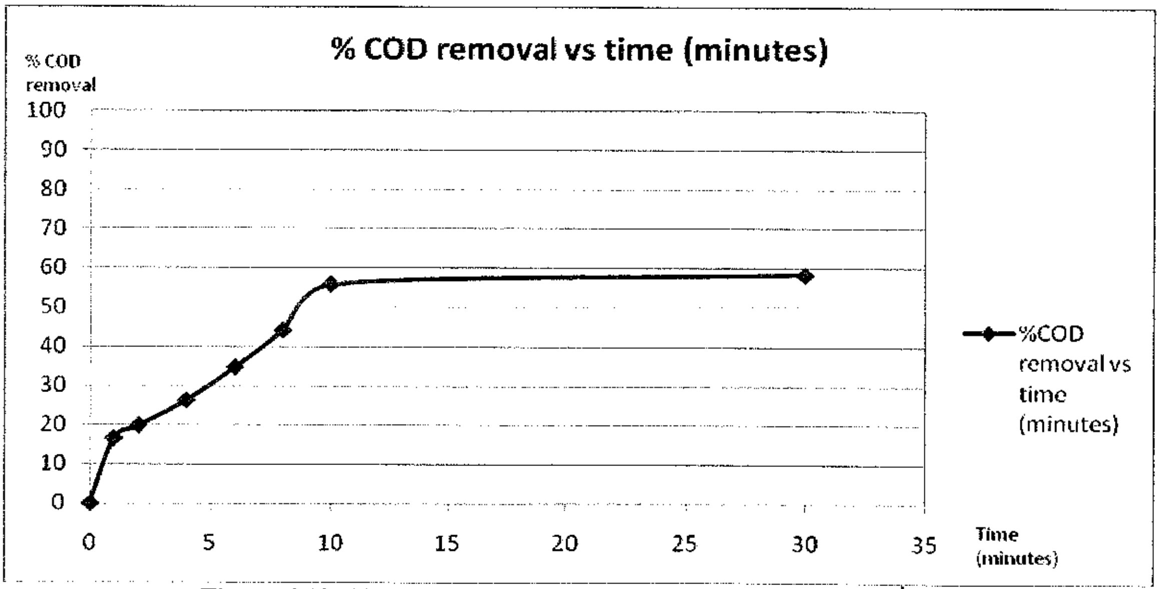

Figure 4.12: %COD removal versus time for test series C: 2nd run

In test series C for the 6th run, it was observed that the reaction of Sulfolane with Fenton reagent is dependent upon the dosages of H_2O_2 and Fe $^{2+}$. At pH 3.00, the Sulfolane COD was reduced by 16.67% after 1 minute of reaction time. At the end of 30 minutes reaction time the COD was reduced by 58.33%.

Effect of pH

Test series D: 1st Run; pH 1.80 - 2.00

H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+})

1st Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	2.00	155	0
1.00	27.9	2.00	154	0.645161
2.00	27.8	1.98	154	0.645161
4.00	27.7	1.92	153	1.290323
6.00	27.5	1.98	154	0.645161
8.00	27.5	2.00	154	0.645161
10.00	27.5	2.00	150	3.225806
30.00	27.5	2.00	150	3.225806

Table 4.7: Result for test series D: 1st run

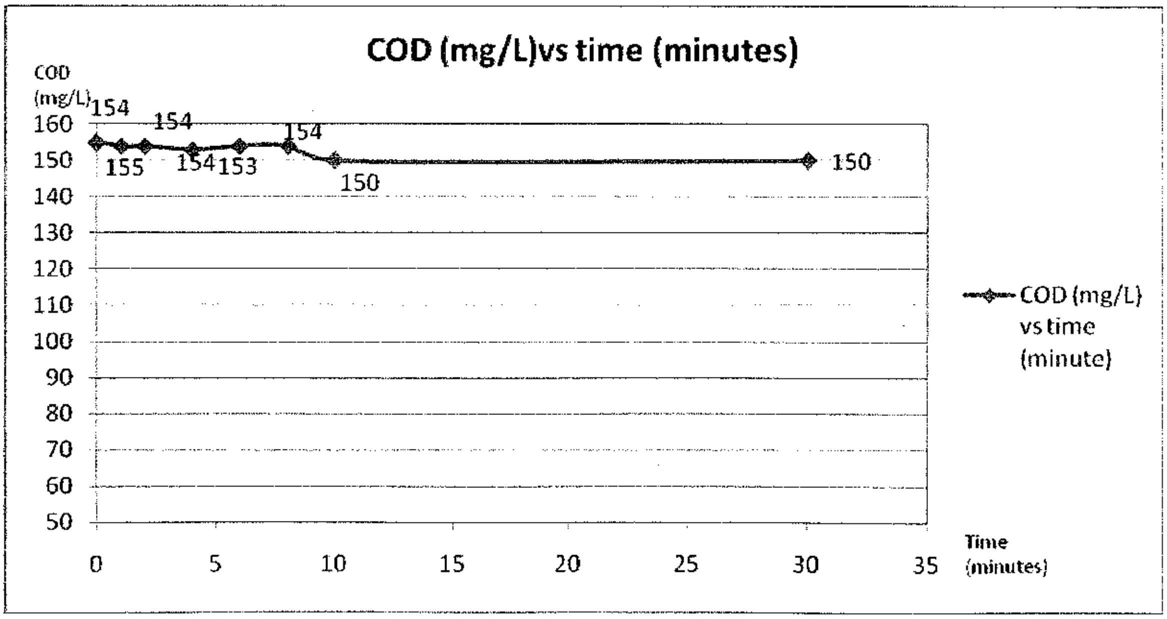

Figure 4.13: Graph of COD versus time for Test series D: 1st Run

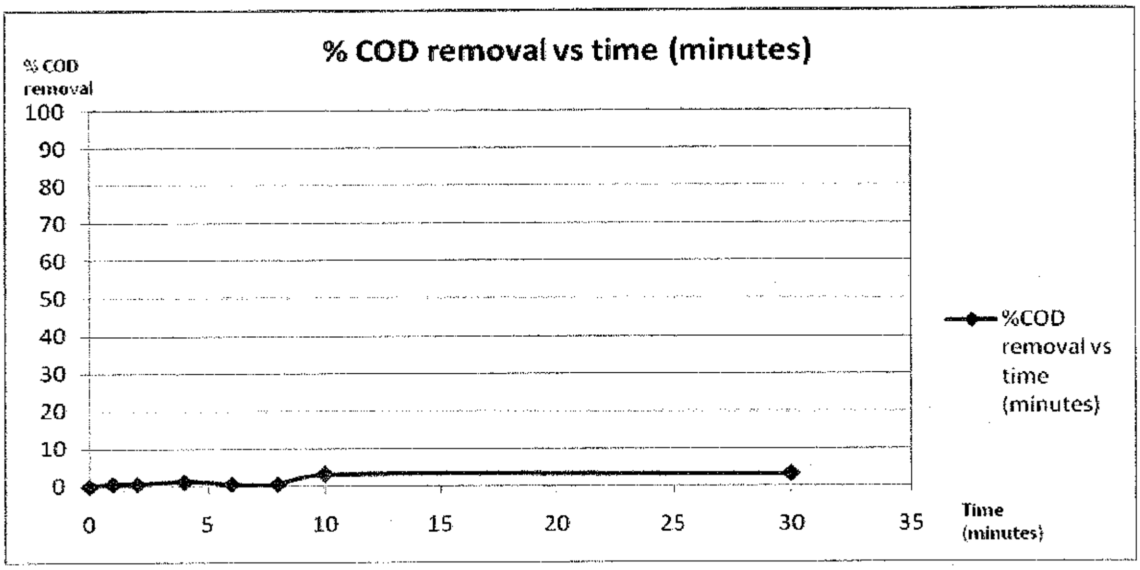

Figure 4.14: %COD removal versus time for Test series D: 1st run

In test series D for 1st run, it was observed that the reaction of Sulfolane with Fenton reagent is pH dependent. At pH 2.00, the Sulfolane COD was reduced by 0.65% after 1 minute of reaction time. At the end of 30 minutes reaction time the COD was reduced by 3.23%. The pH of the mixture is fixed from initial value 2.00. In this test the pH is fixed at range of 1.80 to 2.00 by putting few drops of H_2SO_4 into the mixture in jacketed flask.

Test series D: 2nd Run; pH 2.50

H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+})

2nd Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	2.50	157	0
1.00	27.9	2.47	150	4.458599
2.00	27.8	2.30	150	4.458599
4.00	27.7	2.50	148	5.732484
6.00	27.8	2.55	145	7.643312
8.00	27.5	2.55	146	7.006369
10.00	27.5	2.50	144	8.280255
30.00	27.5	2.50	143	8.917197

Table 4.8: Result for test series D: 2nd run

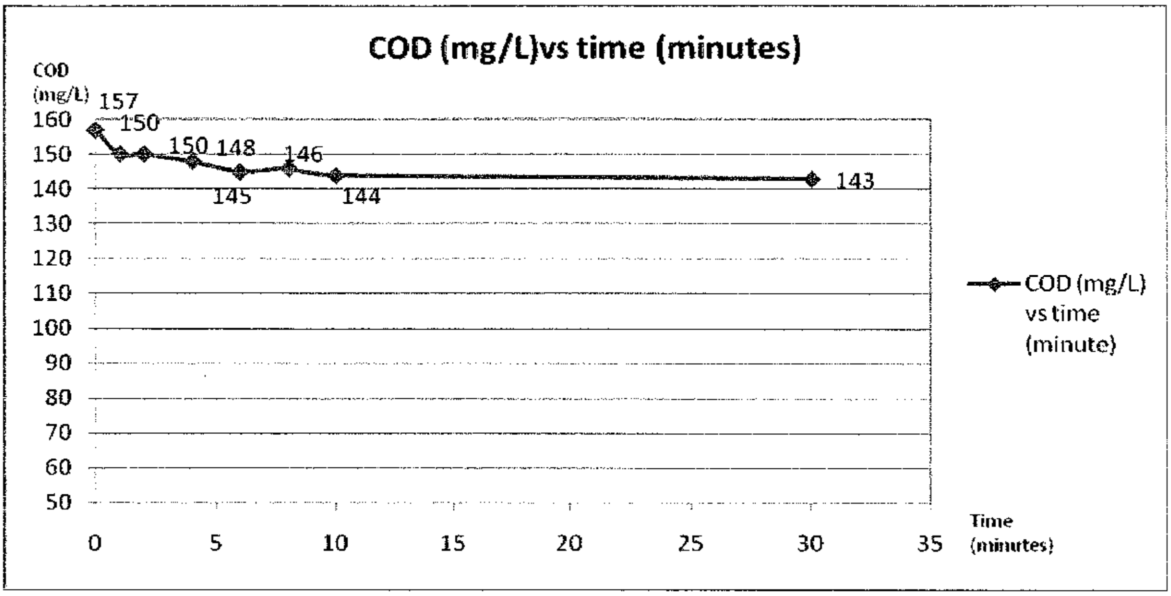

Figure 4.15: Graph of COD versus time for Test series D: 2nd Run

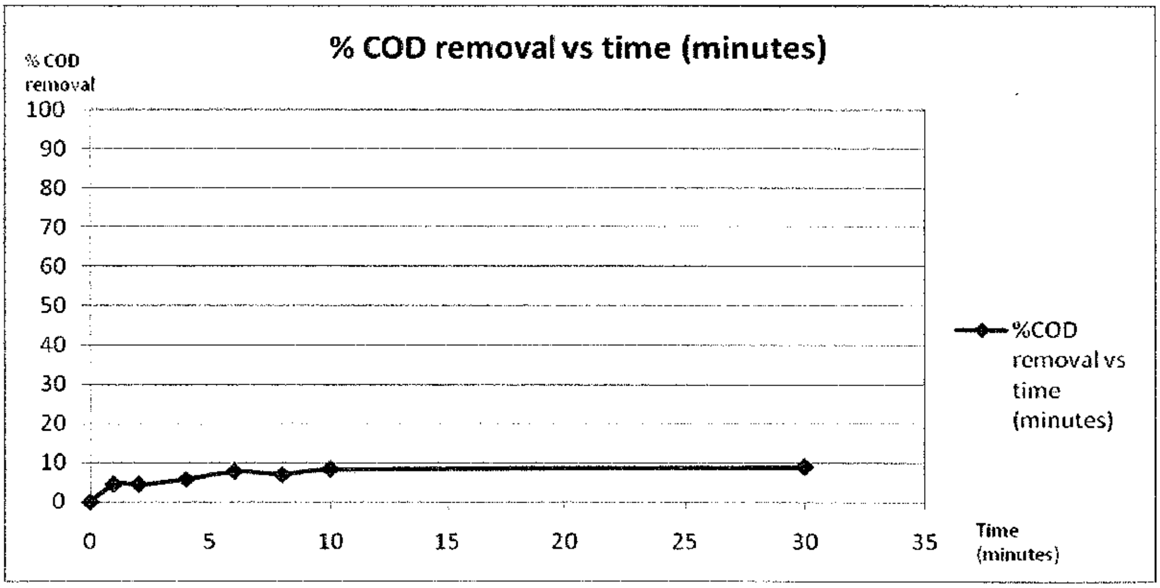

Figure 4.16: %COD removal versus time for Test series D: 2nd run

In test series D for 2nd run, it was observed that the reaction of Sulfolane with Fenton reagent is pH dependent. At pH 2.50, the Sulfolane COD was reduced by 4.46% after 1 minute of reaction time. At the end of 30 minutes reaction time the COD was reduced by 8.92%. The pH of the mixture is fixed from initial value 2.50. In this test the pH is fixed at 2.50 by putting few drops of H_2SO_4 into the mixture in jacketed flask.

Test series D: 3rd Run; pH 3.00

H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+})

3rd Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	3.00	156	0
1.00	27.9	3.00	130	16.66667
2.00	27.8	3.01	125	19.87179
4.00	27.7	3.02	115	26.28205
6.00	27.5	3.00	102	34.61538
8.00	27.5	3.00	87	44.23077
10.00	27.5	3.00	69	55.76923
30.00	27.5	3.00	65	58.33333

Table 4.9: Result for test series D: 3rd run

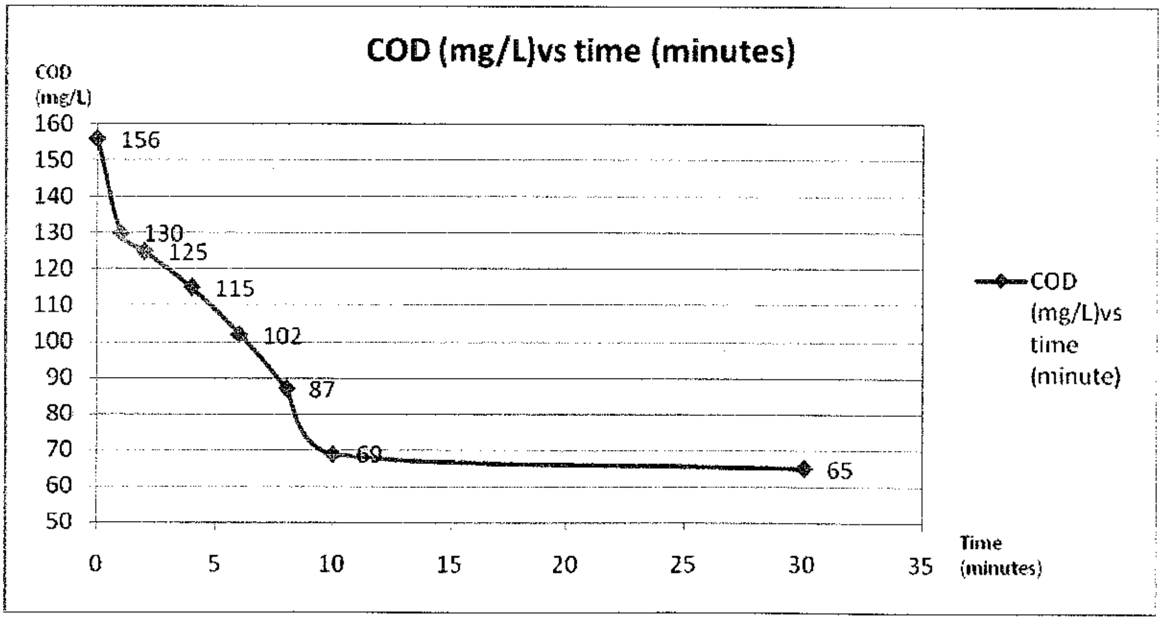

Figure 4.17: Graph of COD versus time for Test series D: 3rd Run

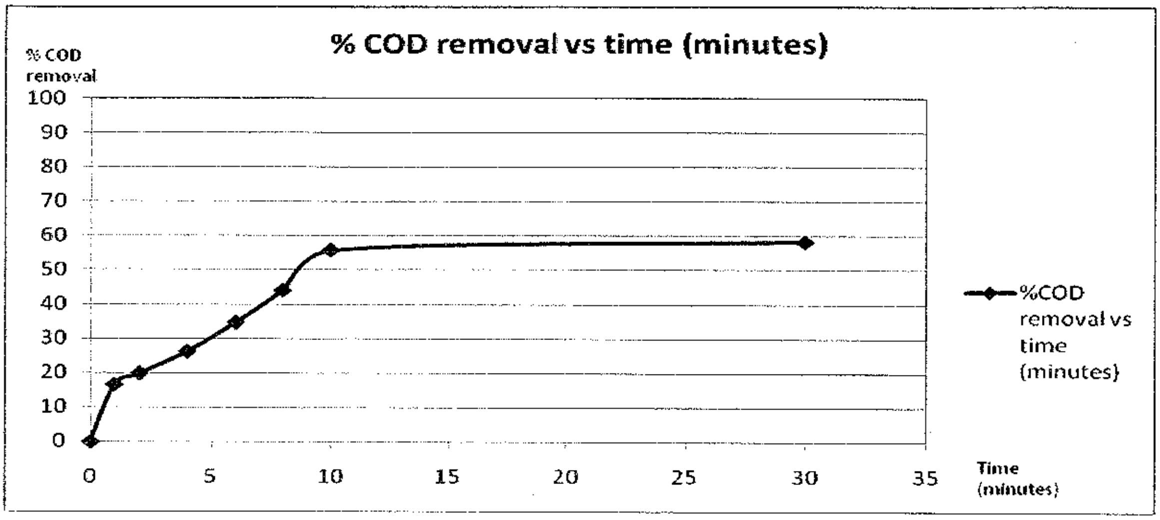

Figure 4.18: %COD removal versus time for Test series D: 3rd run

In test series D for 3rd run, it was observed that the reaction of Sulfolane with Fenton reagent is pH dependent. At pH 3.00, the Sulfolane COD was reduced by 16.67% after 1 minute of reaction time. At the end of 30 minutes reaction time the COD was reduced by 58.33%. The pH of the mixture is fixed at pH 3.00. In this test the pH is maintained at 3.00 by putting few drops of H_2SO_4 and NaOH into the mixture in jacketed flask. The pH is monitored and fixed throughout the test.

Test series D: 4th Run; pH 4.50 – 5.00

H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+})

4th Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	4.50	156	0
1.00	27.9	4.50	150	3.846154
2.00	27.8	4.70	136	12.82051
4.00	27.7	4.90	135	13.46154
6.00	27.0	4.91	131	16.02564
8.00	26.0	4.60	125	19.87179
10.00	27.5	4.58	112	28.20513
30.00	27.5	4.60	111	28.84615

Table 4.10: Result for test series D: 4th run

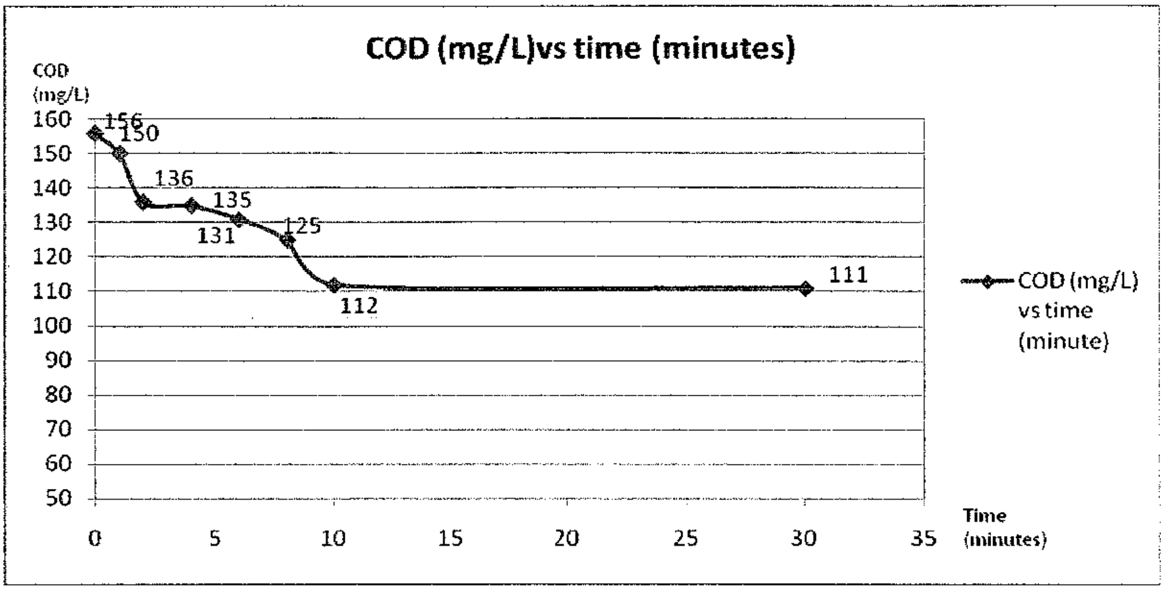

Figure 4.19: Graph of COD versus time for Test series D: 4th Run

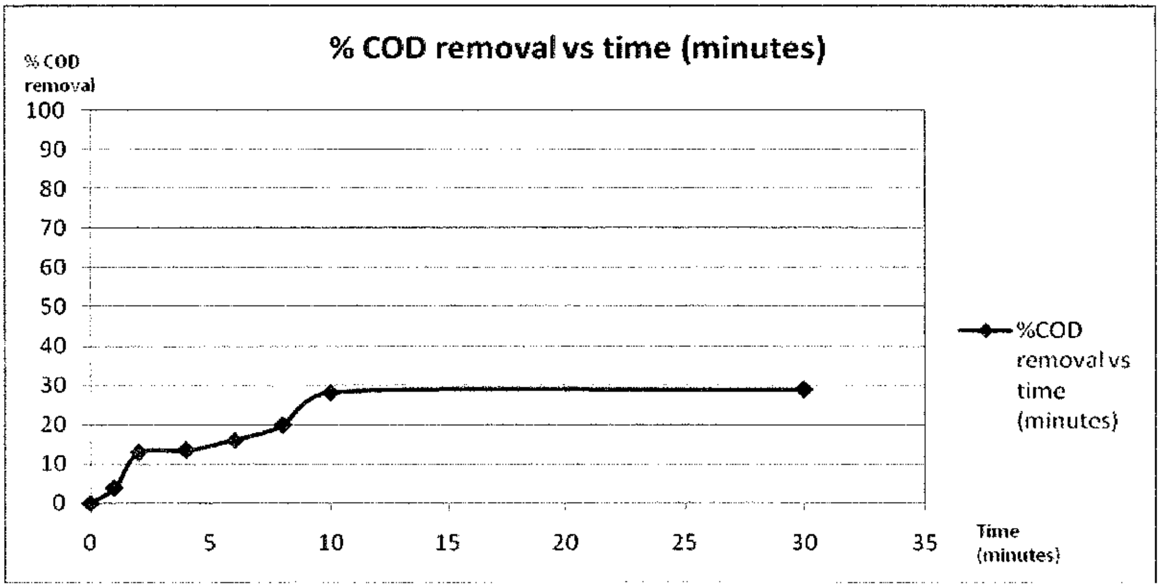

Figure 4.20: %COD removal versus time for Test series D: 4th run

In test series D for 4th run, it was observed that the reaction of Sulfolane with Fenton reagent is pH dependent. At pH 4.00, the Sulfolane COD was reduced by 3.85% after 1 minute of reaction time. At the end of 30 minutes reaction time the COD was reduced by 28.85%. The pH of the mixture is fixed from initial value 4.50. In this test the pH is fixed at the range of pH 4.50 to 5.00 by putting few drops of H_2SO_4 and NaOH into the mixture in jacketed flask. The pH is monitored and fixed throughout the test.

Test series D: 5th Run; pH 7.50 – 8.00

H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+})

5th Run

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal
0.00	28.0	8.00	154	0
1.00	27.9	7.60	136	11.68831
2.00	27.8	7.75	121	21.42857
4.00	27.7	7.78	121	21.42857
6.00	27.7	7.80	118	23.37662
8.00	27.6	7.50	117	24.02597
10.00	27.6	7.90	117	24.02597
30.00	27.5	8.74	115	25.32468

Table 4.11: Result for test series D: 5th run

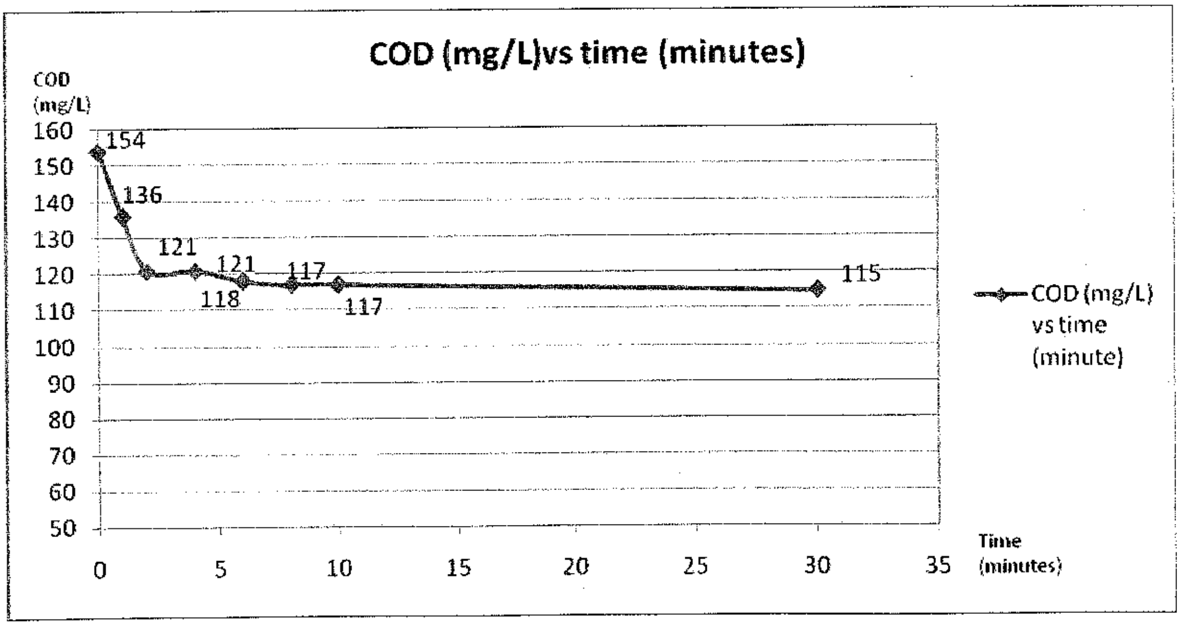

Figure 4.21: Graph of COD vs time for Test series D: 5th Run

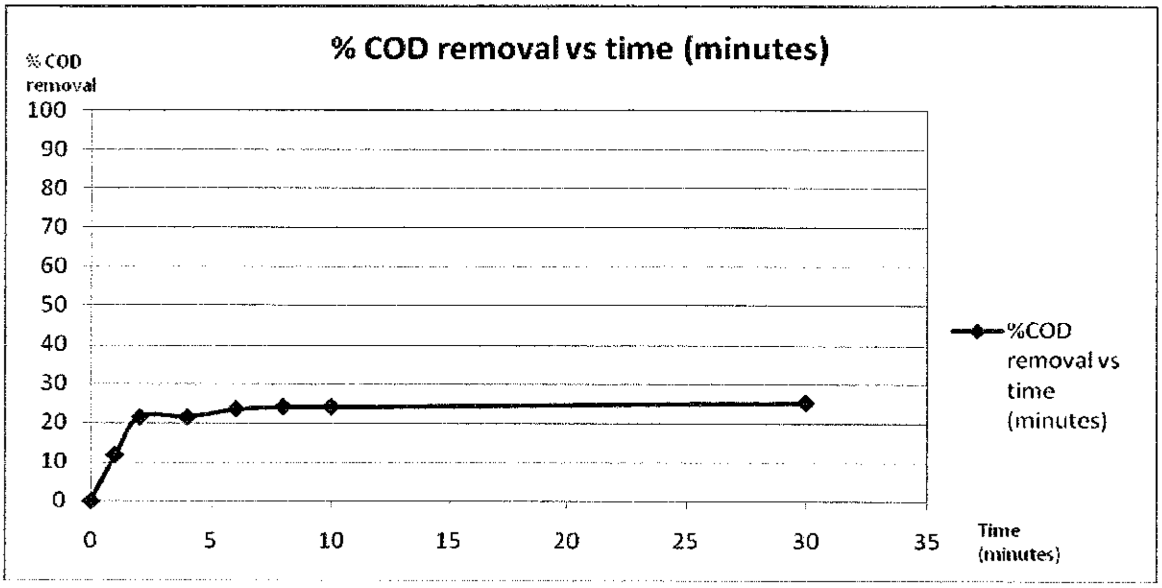

Figure 4.22: %COD removal versus time for Test series D: 5th run

In test series D for 5th run, it was observed that the reaction of Sulfolane with Fenton reagent is pH dependent. At pH 8.00, the Sulfolane COD was reduced by 11.69% after 1 minute of reaction time. At the end of 30 minutes reaction time the COD was reduced by 25.32%. The pH of the mixture is fixed from initial value 8.00. In this test the pH is fixed at the range of pH 7.50 to 8.00 by putting few drops NaOH into the mixture in jacketed flask. The pH is monitored and fixed throughout the test.

Effect of temperature

Test series E: 1st Run; temperature at 27 °C

H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+}) at pH 3.00

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal	log C/C_o	log dx/dt	log x
0.00	28.0	3.00	156	0.0000	1.8579	0.0000	2.1931
1.00	27.9	3.00	130	16.6667	2.0402	2.1139	2.1139
2.00	27.8	3.01	125	19.8718	2.0794	1.7959	2.0969
4.00	27.7	3.02	115	26.2821	2.1628	1.4586	2.0607
6.00	27.5	3.00	102	34.6154	2.2828	1.2304	2.0086
8.00	27.5	3.00	87	44.2308	2.4418	1.0364	1.9395
10.00	27.5	3.00	69	55.7692	2.6736	0.8388	1.8388
30.00	27.5	3.00	65	58.3333	2.7334	0.3358	1.8129

Table 4.12: Result for test series E: 1st run

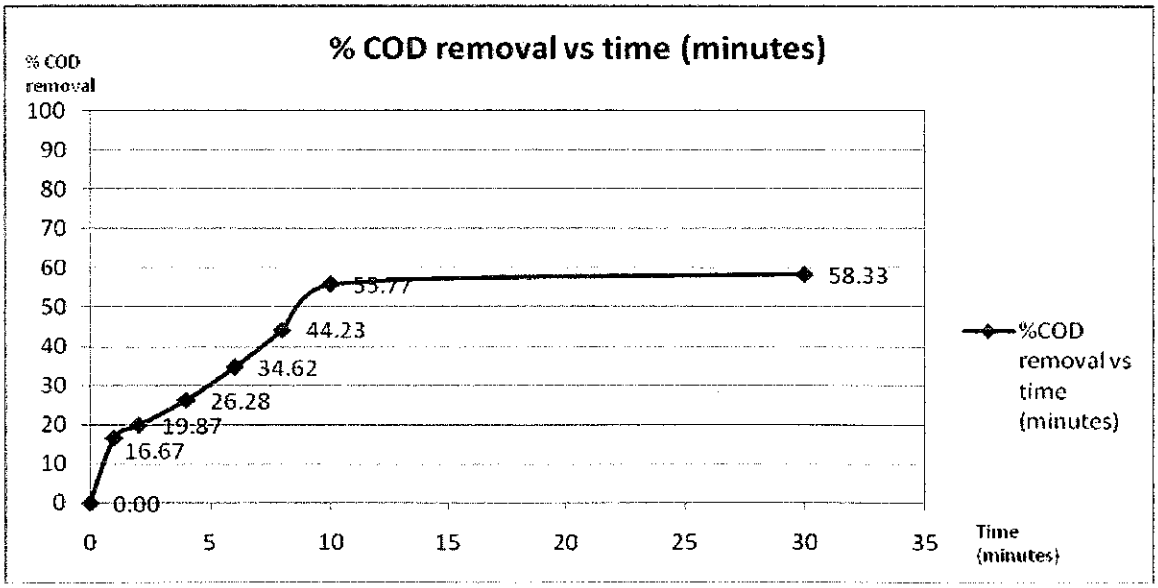

Figure 4.23: %COD removal versus time for Test series E: 1st run

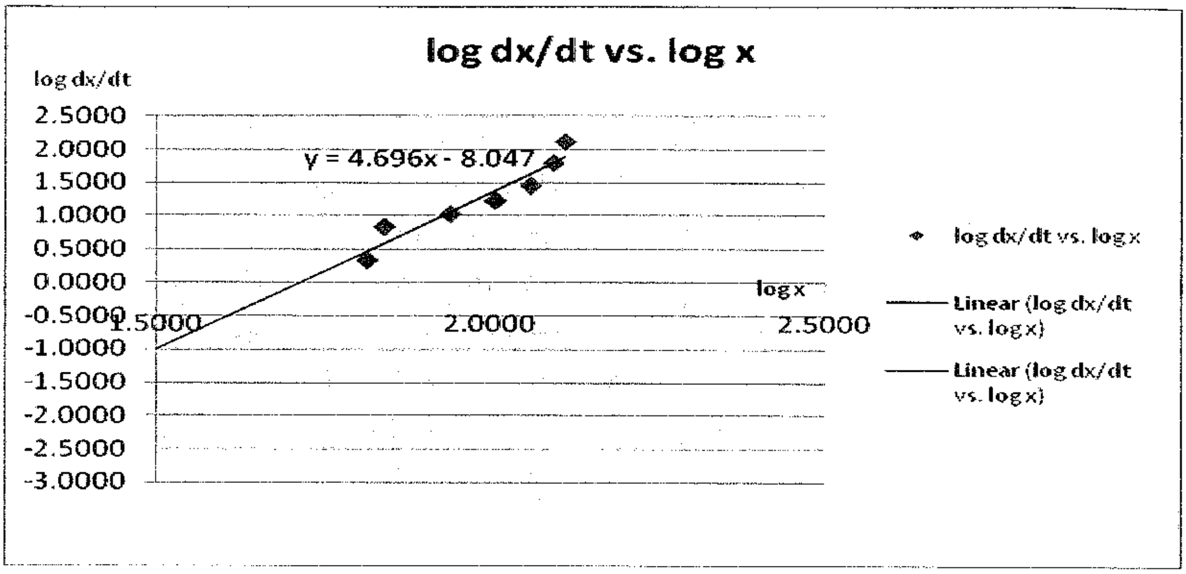

Figure 4.24: log dx/dt versus log x for Test series E: 1st run

The chemical oxidation of Fenton treatment process can be represented by the following mth-order reaction kinetics:

$$\frac{dx}{dt} = k[x]^m$$

where; m = the order of reaction

k = the reaction rate coefficient

t = time

log dx/dt = m log x + log k

From Figure 4.24;

y = 4.696x - 8.047

log k = -8.047

k = 8.97 E-09

Test series E: 2nd Run; temperature at 40 °C

H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+}) at pH 3.00

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal	log C/C$_o$	log dx/dt	log x
0.00	40.0	3.00	156	0.0000	1.8579	0.0000	2.1931
1.00	40.0	3.00	140	10.2564	1.9661	2.1461	2.1461
2.00	40.0	3.00	135	13.4615	2.0025	1.8293	2.1303
4.00	40.1	3.01	126	19.2308	2.0715	1.4983	2.1004
6.00	40.3	3.02	111	28.8462	2.1982	1.2672	2.0453
8.00	40.4	3.01	105	32.6923	2.2538	1.1181	2.0212
10.00	40.4	3.00	90	42.3077	2.4079	0.9542	1.9542
30.00	40.0	3.00	88	43.5897	2.4304	0.4674	1.9445

Table 4.13: Result for test series E: 2nd run

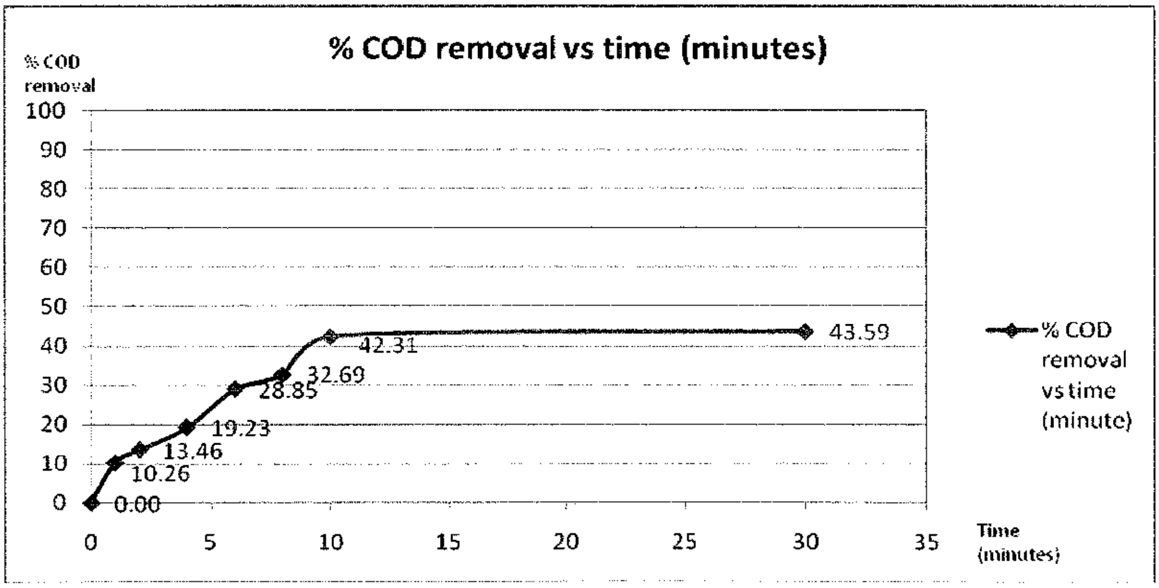

Figure 4.25: %COD removal versus time for Test series E: 2nd run

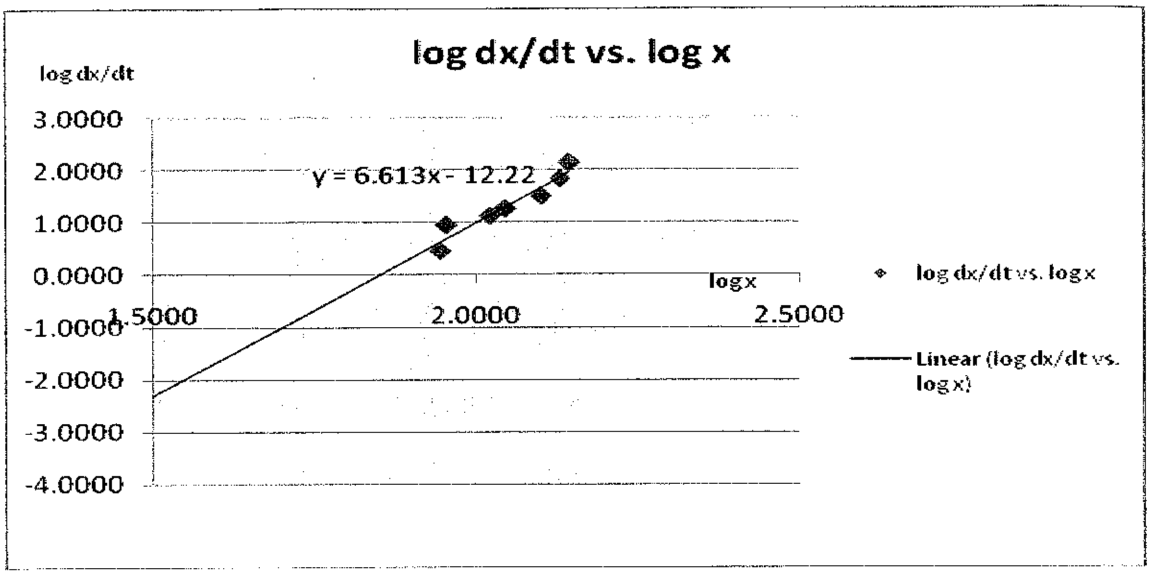

Figure 4.26: log dx/dt versus log x for Test series E: 2nd run

The chemical oxidation of Fenton treatment process can be represented by the following mth-order reaction kinetics:

$$\frac{dx}{dt} = k[x]^m$$

where; m = the order of reaction

k = the reaction rate coefficient

t = time

log dx/dt = m log x + log k

From Figure 4.26;

y = 6.613x - 12.22

log k = -12.22

k = 6.03 E-13

Test series E: 3rd Run; temperature at 60 °C

H_2O_2: Fe^{2+} = 2:1 (2 mole of H_2O_2 to 1 mole of Fe^{2+}) at pH 3.00

Time (minute)	Temperature (°C)	pH	COD (mg/L)	% COD removal	log C/C_o	log dx/dt	log x
0.00	40.0	3.00	156	0.0000	1.8579	0.0000	2.1931
1.00	40.0	3.00	150	3.8462	1.8971	2.1761	2.1761
2.00	40.0	3.00	145	7.0513	1.9310	1.8603	2.1614
4.00	40.1	3.01	136	12.8205	1.9951	1.5315	2.1335
6.00	40.3	3.02	125	19.8718	2.0794	1.3188	2.0969
8.00	40.4	3.01	119	23.7179	2.1286	1.1725	2.0755
10.00	40.4	3.00	110	29.4872	2.2073	1.0414	2.0414
30.00	40.0	3.00	108	30.7692	2.2256	0.5563	2.0334

Table 4.14: Result for test series E: 3rd run

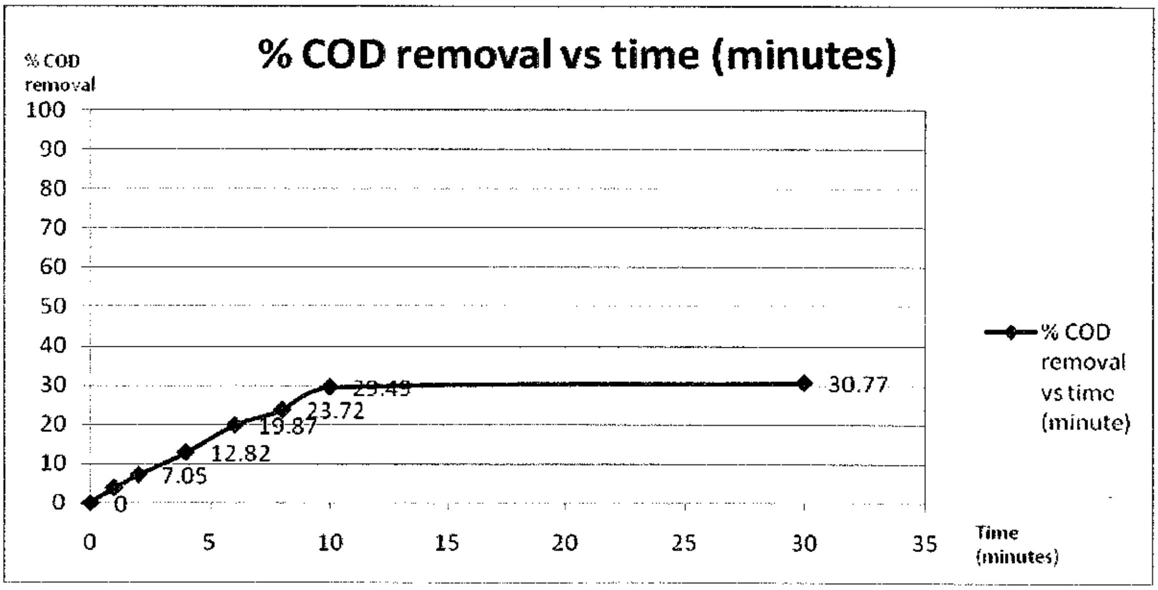

Figure 4.27: %COD removal versus time for Test series E: 3rd run

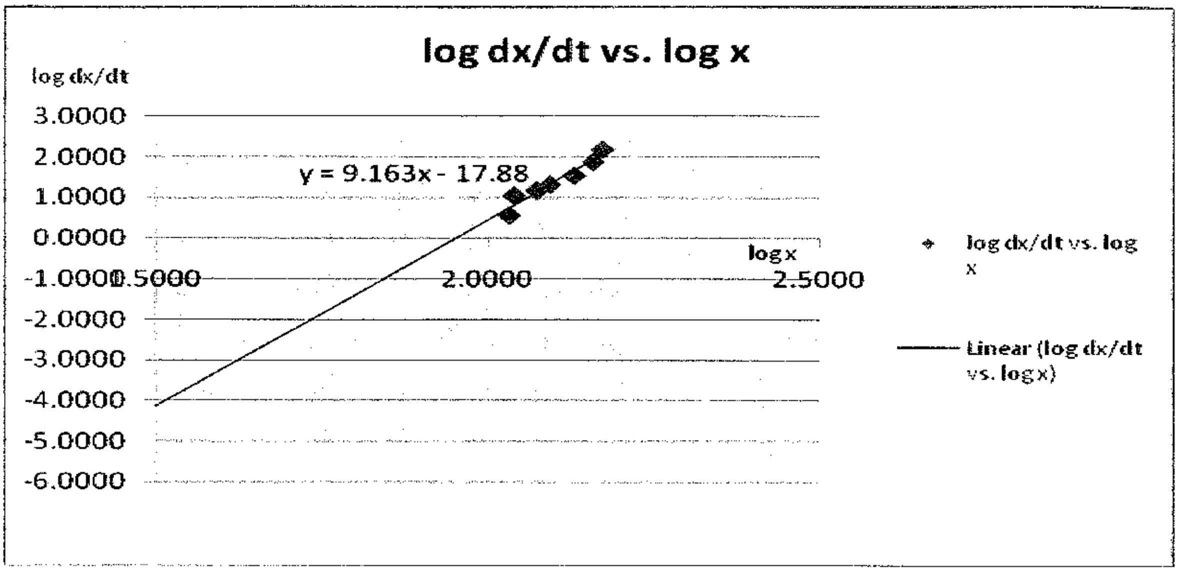

Figure 4.28: log dx/dt versus log x for Test series E: 3rd run

The chemical oxidation of Fenton treatment process can be represented by the following mth-order reaction kinetics:

$$\frac{dx}{dt} = k[x]^m$$

where; m = the order of reaction
k = the reaction rate coefficient
t = time

log dx/dt = m log x + log k
From Figure 4.28;
y = 9.163x - 17.88
log k = -17.88
k = 1.32E-18

From the plotted graphs of log (dx/dt) versus log x for three different temperatures;

Temperature (°C)	log k	k	1/T (K^{-1})
27	-8.047	8.97E-09	0.003288
40	-12.22	6.03E-13	0.003183
60	-17.88	1.32E-18	0.002993

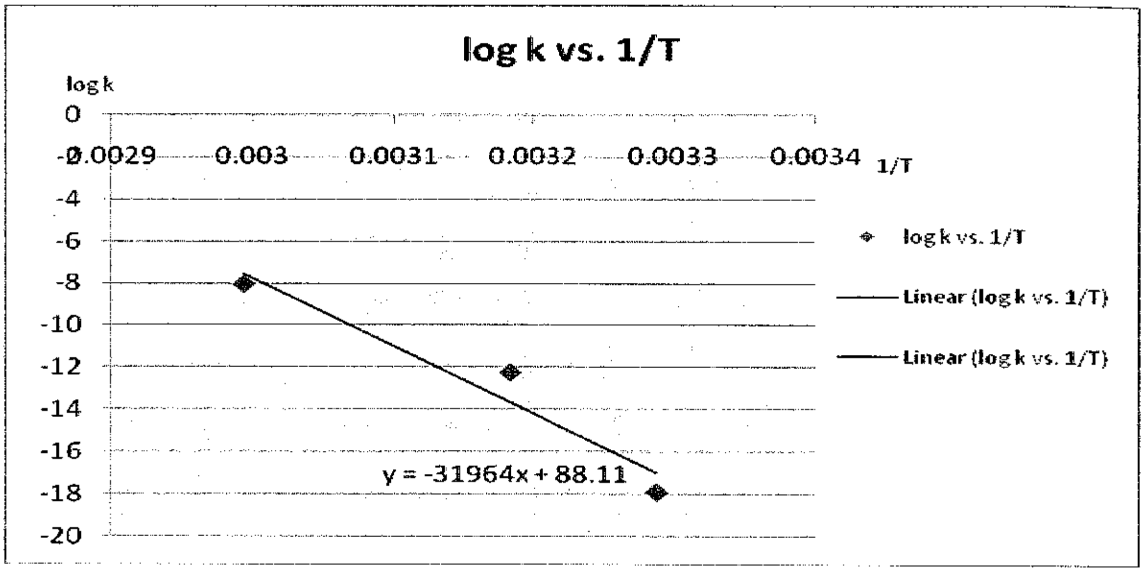

Figure 4.29: log k versus 1/T for Test series E

The first-order reaction rate coefficients are represented by the Arrhenius equation:

k = Ae $^{(-E/RT)}$ where; E_A = activation energy

log k = log A – E_A/RT A = pre-exponential factor

T = temperature (°K)

R = gas constant (8.314 J/mol)

According to the plot;

E_A/R = 31, 964

E_A = 31, 964 x 8.314 J/mol

= **265, 748 J/mol**

log A = -8.11

A = **7.943 x 10^{-12} cm^3/(molecule.second)**

4.2 Discussion

This study demonstrated that Fenton's reagent was successful in reducing the COD in water without generating significant amounts of undesirable byproducts. This reduction can be seen with a contact time of 2 minutes. The reaction was found to be dependent both on the ratio of H_2O_2: Fe $^{2+}$ and the pH of the reaction medium in the Fenton's reagent. In test series A, B and C indicates the effects of H_2O_2 and Fe $^{2+}$ concentration.

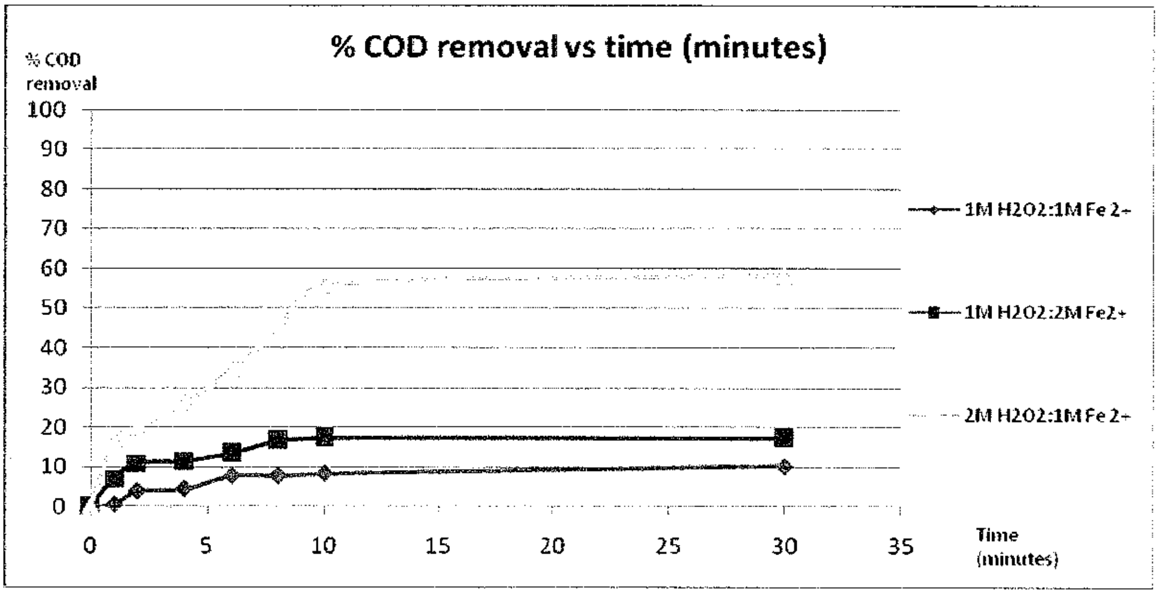

Figure 4.30: Overall %COD removal versus time for different concentration of H_2O_2 and Fe $^{2+}$

In **test series A** (1 mole of H_2O_2 to 1 mole of Fe $^{2+}$), the dosage ratio of H_2O_2: Fe $^{2+}$ is same which is 1:1 based on the calculation of stoichiometric equation.

In **test series B** (1 mole of H_2O_2 to 2 mole of Fe $^{2+}$), the dosage ratio of H_2O_2: Fe $^{2+}$ is 1:2. Higher iron doses improved the COD removal efficiency.

As for **test series C** (2 mole of H_2O_2 to 1 mole of Fe $^{2+}$), the dosage ratio of H_2O_2: Fe $^{2+}$ is 2:1. It is clear that higher H_2O_2 doses generated more hydroxyl radicals which in turn, improved the COD removal efficiency. The reaction of iron salts and hydrogen peroxide;

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

The Fenton reaction begins by producing OH^O radicals from the reaction between ferrous ion and hydrogen peroxide.

A drop in pH of the reaction medium during the progress of the reaction is also observed. This drop in pH which agrees with the results of this study was attributing with the formation of Sulphuric acid. The stoichiometry of the complete oxidation of sulfolane was given by Greene *et al.* (1999) as;

$$C_4H_8O_2S + 6.5O_2 \rightarrow 4CO_2 + 3H_2O + 2H^+ + SO4^{2-}$$

Thus, the release of H_2SO_4, an acid, caused the observed drop in pH.

In **test series D** which indicates the effects of pH in Fenton reagent.

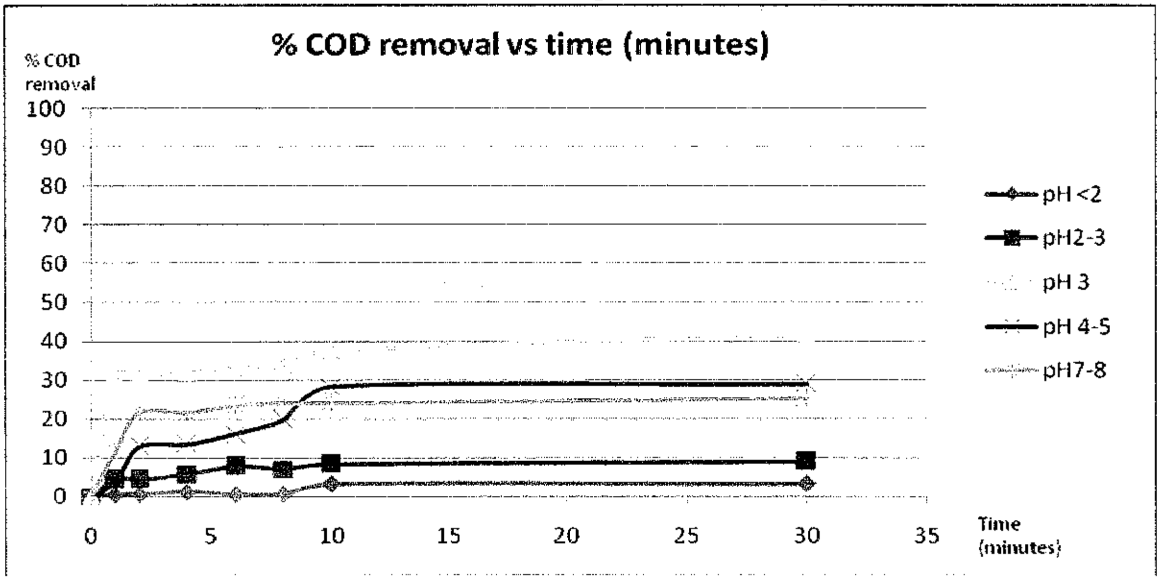

Figure 4.31: Overall %COD removal versus time for different pH

When tested with pH range below than 2, no significant differences in treatment efficiency were observed though at pH range 2-3 produced slightly better result. From the Figure 4.24, at pH 3 produced the highest treatment efficiency. This finding is in line with the test performed by Kochany and Logowski revealed that optimum conditions for Fenton's treatment require pH around 3. It is assumed that the lower conversions is achieved at neutral pH are related to reduction in stability of both Fe^{2+} and H_2O_2 when increasing pH from acidic conditions. Moreover at neutral pH, ferrous iron is readily oxidized by atmospheric and ferric ion precipitates preventing the regeneration of Fe^{2+}.

Test series E indicates the effects of temperature in Fenton Reagent.

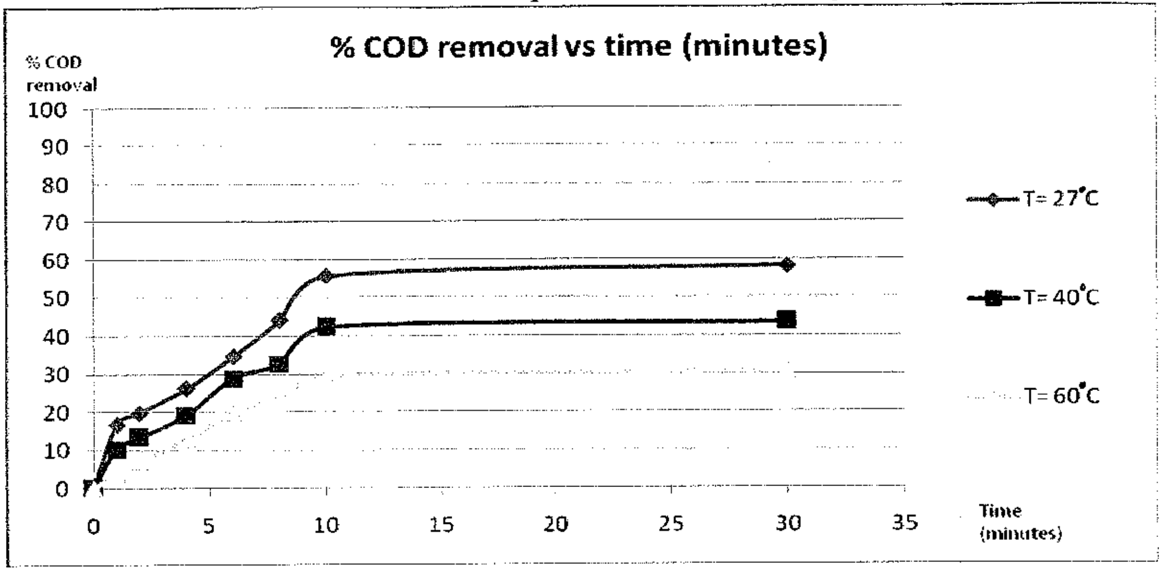

Figure 4.32: Overall %COD removal versus time for different temperature

Figure 4.32 show that there exists an optimal temperature at 27°C for Fenton treatment process. At temperature 27°C, the Sulfolane COD was reduced by 58.33% after 30 minutes of reaction time. While at temperature 40°C and 60°C removed 43.59% and 30.77% COD respectively. The pH of the mixture is fixed at pH 3.00 and the concentration of H_2O_2 to Fe^{2+} is fixed at 2 mole of H_2O_2 to 1 mole of Fe^{2+}, the dosage ratio of H_2O_2: Fe^{2+} is 2:1.

It illustrates Sulfolane COD removal as a function of %COD removal and temperature. As temperature increases beyond 27°C, the %COD removal decreases after 30 minutes of reaction time.

The rate of reaction with Fenton's Reagent increases with the effect more pronounced at temperatures at 27°C. As temperatures increase above 30°C, the efficiency of H_2O_2 utilization declines. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between 20-30°C. Moderating the temperature is important not only for economic reasons, but for safety reasons as well. (Bishop & Walling, 1996).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The project was proven feasible to be implemented in terms of timeliness, apparatus and chemicals. The experiments done in this study could be completed within two semesters of a study year. All apparatus and chemicals can be obtained from the laboratories. Fenton oxidation is a feasible treatment for wastewater containing Sulfinol, allowing a significant decrease of COD.

The experiment also addresses the effects of iron concentration in the Fenton process, hydrogen peroxide concentration in Fenton process and pH in Fenton process. It is observed that higher H_2O_2 doses, 2 mole of H_2O_2 to 1 mole of Fe^{2+} generated more hydroxyl radicals which in turn, improved the COD removal efficiency at reaction pH of range 3.00-3.50. Previous Fenton studies have shown that acidic pH levels near 3.00 are usually optimum for Fenton Oxidation (Hickey et al., 1995).

Experimental results show that there exists an optimal pH at 3.00 and optimal temperature at 27°C for the Fenton treatment process of Sulfolane. As temperature increases above 27°C, the %COD removal of Sulfolane decreases. Temperature plays an important role in process kinetics. The overall rate of Sulfolane degradation presents apparent activation energy around 265.75 kJ/mole. When operated at these optimal conditions, the Fenton treatment process is capable of reducing the COD concentration of the wastewater to the discharge standard.

Fenton oxidation treatment is highly effective at enhancing the biodegradability of wastewater. It is found that a small amount of H_2O_2 can significantly increase the extent of biodegradation of wastewater. Wastewater containing waste like Sulfolane cannot be easily treated by conventional physicochemical and biological processes. Fenton oxidation process provided an elegant and cost-effective way to solve this problem.

5.2 Recommendation and Future Works

In future work, more experiments should be conducted for accuracies. Fenton oxidation is a feasible treatment for wastewater containing Sulfolane, allowing a significant decrease of COD. More attention should be paid to the Fe^{2+}, H_2O_2 dosage, and the pH. The dosage of Fe^{2+} and H_2O_2 and the pH value should varies a lot more to obtain the optimum dosage of Fe^{2+} and H_2O_2 and the pH value AOP of Sulfolane in wastewater. Future FYP students could investigate the AOP of Sulfolane using Fenton reagent by measuring the Biochemical Organic Compound (BOD) and also the Total Organic Compound (TOC).

Students can also collaborate with other external laboratories or research centers such as SIRIM during the experiment implementation to obtain and rectify better results. Students could also get the actual Sulfolane in wastewater sample form plant industry such as MLNG to get more accurate results in series of experiment. In terms of experimental methodology, more series of experiment will be done to familiarize with the lab procedures, chemical and equipments. All series of experiments will use available chemical resources in the laboratory.

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APPENDICES

APPENDIX A: Summary of journals for literature review

Author / Researchers	Research Area	Year	Place
G. Libralato, A Volpi Ghirardini, F. Avezzu	Evaporation and air-stripping to asses and reduce ethanolamine's toxicity in oily wastewater	2007	University of Venice, Italy
Huseyin Tekin, Okan Bilkay, Selale Ataberk, Tolga H. Balta, Haluk Ceribasi, F. Dilek Sanin, Fili B. Dilek, Ulku Yetis	Use of Fenton Oxidation to improve the biodegradability of a pharmaceutical wastewate	2005	Middle East Technical University, Turkey
K. Ntampegliotis, A Riga, V. Karayannis, V. Bontozoglou, G. Papapolymerou	Decoloriation kinetics of Procion H-exl dyes from textile dyeing using Fenton-like reactions	2005	University of Thessaly, Greece
Nora San Sebastian Martinez, Josep Fuguls Fernandez, Xavier Font Segura, Antoni Sanchez Ferrer	Pre-oxidation of an extremely polluted industrial wastewater by Fenton's reagent	2003	Escola University Del Medi Ambient, Spain
E Neyens, J. Baeyens	A review of classic Fenton's peroxidation as an advanced oxidation technique.	2002	Katholieke University, Belgium

Zhimin Qiang, Jih Hsing Chang, Chin-Pao Huang	Electrochemical regeneration of Fe^{2+} in Fenton oxidation processes	2002	University of Delaware, USA
Montserrat Perez, Francesc Torrades, Xavier Domenech, Jose Peral	Fenton and photo-Fenton oxidation of textile effluents	2001	Autonoma de Barcelona University, Spain
Mehmet A. Oturan, Nihal Oturan, Claude Lahitte, Stephane Trevin	Production of hydroxyl radicals by electrochemically assisted Fenton's Reagent	2000	Moleculaire University, Paris
Francisco J Rivas, Fernando J Beltran, Jesus Frades, Paco Buxeda	Oxidation of P-Hydroxybenzoic Acid by Fenton's Reagent	2000	Castilla la Mancha University, Spain
E. Anne Greene, Debora L. Coy, Phillip M. Fedorak	Sulfolane Biodegradation Potential in Aquifer Sediments at Sour Natural Gas Plant Sites	1998	University of Alberta, Edmonton, Alta., Canada
J.C Lou, S.S Lee	Chemical Oxidation of BTX Using Fenton Reagent	1995	National Sant Yat-Sen University, Taiwan

APPENDIX B: Gantt Chart for FYP II

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continue		▨	▨											
	-Practical/Laboratory Work														
2	Submission of Progress Report 1				●										
3	Project Work Continue				▨	▨	▨	▨							
	-Practical/Laboratory Work														
4	Submission of Progress Report 2											●			
5	Project work continue								▨	▨	▨	▨			
	-Practical/Laboratory Work														
6	Poster Presentation (Pre-Edx)												●		
7	Submission of Project Dissertation													●	
8	Oral Presentation	25th May 2009 – 3rd June 2009													

● Suggested milestone
▨ Process

APPENDIX C: Pictures of AOP of Sulfolane in Wastewater Experiment

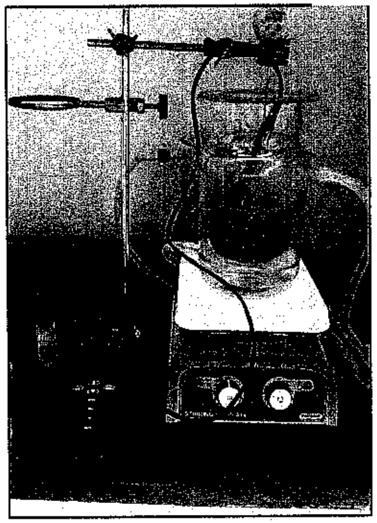

Figure I: Reaction of Sulfolane with Fenton's Reagent

Figure II: Sample is dissolved with NaOH to stop further reaction

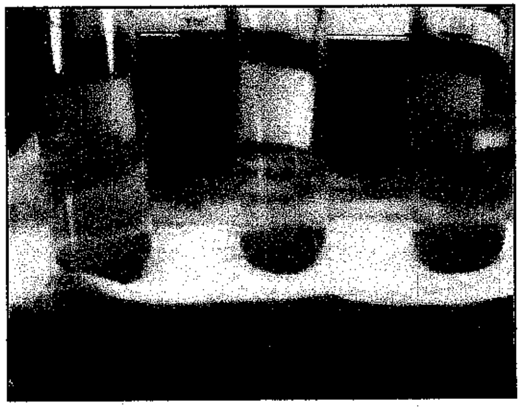

Figure III: Precipitate formed

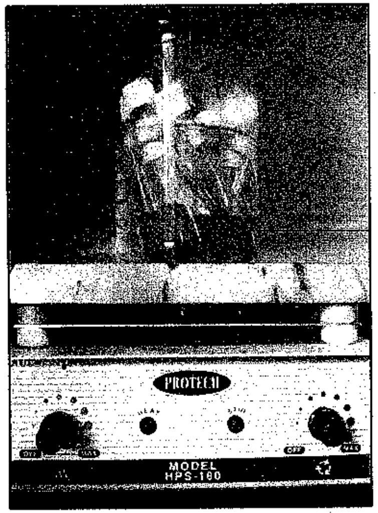

Figure IV: Heated in hot bath to remove excess H_2O_2

Figure V: Cooling down the precipitate

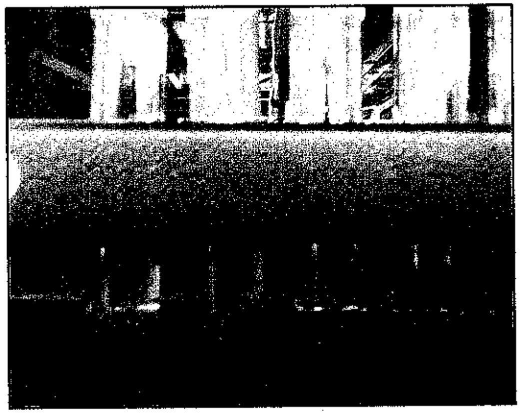

Figure VI: Filter out the solution leaving the precipitate behind

APPENDIX D: COD Determination for Sulfolane (Preparation COD of Sulfonane Wastewater)