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UNIVERSITI TEKNOLOGI PETRONAS

DEGRADATION OF DIISOPROPANOLAMINE USING FENTON’S REAGENT

by

RAIHAN MAHIRAH BINTI RAMLI

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DEGRADATION OF DIISOPROPANOLAMINE USING FENTON'S REAGENT

by

RAIHAN MAHIRAH BINTI RAMLI

A Thesis

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BANDAR SRI ISKANDAR,

PERAK

MARCH, 2010

DECLARATION OF THESIS

Title of thesis	Degradation of Diisopropanolamine using Fenton's Reagent

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ABSTRACT

Diisopropanolamine (DIPA) has been widely used as an additive in cosmetic and personal care products, as corrosion inhibitor and lubricating agent in metalworking fluids, as drug intermediates in pharmaceutical industry and as solvent to remove acid gas from raw natural gas. Thus, wastewater contaminated of DIPA is constantly generated. However, despite the facts, a treatment method to treat the DIPA contaminated wastewater has yet to be developed. Most industrial wastewater treatment plant use conventional biological treatment system to treat wastewater because the system can handle large volume of wastewater at a time. Unfortunately, this system could not treat recalcitrant pollutant such as organic compounds. The DIPA contaminated wastewater is characterized as having high chemical oxygen demand (COD) which makes it impossible to be treated by the conventional wastewater treatment system. Shock loading of COD into the system may cause process upset. Due to this fact, a new way to treat these recalcitrant components has to be identified. The pretreatment of the waste is necessary prior entering the wastewater treatment plant to meet the local standard requirement. In latter decades, advanced oxidation processes (AOP) has been identified to be able to degrade wide range of recalcitrant organic compounds. The simplest AOP that has been applied is Fenton oxidation process. The applicability of this process to degrade organic compounds to biodegradable or harmless products has been widely reported. In this research, viability of Fenton’s reagent to degrade DIPA to biodegradable products was studied. The degradability of DIPA was measured by the reduction of COD in the treated wastewater sample. The percentage COD reduction was found to be higher with higher initial concentration of amine. Highest COD reduction (74 %) in Fenton oxidation of synthetic wastewater was achieved at initial pH of 2 with H_2O_2/Fe^{2+} molar ratio of 10, while for real wastewater sample degradation (72 % COD removal) is most favored at pH of 3 with H_2O_2/Fe^{2+} molar ratio of 12. Continuous addition of Fenton’s reagents is much more effective with better utilization of hydrogen peroxide compared to single addition. In the research, significant COD reduction was observed at the optimum condition and parameters. Carboxylic acids (formic, oxalic and acetic) and glycine were identified as the degradation products. The residual COD could be further decrease in biological treatment system due to the presence of carboxylic acid which is more biodegradable intermediates.

ABSTRAK

Diisopropanolamine (DIPA) telah digunakan secara meluas sebagai bahan tambahan di dalam pembuatan produk penjagaan kosmetik dan peribadi, sebagai pencegah kakisan dan agen pelincir dalam cecair pengerjaan logam, sebagai dadah perantaraan dalam industri farmaseutikal dan sebagai pelarut untuk membuang gas asid daripada gas asli mentah. Oleh kerana itu, air kumbahan yang mengandungi DIPA dihasilkan secara berterusan. Meskipun penggunaan DIPA di dalam industri pembuatan dan pemprosesan semakin meluas, kaedah perawatan khusus untuk merawati air kumbahan yang tercemar oleh sisa DIPA masih belum dibangunkan. Buat masa ini. Kebanyakan industri menggunakan kaedah perawatan air kumbahan secara biologi memndangkan sistem ini mampu merawat air kumbahan dalam jumlah yang banyak pada satu-satu masa. Namun begitu, sistem ini hanya mampu merawati air kumbahan yang mempunyai nilai BOD yang rendah. Air kumbahan yang dicemari oleh DIPA mempunyai nilai COD yang sangat tinggi yang tidak mampu dirawat secara terus oleh sistem perawatan biologi. Nilai COD yang tinggi memasuki system biologi berkemungkinan besar mampu menyebabkan proses perawatan sstem biologi terganggu. Disebabkan itu, satu kaedah rawatan baru untuk merawati bahan pencemar yang susah diurai oleh mikroorganisma peril dikenalpasti. Beberapa dekad kebelakangan ini, 'advanced oxidation process' (AOP) telah dikenalpasti mampu mengurai bermacam-macam bahan pencemar yang sukar untuk diurai oleh mikroorganisma. AOP yang paling ringkas dan mudah dijalankan adalah Fenton oxidation. Penggunaan proses ini untuk mengurai sebatian organic yang berbahaya telah banyak dilaporkan. Dalam kajian yang dijalankan ini, kemampuan Fenton reagen untuk mengurai DIPA kepada bahan yang lebih ringkas dan mudah terurai telah dikenalpasti. Tahap penguraian DIPA diukur melalui nilai COD yang mampu dikurangkan. Peratusan penurunan didapati lebih tinggi apabila tahap kepekatan DIPA yang digunakan adalah tinggi. Peratusan penurunan nilai COD yang paling tinggi (74%) bagi air kumbahan sintetik dicapai pada pH awal 2 dengan nisbah molar H_2O_2/Fe^{2+} 8, sedangkan untuk air kumbahan dari industri, tahap penguraian sebanyak 72% (yang paling tinggi mampu dicapai) pada pH 3 dengan H_2O_2/Fe^{2+} molar nisbah 10. Cara penambahan reagen yang perlahan dan berterusan didapati menghasilkan lebih banyak pengurangan COD berbanding apabila reagen ditambah secara serentak di awal eksperimen. Penambahan reagen dengan cara ini jauh lebih berkesan kerana hydrogen peroksida yang disalurkan dimanfaatkan dengan lebih baik untuk menguraikan sebatian organic. Melalui proses penguraian ini, asid karboksilik (format, oksalat dan asetik) dan glisin dikenalpasti sebagai produk penguraian. Nilai COD yang masih tersisa boleh dikurangkan dengan merawat air kumbahan menggunakan kaedah perawatn tradisional iaitu secara biologi kerana asid karboksilik lebih mudah terurai melalui cara ini.

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CHAPTER 1

INTRODUCTION AND BACKGROUND OF THESIS

1.1 Fundamentals of Wastewater

Wastewater is used water or liquid waste generated by various human activities and contains impurities in excess of the allowable statutory limits. It can also be defined as any water or liquid that contains impurities or pollutants in any form of solids, liquids and/or gases in such a concentration that is harmful if disposed into the environment. For safe disposal of wastewater to the receiving bodies of water such as streams, lakes, ponds, canals, rivers, seas and estuaries, the wastewater is routed to treatment system to remove the pollutants to the dischargeable limits.

Wastewater can be broadly categorized into two groups, depending on its source of generation. Domestic wastewater, also known as sewage, is the used water discharged from the residential, commercial and institutional areas of a city. It is collected through sewerage system. Generally, domestic wastewater contains organic and inorganic solids and microorganism. On the other hand, industrial wastewaters are generated by medium and large scale industries. These wastewaters vary in quantity and quality depending on the industry as well as the process within the same industry. Generally, majority of the wastewater produced by manufacturing and processing industries are highly contaminated wastewaters.

1.1.1 Generation of Industrial Wastewaters

Even though recent trend in industries have been to minimize waste production or recycle such waste within the production process, still many industries remain dependent on process that produce wastewater during operations. Typically, water that has been used for an industrial application requires some degree of treatment before it can be discharged either to a municipal sewer or to a receiving body water. Thus, water itself can represent a major industrial process cost. Treatment of wastewater produced by industry is the most challenging tasks due to the wide variety of pollutants. Selection of treatment technologies depends on the target pollutants as well as degree of treatment to be achieved. Table 1.1 listed some example of the industries with their respective pollutants in the generated wastewater.

Table 1.1: Types of pollutants based on industry

Industry	**Types of pollutants**
Iron and steel	• Gasification products such as benzene, naphthalene, anthracene, cyanide, ammonia, polycyclic aromatic hydrocarbons (PAH). • Hydraulic oils, tallow and particulate solids.
Mines and quarries	• For metal mines, zinc and other materials such as arsenic. • Extraction of high value metals such as gold and silver may generate slimes containing very fine particles in where physical removal of contaminants becomes particularly difficult.
Food industry	• Vegetable washing generates waters with high loads of particulate matter, dissolved organics, and surfactants. • Animal slaughter and processing produces very strong organic waste from body fluids frequently with significant levels of antibiotics and growth hormones • Variety of pesticides used to control parasites • Processing food generates waste contains organic material, salt, flavorings, coloring material, acid and alkali. Significant quantities of oil and fats also present.
Complex organic chemical industry	• Contaminations vary depending on type of process and chemical used. • These include pesticides, pharmaceuticals, paints and dyes, petrochemicals, detergents, plastics. • Waste waters can be contaminated by feed-stock materials, by-products, product material in soluble or particulate form, washing and cleaning agents and solvents.
Nuclear industry	• Radioactive waste

Source: Wikipedia, 2009

1.1.2 Natural Gas Processing Plants

Raw natural gas extracted from reservoir contains impurities that must be removed before it can be used. After the treatment, the processed natural gas will contain almost pure methane and it is used as fuel by residential, commercial and industrial consumers. Meanwhile, the raw natural gas which primarily consists of methane also contains varying amounts of other components such as heavier gaseous hydrocarbons (ethane, propane, butane etc.), acid gases (carbon dioxide, hydrogen sulfide, mercaptans etc.), water (vapor and liquid) and liquid hydrocarbons.

Development of alkanolamines as absorbent for acidic gases was discovered by R. R. Bottoms in 1930. In the same year, he was granted a patent covering the application of alkanolamines. The first alkanolamine commercially available for acid gas treatment was triethanolamine (TEA). Since then, the other members of alkanolamines were introduced in the market and evaluated as possible acid gas absorbents (Kohl and Nielsen, 1997). Various amines are now available such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), methyldiethanolamine (MDEA) and TEA. MEA is primary amine, while DEA and DIPA are secondary amines. On the other hand, MDEA and TEA are grouped under tertiary amines.

Amine gas treating, also known as gas sweetening and acid gas removal, refers to a group of processes that use aqueous solutions of various alkanolamines to remove hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from natural gas. This treating unit is commonly used in refineries, petrochemical plants, natural gas processing plants and also some other industries. Fig 1.1 shows a typical amine gas treating unit. Typically, the unit includes an absorber and regenerator unit as well as accessory equipment. In the absorber, the downflowing amine solution will absorb acid gases from the upflowing sour gas. The sweetened gas stream (acid gases free gas) will leave the amine unit as product while the amine solution rich in the absorbed acid gases will flow into regenerator (a stripper with a reboiler) to remove acid gases. After the regeneration process, lean amine solution is recycled for reuse in the absorber.

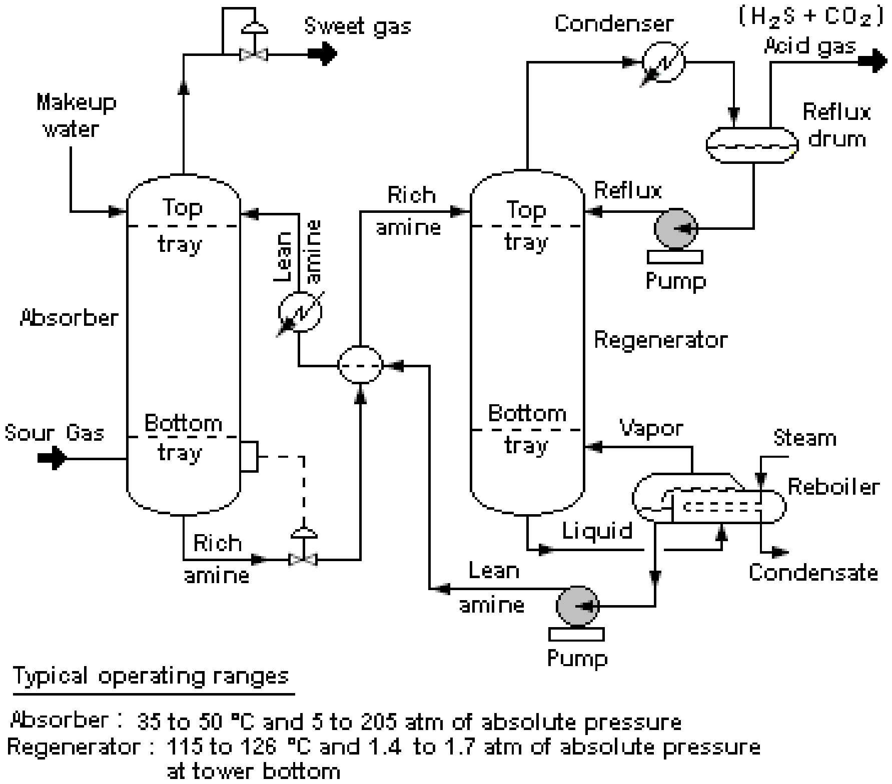


Figure 1.1: **Process flow diagram of a typical amine treating unit**

Source: Wikipedia, 2009

Even though amine solutions are regenerated and recycled within the system, some of it may be carried over in water to the wastewater treatment system. The amine can also be carried in wastewater during the turnaround for safety inspection of amine treating unit. During this period, the amine solution will be flushed off from the absorption and regeneration tower. Then high pressure water is used to clean the inside of tower. This water with traces of amines will be routed to wastewater treatment plant. Unfortunately, traces of amines in the wastewater increase the chemical oxygen demand (COD). High COD loading to the biological treatment plant upset the system. Consequently, wastewater discharged will violate the regulation.

1.1.3 Treatment of Amines Contaminated Wastewater

Despite the common usage of alkanolamines in industry, the treatment of wastewater contaminated with the amines has yet to be developed. The contaminated wastewater is characterized as having high COD which makes it impossible to be treated by current wastewater treatment facility. Due to this fact, a new way to treat these recalcitrant components has to be identified. The pretreatment of the waste is necessary prior entering the wastewater treatment plant to meet the local standard requirement. One of the pretreatment methods that have been widely utilized in recent wastewater plant development is advanced oxidation processes (AOPs).

In the past few decades, AOPs have attracted many researchers due to its ability to degrade wide range of recalcitrant organics that is impossible to be degraded by other methods. Compared to other wastewater treatment processes such as biological, classical chemical and physical-mechanical, AOPs have proved their abilities to mineralize organic contaminants present in wastewater. They have been used to degrade 99.25% of azo dye Amido black (Sun *et al.*, 2006), 90% of cork cooking (Guedes *et al.*, 2006), and 87.3% of pharmaceutical waste (Huseyin *et al.*, 2006). However, the research on applicability of AOPs to degrade alkanolamines has yet to be conducted. Very little research on amine itself is available and none is on alkanolamines.

1.2 Thesis Statement

Alkanolamines have been widely applied in natural gas processing plants to remove acid gas and improve quality of natural gas for commercial use. Despite its wide application, a treatment system to handle wastewater contaminated with this organic solvent or the solvent itself has yet to be developed. Wastewater contaminated with alkanolamines has an extremely high COD which exceeds the limits set by local authorities. High COD in the influent stream makes the treatment by biological method not viable. Current practice shows that these wastes are stored in buffer tank and sent to licensed contractor for disposal. However, due to large volume of wastewater generated, this practice in not economically feasible to be implemented.

AOPs have shown great efficiency as a tool to degrade organic pollutants to readily biodegradable products. Its applicability as a pretreatment step before biological system has been studied and reported to be very feasible. Although there are many literatures related on the applicability of AOPs to degrade variety of organic pollutants, very little research on amine itself is available and none is on alkanolamines. For that reason, this study intends to investigate the applicability of Fenton oxidation, an advanced oxidation process, to degrade an alkanolamine. The application of Fenton process in wastewater treatment is still new but this process is attractive due to the highly abundant and non-toxic element of iron (Buzzi, 1992), and environmentally benign of hydrogen peroxide. Furthermore, many literatures are available on the applicability of Fenton process to convert a broad range of pollutants to harmless or biodegradable products (Koprivanac and Kusic, 2007). The effectiveness of Fenton's reagent for the degradation of organic contaminants has been widely reported which include aromatic hydrocarbons and other compounds such as amines, phenol and substituted phenols, polycyclic aromatics, chlorinated hydrocarbons and more complex molecules like dyes, pharmaceuticals, amines, alcohols, mineral oils, etc. A very fast reaction using Fenton's reagent within 10 minutes with almost complete destruction of benzene, toluene and xylene (BTX) was reported by Lou and Lee (1995). Ray et al. (2003) also reported an almost complete destruction of MTBE in wastewater within 10 minutes of reaction. Quite a few studies were reported on degradation of residual dyes or dyeing wastewater using the Fenton's reagent. Gulkaya et al (2006) reported that with optimal ratio of H_2O_2/Fe^{2+} concentration, up to 95% of COD removal in carpet dyeing wastewater was achieved. Treatment of synthetic wastewater in laboratory containing azo dyes was studied by Sun et al. (2007) by using Fenton's reagent. Under optimal conditions (pH = 3.50, $[Fe^{2+}]_o:[H_2O_2]_o = 1:10$, $[dye]_o = 50$ mg/L, temperature = 25°C), 99.25% degradation efficiency of dye was achieved. A comparison between UV-H_2O_2 and Fenton's reagent was reported by Alshamsi et al. (2007) who studied efficiencies of degradation of Crystal Violet and also by Alnuaimi et al (2007) who studied about the decolorations of Neutral Red. In these two reports, Fenton's reagent was proved to be more effective than the photo-chemical route. In situ remediation of contaminated soil by Fenton's oxidation has been applied at many sites (Matthew, 2003). Typical applications include degradation of light nonaqueous phase liquid (LNAPLs), dense nonaqueous phase liquids (DNAPLs) and some other larger molecules such as energetic compounds. In a laboratory study conducted by Ravikumar and Gurol (1994), pentachlorophenol (PCP) and trichloroethylene (TCE) were successfully treated with Fenton' reagent with TCE showed better degradation.

Fenton’s reagent has also been applied as pretreatment before biological treatment to enhance the biodegradability of the pollutant. Alaton and Teksoy (2005) studied the effectiveness of Fenton’s reagent to pre-treat acid dye-bath effluents of a textile industry before conventional biological treatment. Gotvajn and Zagorc-Konca (2005) combined Fenton’s reagent and biological oxidation for heavily polluted fermentation broth waste. Biodegradation of a pharmaceutical wastewater was greatly improved by Fenton’s treatment as reported by Tekin et al. (2006) since of breakdown of the organics into smaller fragments makes it amenable to normal biological oxidation. Application of Fenton oxidation to the amines compound has also been studied and reported. Oxidation of a tertiary amine by hydrogen peroxide was studied by Hoh et al. (1963) where they reported an extra of 10% hydrogen peroxide was required for complete conversion of dimethyldodecylamine. Casero et al. (1997) then reported a study on the degradation of aromatic amines (aniline and a few substituted anilines). They identified the intermediates by mass spectrometry. Complete mineralization was achieved within one to three hours. Mineralization of aniline was also studied by Brillas et al (1997) by using a few advanced oxidation techniques – such as anodic oxidation, photo-catalysis, electro-Fenton and photo-Fenton techniques. UV irradiation was found to accelerate each of the processes. The latest study on the application of Fenton oxidation to enhance the biodegradability of alkanolamine was reported by Harimurti et al. (2009). They reported the effectiveness of Fenton’s reagent to partially degrade monoethanolamine (MEA) before introducing to the conventional biological treatment. Almost complete COD removal was successfully achieved within 24 hours of treatment. With the recent reports on the successful application of Fenton’s reagent to a broad range of organic contaminant and the ease of assess of the reagents, Fenton’s reagent is chosen as the treatment process to degrade DIPA to the acceptable level of conventional biological treatment system.

In this study, a secondary alkanolamine (diisopropanolamine, DIPA) is selected as the subject of the research. DIPA is chosen over other alkanolamines due to its wide application in industry as well as toxicity of it reported by others (CCME, 2006; Dow, 1984). The application of DIPA in industry include as solvent in natural gas treatment plant where Sulfinol contains 50 percent of DIPA. Besides, this amine has been used as an ingredient in cosmetics and detergent products which have been used everyday. Thus, wastewater containing DIPA has been continuously generated. A small amount of DIPA in wastewater will contribute to high value of COD. Even with only one gram of DIPA in a liter of wastewater will contribute to nearly 2,000 mg/L of COD (Appendix A). This level of COD is obviously exceeding the discharged limit for disposal to water bodies. The presence of DIPA in water will be harmful to the livings. Ingestion of DIPA will cause a series of health problems, from the burning sensation to abdominal cramps and the person eventually will collapse. Meanwhile, inhalation of it may cause respiratory tract irritation as well as fatalism due to spasm, inflammation, chemical pneumonitis and pulmonary edema (Chemwatch, 2006).

1.3 Objectives

This thesis aims at investigating the applicability of Fenton oxidation for the mineralization of DIPA contaminated wastewater. The objectives are:

1. To investigate the applicability of Fenton’s reagent to reduce COD and degrade DIPA in synthetic wastewater and industrial wastewater samples,
2. To investigate the effect of various process parameters on the rate and extent of degradation of the amines and determine optimum parameters for the degradation of DIPA,
3. To identify the byproducts produced from the degradation process, and
4. To prove the improvement of biodegradability of wastewater after Fenton oxidation.

1.4 Scope of Work

In the above context, this work has been undertaken to experimentally investigate the degradability of alkanolamines using Fenton’s reagent. Diisopropanolamine (DIPA) is selected as the research subject. Effects of different process parameters such as the initial concentration of the amine, the dosage of Fenton’s reagent, pH and the mode of addition of the reagents (single or continuous dosing) are to be studied. Later, the applicability of Fenton’s reagent is investigated using real wastewater containing DIPA. The treatment conditions between synthetic and real wastewater samples are compared.

1.5 Thesis Outline

- Chapter 2 reviews the process selection. Possible treatment technologies for organic compounds. Each treatment technology is evaluated to select the best option for the treatment of DIPA contaminated wastewater. The theory of the selected treatment method is explained in details as well as the significant application in industrial wastewater treatment.

- Chapter 3 gives the details on the materials for the study, experimental and analytical procedure for the research. Experimental procedure is summarized in a flowchart followed by a detailed explanation.

- Chapter 4 provides the findings for the degradation of DIPA. Each factor was discussed and comparison with the available literature was studied.

- Chapter 5 provides general discussions based on the discussion of each factors. Comparison between synthetic and industrial wastewater was also discussed.

- Chapter 6 concludes the research work based on the objectives of the study.

- Chapter 7 provides future avenues for the research on this topic.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Justification for wastewater treatment process selection is detailed in this chapter. Possible treatment technologies for organic compounds are identified and each treatment technology is evaluated to select the best option for the treatment of DIPA contaminated wastewater. The selected treatment should be applicable to treat industrial wastewater which is more polluted compared to domestic wastewater due to the nature of chemicals used.

Industrial wastewater is very different in composition compared to domestic wastewater. The waste coming from industry varies in composition depending on the type of industry and the material processed itself. It can be organic, easily biodegradable, largely inorganic or potentially inhibitory. On the other hand, domestic wastewater comprise primarily water which is approximately 99% with a complex mixture of organic or/and inorganic constituent. As they are also from human waste, they may contain microorganisms which can be pathogenic. Generally, wastewater that has COD:BOD_5 ratio of 3 or lower can be fully treated by biological process (Ng, 2006). Meanwhile, other wastewaters may need different treatment methods to achieve desired degree of purification.

2.2 Organic Compounds Treatment Technologies

There are many treatment technologies available to treat industrial wastewater before it can be discharged. In general, the wastewater treatment can be categorized into three main groups which are chemical, physical and biological methods. Stephenson and Blackburn (1997) identified several treatment methods for removal of organics from wastewater. Some of the treatment technologies suitable for treating organic compounds include steam and air stripping, biological removal, adsorption and chemical oxidation. The selection of treatment method depends on the characterization of the pollutants that are subjected to be treated and degree of treatment. In the next section, the advantages and disadvantages of several treatments methods will be discussed in detail.

2.2.1 Biological Treatment

Biological methods involve living organisms using organic or inorganic substances for their food. By doing so, the chemical or physical characteristics of organic or inorganic substances will change. This method has been widely applied in industry due to its low operating cost. The living organisms used in the industrial wastewater treatment include bacteria, fungi, protozoa and algae. The most active agents in the biodegradation of organic matter are bacteria which typically range from 1 to 5 µm in size. The organic matter present in wastewater is composed of the elements carbon, hydrogen, nitrogen, phosphorus, and many additional elements in a much smaller amount. These elements are connected by chemical bonds, which is defined by a certain amount of energy known as “bond energy”. During the biodegradation process, the amount of organic pollutant will decrease while quantity of microorganisms, carbon dioxide, water and other byproducts of microbial metabolism will increase (Woodard and Currant, 2006).

Industrial wastewater treatment by microorganisms can be divided into two technologies. In aerobic technology, oxygen is introduced into the aeration tank. The oxygen will be used by microorganism to oxidize organic matter. Meanwhile, anaerobic technology is working in the absent of oxygen. The types of microorganism used in these two technologies are different depending on the system (Eckenfelder and Musterman, 1995)

Comparing to other treatment methods, the major advantage of biological treatment is the least of cost to build the plant. Besides, large volume of wastewater can be treated simultaneously compared to other methods. However, the major drawback is the length of time involve because this treatments can take days to months to complete the process. Unfortunately, oxidizing organic matter by microorganisms is not a 100 percent complete process. There are some organic molecules that are unable to be degraded by microorganism. They may prefer some compounds more than others, so this process is selective and depends on the compound matrix (Stephenson and Blackburn, 1997). This type of polluted wastewater needs another treatment step before biodegradation.

2.2.2 Stripping

Stripping process involve no chemical reactions, which make it purely physical treatment technology. It involves only the movement of one or more chemical substances from one medium to another medium which normally the opposite of the first medium. Stripping agents can be either steam or air. Frequently, stripping is coupled with absorption whereby absorption is used to remove soluble components from gas stream and stripping is used to regenerate the solvent by removing the dissolved components from the spent solvent. The basic design of strippers and absorbers are basically the same. It is a gas-liquid contactor which use continuous flow of gas and either batch or continuous flow of liquid.

Environmental applications of stripping includes regeneration of absorber solvents for recycling, removing of volatile organic compounds (VOCs) such as solvents, gasoline, and diesel fuel from contaminated soil or groundwater during soil venting, removing VOCs, odors and ammonia from wastewater, recovery of organic chemicals from solvents and recycle oil by steam stripping, and inert gas stripping of reactive materials from water and solvent which use nitrogen, carbon dioxide or steam as stripping agents. Besides the listed application, stripping process is also widely applied in manufacturing processes (Stephenson and Blackburn, 1997).

In steam stripping, the basic operating principle is the direct contact of wastewater with steam. During the contact, the heat from steam will vaporize the more volatile organic compounds. Then, the overhead vapor, the mixture of water and organic compounds, is condensed and separated to recover the organic compounds. Depending on the industry, the recovered organic are either recycled back to the process or incinerated in an onsite combustion device.

Unlike steam stripping, the basic principle of air stripping is the vapor-liquid equilibrium. A large amount of air is forced through the contaminated water thus provided a large air-water interface which results in an increase of transfer rate of the organic compounds into vapor phase. Air stripping is applicable in a wider range of volatilities compared to steam stripping. However, the air used to remove organic compounds from wastewater must be vented. Practically, air stripping is applied for the streams containing dilute organic compound such as pulp and paper wastewaters or contaminated ground water. It works most efficiently in the removal of highly volatile, water insoluble compounds (Watson, 1999).

As stated before, stripping has been widely applied in industry either for environmental application or manufacturing process. The technology has proved to be efficient to recover or remove volatile organic compounds from spent solvent or contaminated water. Despite the advantage of stripping in the VOCs recovery or removal, there are a few drawbacks of the technology. This technology is only effective to remove solute which has low boiling point, low solubility and low heat of vaporization. The inadequate purity in the stripping gas may cause impurities to the liquid being stripped during the final contact between the liquid and gas (Watson, 1999).

2.2.3 Adsorption

Similar to absorption, adsorption process happens when a substance in either gas or liquid becomes attached to a solid. Special solid surface, called adsorbent will attract pollutant, called adsorbate. Early humans found adsorption process occurred naturally in daily life process. This process was then perfected to be used in industry to clean up hazardous waste or purify drinking water (Binnie *et al.*, 2002).

The basic principle of adsorption is based on the attractive forces between solid surface and the adsorbed molecules. Physical adsorption occurs when the attraction between adsorbent surface and adsorbed molecules are purely physical. This adsorbent can be easily regenerated by reducing pressure, raising temperature, or flushing with solvents. However, if the attractive forces resulted in a chemical bond between the adsorbent surface and adsorbed molecules, the adsorption is called chemical adsorption or chemisorption. The regeneration of spent adsorbent is more difficult where it may require chemical reactions to reactivate the adsorbent (Watson, 1999).

There are various kinds of adsorbents available for different type of adsorption application. For commercial applications, a sorbent should have high selectivity so that optimum separation can be achieved, high capacity to minimize the amount of sorbent required, favorable kinetic and transport properties for rapid sorption, and relatively low cost. The most common adsorbent used for industrial wastewater treatment is activated carbon. Other adsorbents include synthetic resins, activated alumina, silica gel, and molecular sieves (Seader and Henley, 1998).

Adsorption process is practical as a separation technique due to the ability to produce adsorbents that have high surface area per unit weight (Seader and Henley, 1998). Besides, the target adsorbate can be removed by using very selective adsorbent. Depending on the physico-chemical properties of adsorbate, adsorption is only practical if the substrate to be removed is moderately soluble in water. Plugging of adsorbent bed can be a major problem if the feed inlet contains dirt or fine particulate. For high degree of separation, very selective adsorbent can be used but it will be non economical if a mixture of organics or pollutants present in the wastewater. Since the organics are only removed or concentrated, further treatment is required before disposal. The use of solvent for regeneration of adsorbent for less volatile adsorbate will increase the amount of chemical in the wastewater. Although the solvent can be recovered, the trace of it can still contribute to high value of chemical oxygen demand (Watson, 1999).

2.2.4 Chemical Oxidation

Treatment system by oxidation is usually the last resort due to its cost. However, in most cases, the process is very effective. Due to the fact, it has been commercialized to treat recalcitrant chemicals that are untreatable by other treatment systems. Chemical oxidation involves chemical reactions between the organic compounds and oxidants such as ozone, hydrogen peroxide, permanganate, or chlorine dioxide. Depends on the oxidants and types of pollutant, oxidation have proved to be effective in reducing contaminants. Selection of oxidant to be used depends on the types of pollutants to be treated. Chlorine is the most common oxidant, but it has found to form carcinogenic compounds during oxidation with organics. On the other hand, permanganate is relatively expensive but more effective under certain conditions. It can be used to oxidize organic compounds over a wide pH range (EPA, 2004).

Ozone is another oxidant that has proved to be effective for organic reduction. It was first used in drinking water treatment as disinfectant and oxidant. Then, its application has been widening to the treatment of inorganic pollutant such as iron, manganese, and sulfide; organic micropollutant oxidation, including taste and odor compounds, phenolic pollutants, and some pesticides; and organic macropollutant oxidation such as for color removal, increasing biodegradability of organic compounds, and reduction of chlorine demand.

Compared to other oxidants such as chlorine, chloroamines and chlorine dioxide, ozone acts as a general oxidizing agent and more effective for inactivation of viruses such as Cryptosporidium and Giardia (Langlais *et al.*, 1991). Besides, it can oxidize iron, manganese and sulfides, enhance clarification process and turbidity removal, control color, taste and odors. Additionally, it requires very short contact time and only produces dissolved oxygen upon decomposition. Despite all the advantages, where cost dominates over other engineering factors at a site, ozone is the last resort due to its high cost for initial ozonation equipment, operating and maintenance. Generation of ozone requires high energy and should be generated onsite. Ozone has strong oxidation potential of 1.4 times higher than hydrogen peroxide, so it is highly corrosive. At high pH and temperature, ozone decays rapidly (Gottchalk *et al.,* 2001).

In the last few years, hydrogen peroxide has been found to be more applicable and less expensive (Stephenson and Blackburn, 1997). It is effective to reduce organics, such as COD and worthwhile to be considered as the remediation technique to the COD and organics reduction problems. Due to this, it has attracted many researchers to deeply dig its capability as an oxidant. Dye contaminated wastewater is one of the biggest volume accumulated in the world due to the fact that it is the main ingredient in textile manufacturing process. Therefore, the research for that particular pollutant has been conducted for years. Dutta *et. al* (2001) reported the effectiveness of hydrogen peroxide as oxidant coupled with ferrous sulfate as catalyst to oxidize methylene blue with more that 98% reduction in only one hour. Aside from dye, phenol is also another major pollutant produced by industry due to its wide application in textile, pesticides plants, paint, chemical, etc. Treatment of phenol contaminated wastewater was studied by Chamarro *et. al* (2000) who found that the biodegradability of the treated water increased after the treatment with Fenton’s reagents, which consist of hydrogen peroxide and ferrous salt. Reaction of organic with hydrogen peroxide only takes very short time when catalyzed and the peroxide itself is environmental friendly where it will decompose to oxygen and water.

Application of chemical oxidation as one of advanced oxidation technology to treat wide range of organic pollutants has attracted many researcher to contribute in this field. This technology can be applied for in-situ treatment with rapid destruction of organic contaminants. The degradation products are harmless and biodegradable (Chamarro *et. al,* 2000) with the ability to completely mineralized the organics when right oxidant is used. Although the initial cost is relatively higher compared to other treatment technologies, the short reaction time will reduce the size of the equipments thus reducing the disturbance to site operations when it is built on site.

2.3 Chemical Oxidation as the Most Applicable Technology

In previous section, four different methods available to treat wastewater containing organic compounds were discussed. The advantages and disadvantages of each treatment method were summarized in Table 2.1. From the table, chemical oxidation method is the most suitable technique for the treatment of wastewater containing DIPA. As an organic solvent, complete degradation of DIPA is possible with adequate amount of reagents. In chemical oxidation, wide range of organic compounds can be mineralized to harmless byproducts. Furthermore, recalcitrant organic compounds are degraded to biodegradable product which can be further mineralized by microorganisms. Compared to other treatment technologies, large volume of wastewater can be treated in shorter time.

Table 2.1: Comparison of different treatment method

Treatment Method	Advantage(s)	Disadvantage(s)
Biological Treatment	• Low cost to build treatment facility • A large volume of wastewater can be treated simultaneously	• Degradation may take days to months depends on degree of treatment • Not all organic can be degraded by microorganism, not a 100 percent complete process • For high COD wastewater, it will require further treatment process to ensure the final COD value is below the limit for discharge
Stripping	• Proven to be efficient to recover or remove volatile organic compounds	• Only effective to remove solute which has low boiling point, low solubility and low heat of vaporization. • Inadequate purity in the stripping gas may cause impurities to the liquid being stripped during the final contact between the liquid and gas. • Recovered organic pollutant still need to treated
Adsorption	• Practical as a separation technique due to the ability to produce adsorbents that have high surface area per unit weight • Can remove the target pollutant effectively due to very selective adsorbent	• Only practical if the substrate to be removed is moderately soluble in water • Fine dirt or particulate can plug in the adsorbent bed • Non-economical if a very selective adsorbent is used for high degree of separation when the wastewater contains a mixture of pollutants • The use of solvent to regenerate adsorbent will increase the amount of chemicals in wastewater
Chemical Oxidation	• Short reaction time will reduce the size of the equipments, so reducing the disturbance to site operations when it is built in-situ • The degradation products are harmless and biodegradable for some process • Complete mineralization can be obtained with right amount of reagents • Wide range of organic compounds can be mineralized • Contaminant can be destroyed in-situ • Some processes can be applied at ambient condition (normal pressure and temperature)	• Relatively higher initial cost compared to other technologies • Requires highly skilled operators

Most of the wastes produced from industry are hazardous organic wastes where the greatest challenge is to treat the waste safely and effectively. The inability of the conventional biological wastewater treatment to effectively remove the toxic pollutants shows that new wastewater treatment system is in great demand. In the recent study done by many scholars, advanced oxidation processes (AOPs) showed a great potential to become the most favorable process in the near future.

Glaze et al (1987) defined AOPs as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”. The main feature of AOPs is hydroxyl radical (·OH) which has a high oxidation potential and acts rapidly with most organic compounds. Table 2-2 below shows that hydroxyl radicals have the second largest standard redox potential after fluorine.

Table 2.2: Standard Redox Potential of Some Oxidant Species

Source: Matthew, 2003

Oxidant	**E^o, V**
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Permanganate ion	1.67
Hypochlorous acid	1.49
Chlorine	1.36
Chlorine oxide	1.27
Bromine	1.09

The attack by the ·OH radical initiates a complex cascade of oxidative reactions leading to mineralization of the organic compound. Generally, three common reaction pathways are known:

a) hydroxyl radical addition to unsaturated systems
b) hydrogen abstraction (typically from alkyl or hydroxyl groups), and
c) direct electron transfer.

Due to the reactivity of hydroxyl radicals, they can react with almost all types of organics (ethylenic, lipid, aromatic, aliphatic) and inorganics (anions and cations) (Hordern *et al.,* 2003). In a report by Matthew (2003), the reactions by ·OH radicals typically follow second order kinetics with most compounds studied have rate constant between 10^7 and 10^{10} M^{-1} sec^{-1}. Many ways have been identified to generate the highly reactive ·OH radicals. These include both non-photochemical and photochemical methods.

2.3.1 Non-photochemical Oxidation

Three well known methods to produce ·OH radicals without the use of light energy are combination of ozone with hydrogen peroxide, ozonation with catalyst, and Fenton system.

2.3.1.1 Ozone-Hydrogen Peroxide

The combination of ozone with hydrogen peroxide is also known as the peroxone system. Ozone itself can decompose to produce hydroxyl radicals. However, oxidation of organic with ozone alone is not effective. In this system, the addition of hydrogen peroxide accelerates the dissociation of ozone and increase the concentration of hydroxyl free radicals. Brunet *et al.* (1984) and Duguet *et al.* (1985) found that the addition of hydrogen peroxide enhanced the oxidation efficiency of several organic compounds.

Successful application of peroxone for the destruction of recalcitrant pollutants was reported by Mahar *et al.* (1999). Many contaminants such as 1,4 dioxane, methyl tertiary-butyl ether (MTBE), trichloroethylene (TCE), perchloroethylene (PCE), N-nitrosodimethylamine (NDMA) can be oxidized by peroxone. Besides the application as a powerful oxidant, the oxidizing potential of peroxone also makes it a great disinfectant.

Comparing to ozone only system, oxidation is more reactive and faster in peroxone process. It is also more effective in oxidizing refractory organics such as taste and odor compounds. In addition, halogenated compounds were also reported to be destructible by peroxone process (Gottchalk *et al.,* 2001). With the right amount of hydrogen peroxide supplied, mineralization of organic carbon compounds to readily biodegradable components can be achieved. Despites all the advantages, the application of peroxone system will require high initial cost for ozonation equipment. The generation of ozone also requires high energy and should be generated on-site. At high pH and warm temperature, ozone will decay rapidly and leave no residual. Operation of ozone producing equipment requires high level of maintenance and operator skills.

2.3.1.2 Ozone-Catalyst

Addition of metal oxides and metal ions to ozonation reaction is one way to increase the capability of ozone as oxidizing agent. Metal oxides and metal ions such as TiO_2, Fe_2O_3, Al_2O_3-Me, MnO_2, Fe^{2+}, Fe^{3+}, Mn^{2+} have been studied and reported to have potential in oxidation of contaminants (Munter, 2001). Similar to ozone-hydrogen peroxide system, the use of catalyst accelerates the dissociation of ozone thus increase the concentration of hydroxyl free radicals. Homogeneous catalytic ozonation is based on the use of aqueous metal ions for activation of ozone, while heterogeneous catalytic ozonation occur in the presence of metal oxides or metals/metal oxides on support.

Quispe *et al.,* (2006) studied the applicability of catalytic ozonation for the degradation of refractory organic compound oxalic acid. Comparison between catalytic and non-catalytic ozonation showed that degradation was more efficient with the presence of catalysts MnO_2/TiO_2 and Rh/TiO_2.

The use of ozone in wastewater treatment is attractive when only selective pollutant is to be destroyed. Thus, the degradation will not be hindered by competitive reactions unlike in case of hydroxyl radicals (Hordern *et al.,* 2003). However, the limits application in water treatment technology is due to the low solubility and stability of ozone in water. The high cost of ozone production and selective oxidation of organic make it not feasible from economic point of view.

2.3.1.3 Fenton oxidation

Fenton's reagent had been applied to degrade a wide range of contaminants, mainly recalcitrant organic pollutants. The Fenton's reagent consists of a mixture of ferrous catalyst and hydrogen peroxide. It was first reported by Fenton (Fenton HJH, 1876, *as cited by* Matthew, 2003) in 1876.

Since then, the applicability of Fenton's reagent to the degradation of many recalcitrant organic compounds has been reported and the research is still going. Kavitha and Palanivelu (2005) reported that destruction of cresols can be done by using Fenton oxidation, where the degradation efficiency was as high as 82%. Meanwhile, degradation of azo dye Amido black 10B by this process accompanied by optimal conditions can increase the degradation efficiency up to 99.25% (Jian *et al*, 2006).

The application of Fenton's reagent in oxidation of organic compounds is very attractive due to the ability to convert a wide range of pollutants to nontoxic or biodegradable products. Also, the environmentally benign of reagents do not pose any threat. Abundant amount and nontoxic nature of ferrous catalyst is also an added advantage of Fenton system. Besides, the cost for the reagents is also relatively low. Despite the advantages, the major drawback of this system is the generation of excessive or explosive heat under aggressive conditions (Matthew, 2003).

2.3.2 Photochemical Oxidation

Five photochemical oxidation methods are being studied to determine the effectiveness of the process to completely oxidize the pollutants. The processes are ozone with UV radiation, hydrogen peroxide with UV radiation, combination of ozone, hydrogen peroxide and UV radiation, photo-Fenton system and photocatalytic oxidation.

2.3.2.1 UV Radiation-Hydrogen Peroxide

Direct photolysis of organic is not effective with insignificant reduction of organic concentration was reported (Al Momani *et al.,* 2004; Lee *et al.,* 2004; Xu *et al.,* 2007). However, when the UV radiation was combined with hydrogen peroxide, the degradation significantly increased. When used alone in the oxidation of organic compounds, oxidizing power of hydrogen peroxide is 1.77V (Table 2.2). But with the addition of UV radiation, the peroxide will be dissociated into more reactive hydroxyl radicals with oxidizing potential of 2.8V (Matthew, 2003). In this system, UV light serves as the initiator for dissociation of hydrogen peroxide to two hydroxyl radicals (reaction 2.1).

$$H_2O_2 \xrightarrow{UV} 2^{\bullet}OH \qquad (2.1)$$

Oxidation of organics by this method happens in two ways. Some organic chemicals can be destructed by the absorption of direct UV light (Schwarzenbach *et al.,* 2003). Meanwhile, other organics will be transformed by more reactive hydroxyl radicals produced by the reaction of UV light with hydrogen peroxide (Bolton and Cater, 1994). The employment of UV/H_2O_2 process for degradation of dye pollutants was found to be effective (Colonna *et al.*, 1999; Mohey *et al.*, 2003; Georgiou *et al.,* 2005).

UV/H_2O_2 process has several advantages that make it attractive. There is no sludge formation during the treatment. So, sludge disposal will not be a problem. This process can be carried out at under ambient conditions. If this process is to be combined with biological system, the oxygen formed in this pre-treatment step will be useful for the subsequent treatment (Marechal *et al.,* 1997). However, the absorption of UV light will be affected if the wastewater to be treated has high turbidity and solid particles the aqueous. The aqueous stream may need pretreatment to remove all these substances which will further add to the initial setup and operating cost.

2.3.2.2 Ozone-UV Radiation-Hydrogen Peroxide

As in UV radiation-hydrogen peroxide process, this process is quite similar except for an additional component. The name ozone-UV radiation-hydrogen peroxide implies that the treatment process consists of three individual components; UV radiation, ozone gas, and hydrogen peroxide solution. The use of these three components together can destroy a broad range of contaminants. With a wavelength of 254 nm, UV radiation is absorbed by ozone to produce H_2O_2 as intermediate which then decomposes to hydroxyl radicals. At the same time, the hydrogen peroxide is also supplied. Thus the formation rate of powerful hydroxyl radicals is high which then oxidize the organic contaminants. In many cases, conventional ozone or hydrogen peroxide oxidation only does not completely oxidize organics to CO_2 and H_2O. The reactions may produce intermediate products that may be as toxic as or even more toxic than the initial pollutants. However, with a combination of these three components, a very powerful method is produced which allows the fast and complete mineralization of pollutants (Esplugas *et al.*, 2002).

There are numerous advantages of treatment process using ultraviolet light, ozone, and hydrogen peroxide. High molecular weight substances can be transformed into readily biodegradable byproducts which then increase the BOD (Fernando, 2003). The process is able to destruct the pollutants to the final products which are CO_2, H_2O and inert salts. Therefore, the process residuals do not require any additional treatment, as they might in conventional systems. The use of ozone instead of chlorine as an oxidant is safer as ozone is a better disinfectant than chlorine and is not known to produce mutagenic substances (Gottchalk *et al.*, 2001). Besides, storage area is not required since ozone is generated on site. The addition of hydrogen peroxide reduces the size of ozone generator and oxidant amounts thus lower the initial cost for equipment and setup. The combination of these three components overcomes the limitations of individual component.

Despite the long list of advantages, there are still a few limitations and drawbacks of this system. High turbidity, solid particles, and heavy metal ions in the aqueous stream are all interferences that reduce the effectiveness of the treatment. Therefore, the aqueous stream may need pretreatment to remove all these substances.

Since ozone decays rapidly, on site generation of ozone and also UV radiation are necessary and the size of equipments depend on the required production rate. Unfortunately, this system can be expensive due to the equipment needed (ozone generator, UV lamps, photoreactor and ozonation chambers, process control building), and operating and maintenance cost (power requirement, higher skills operator). Ozone levels must be monitored to ensure it not exceeding the regulatory limits as ozone is also an air pollutants.

2.3.2.3 Fe-UV Radiation-Hydrogen Peroxide

This Fe-UV radiation-hydrogen peroxide system is basically known as photo-Fenton oxidation process. The basic of this process is similar to Fenton's oxidation except with an additional feature; the UV radiation. With the presence of light, the production rate of hydroxyl radicals increases due to additional reactions occurs (2.1-2.3):

$$H_2O_2 \xrightarrow{UV} 2^{\bullet}OH \qquad (2.1)$$

$$Fe(OH)^{2+} \xrightarrow{UV} Fe^{2+} + {}^{\bullet}OH \qquad (2.2)$$

$$Fe^{3+}(L^{-}) \xrightarrow{UV} Fe^{2+} + L^{\bullet} \qquad (2.3)$$

where L is organic ligand (Matthew, 2003). In a study of nitrophenols degradation, Goi and Trapido (2002) reported that at the same concentration of hydrogen peroxide, the presence of UV light improved the action of Fenton's system. This is proven by Goi and Trapido, where decomposition of nitrophenols was faster in photo-Fenton than in Fenton's system.

The interesting fact of this system is the ability of UV light to regenerate the ferrous catalyst (reactions 2.2-2.3). Ming *et al.* (2003) concluded that UV light promotes higher degradation efficiency than dark Fenton system but only when the concentration of ferrous ion is low due to its low turbidity. On the other hand, it is not effective at high concentration of pollutants as the ferrous catalyst required for the treatment will be high as well. The addition of UV light can further degrade partial oxidized organic matter by Fenton's system, thus the pollutants can be completely mineralized. Besides, the ferric sludge formed during the treatment can de reduced to ferrous ion and recycled into the system.

2.3.3 Justification of process selection

The advantages and disadvantages of each AOP were summarized in Table 2.3. The comparison conducted by Esplugas *et al.* (2002) for several AOPs (ozone and its combination, photolysis and UV/H_2O_2, Fenton and photocatalysis) reported that Fenton's reagent gave the fastest degradation rate among other methods. Besides, UV based AOPs will be less attractive if the aqueous stream has high turbidity and solid particles. Combination of the report and Table 2.3 shows that Fenton's reagent is the most appealing option for the treatment of organic contaminants and will be discussed further in the next section.

Table 2.3: Comparison of advanced oxidation processes

Advanced Oxidation Process	Advantage(s)	Disadvantage(s)
Ozone/Hydrogen Peroxide (O_3/H_2O_2)	• Oxidation is more reactive and faster in peroxone process than ozone only • More effective in oxidizing refractory organics such as taste and odor compounds. • Halogenated compounds were also reported to be destructible by peroxone process. • Mineralization of organic carbon compounds to readily biodegradable components can be achieved with the right amount of hydrogen peroxide supplied	• Require high initial cost for ozonation equipment. • Generation of ozone also requires high energy and should be generated on-site. • Ozone will decay rapidly and left no residual at high pH and warm temperature. • Operation of ozone requires high level of maintenance and operator skills.
Ozone/Catalyst (O_3/CAT)	• Able to attack target pollutant • Degradation will not be hindered by competitive reactions unlike in case of hydroxyl radicals (Hordern *et al.*, 2003).	• Application in water treatment technology is limited due to the low solubility and stability of ozone in water. • The high cost of ozone production and selective oxidation of organic make it not feasible from economic point of view.
Fenton's Oxidation (Fe^{2+}/H_2O_2)	• Able to convert a wide range of pollutants to nontoxic or biodegradable products.	• Generation of excessive or explosive heat under aggressive conditions.

	• Environmentally benign of reagents do not pose any threat • Abundant amount and nontoxic nature of ferrous catalyst • The cost for the reagents is also relatively low (Matthew, 2003) • Reactor design is less complicated • Residual iron can be removed by alkalization and subsequent precipitation • Ferric sludge can be reduce to ferrous ion and recycle to the system	• Sludge formation during the treatment may need treatment before disposal.

Table 2.3 (continued)

UV Radiation/ Hydrogen Peroxide (UV/ H_2O_2)	• No sludge formation during the treatment. • Can be carried out at under ambient conditions • Oxygen formed this process will be useful for the subsequent treatment (Marechal *et al.,* 1997) if it is to be combined with biological system	• Absorption of UV light will be affected if the wastewater to be treated has high turbidity and solid particles the aqueous. • The aqueous stream may need pretreatment to remove all these substances which will further add to the initial setup and operating cost.
UV Radiation/ Ozone/Hydrogen Peroxide ($UV/O_3/H_2O_2$)	• High molecular weight substances can be transformed into readily biodegradable byproducts thus increase the BOD (Fernando, 2003). • Able to destruct the pollutants to the final products which are CO_2, H_2O and inert salts, thus no further treatment required. • Storage area is not required for the oxidant as ozone must be generated on site.	• High turbidity, solid particles, and heavy metal ions in the aqueous stream will reduce the effectiveness of the treatment. • Aqueous stream may need pretreatment to remove all these substances. • As ozone decays rapidly, on site generation of ozone and also UV radiation are necessary, size of equipments depend on the required production rate. • System may be expensive due to the equipment needed (ozone generator, UV lamps, photoreactor and ozonation chambers, process control building), and operating and maintenance cost (power requirement, higher skills operator). • Ozone levels must be monitored to ensure it not exceeding the regulatory limits as ozone is also an air pollutants.
UV Radiation/ Ferrous Ion/ Hydrogen Peroxide ($UV/Fe^{2+}/H_2O_2$)	• Able to regenerate the ferrous catalyst (Ming *et al.,* 2003). • The ferrous ion is available through out the process. • Less amount of catalyst required. • Able to convert a wide range of pollutants to nontoxic or biodegradable products. • Ferric sludge can be reduce to ferrous ion and recycle to the system.	• Only effective at low concentration of ferrous catalyst • High turbidity, solid particles, and heavy metal ions in the aqueous stream will reduce the effectiveness of the treatment. • Aqueous stream may need pretreatment to remove all these substances.

2.4 Fenton's Reagent: Fundamentals and Applications

2.4.1 Fundamentals

Fenton's reagent is a mixture of ferrous catalyst and hydrogen peroxide which through a series of reactions will oxidize the broad range of organic pollutants. The mechanism of the Fenton's process is reported below (Neyens and Baeyens, 2003; Matthew, 2003).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \tag{2.4}$$

$$RH + {}^{\bullet}OH \rightarrow H_2O + R^{\bullet} \tag{2.5}$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \tag{2.6}$$

Apart from the above reactions, several other reactions also occur simultaneously. Aside from being reagents for generation of hydroxyl radicals, ferrous ions and hydrogen peroxide also act as hydroxyl radicals' scavengers.

$${}^{\bullet}OH + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \tag{2.7}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{2.8}$$

The formed ferric ions will catalyze hydrogen peroxide to decompose into water and oxygen. This reaction is known as Fenton-like reaction. During this, ferrous ions are regenerated back as in reactions (2.6 and 2.10).

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^{+} \tag{2.9}$$

$$Fe-OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \tag{2.10}$$

There are a few factors that directly affect the efficiency of Fenton's oxidation. The major parameters are solution's pH, amount of ferrous ions, concentration of H_2O_2, and initial concentration of pollutants. Temperature however, only showed mild effect to the rates and degradation of the reaction when the reaction was conducted in temperature range of 25 to 75^{o}C (Dutta *et al.*, 2001; Martinez *et al.*, 2003).

2.4.2 Applications

Fenton's oxidation is applied as a pretreatment step by transforming toxic pollutants to byproducts that are more readily biodegradable. In a study by Tekin *et al.* (2006), pretreatment of pharmaceutical wastewater by Fenton's oxidation was found to be effective to improve biodegradability of the waste. The wastewater used was from a drug manufacturing plant producing various disinfectants, tincture of iodines, hydrogen peroxide and antiseptics. With the optimum conditions (initial pH of 3.5, H_2O_2/Fe^{2+} molar ratio of 150, initial COD between 900 to 7,000 mg/L), 45 to 65% COD was removed in Fenton's process and residual COD was removed by sequential batch reactor (SBR). Total of 98% COD removal was achieved by using combination of Fenton's oxidation with SBR system.

Agriculture industry produces large volumes of livestock wastewater which will be a problem to the conventional wastewater treatment system if the strength of the wastewater is high. Heavy contamination of livestock wastewater is characterized by high suspended solids, high COD, high BOD and high nitrogen, which affected the surface water if it is not treated (Shin *et al.*, 2005). A study by Lee and Shoda (2007) using livestock wastewater from Japan revealed that the wastewater was characterized as high COD using chromate (CODcr of 5,000 to 5,700 mg/L), high total solid (5,126 to 5,900 mg/L), pH in the range of 8.4 to 8.7, and the color was dark grey. The treatment of the wastewater by Fenton's reagent has reduced more than 80 percent of CODcr and 95 percent of color with only single addition of reagents under optimal condition.

In textile industry, the reagents used are very diverse in chemical compositions which are not easily amenable by biological treatment. Among the compounds found by GC-MS are 3-methyl-benzoic acid, ethyl ester 4-ethoxy-benzoic acid, and 2,8-dimethyl-4-methylene-nonane (Perez *et al.*, 2002). Treatment of synthetic wastewater in laboratory containing azo dyes was studied by Sun *et al.* (2007) by using Fenton's reagent. Under optimal conditions (pH = 3.50, $[Fe^{2+}]_o:[H_2O_2]_o = 1:10$, $[dye]_o = 50$ mg/L, temperature = 25°C), 99.25 percent degradation efficiency of dye was achieved.

Various types of phenol have been introduced in production since 1860s. Early use of phenol was as an antiseptic. As time moved, new uses of phenol were found in the synthesis of dyes, aspirin and picric acid. Nowadays, phenol is commercially used to make chemical intermediates for broad range of other applications, ranging from plastics to pharmaceuticals and agricultural chemicals. Due to the extensive application of phenols, large volume of wastewater contaminated with high concentration of phenols constantly produced. Treating phenolic wastewater to harmless level is an arduous process for many biological and chemical processes due to its high solubility and stability in water (Keating *et al.*, 1978). As a result, increasing research has focused on the applicability of Fenton's oxidation to completely mineralize the phenol pollutants to harmless products. Goi and Trapido (2002) studied the degradation of seven nitrophenols by comparing of Fenton's oxidation with photo-Fenton and hydrogen peroxide photolysis. From the study, they found that Fenton's oxidation was the best option in terms of degradation efficiency and economic point of view.

In situ remediation of contaminated soil by Fenton's oxidation has been applied at many sites (Matthew, 2003). Typical applications include degradation of light nonaqueous phase liquid (LNAPLs), dense nonaqueous phase liquids (DNAPLs) and some other larger molecules such as energetic compounds. In laboratory, a study was conducted by Ravikumar and Gurol (1994) to investigate the application of Fenton's oxidation to treat contaminated soil. Their study demonstrated that soils contaminated with pentachlorophenol (PCP) and trichloroethylene (TCE) was successfully treated with Fenton' reagent with TCE showed better degradation.

The applications of Fenton's oxidation described previously are only a small part. There are many ongoing researches being conducted to disclose the possibility of Fenton's reagent for treatment of other organic compounds. The evidence of increasing study that is going on, the popularity of Fenton's reagents as the most attractive option for the treatment of recalcitrant pollutants will increase. Based on the comparison of different methods previously, Fenton's oxidation is selected as the treatment method to study its applicability to oxidize diisopropanolamine and reduce the COD of the wastewater.

2.5 Characteristic of Diisopropanolamine as Subject of Research

2.5.1 Fundamentals

Diisopropanolamine (DIPA) is a secondary alkanolamine. Alkanolamines are organic derivatives of ammonia and they are categorized based on the number of substituent groups that attached to the nitrogen atom. In his book, Kirk Othmer (1999) has discussed in detail on the production of DIPA. It has been commercialized over 40 years. In the synthesis of DIPA, propylene oxide (C_3H_6O) is reacted with ammonia (NH_3). Figure 3.1 shows the reaction path for synthesis of DIPA.

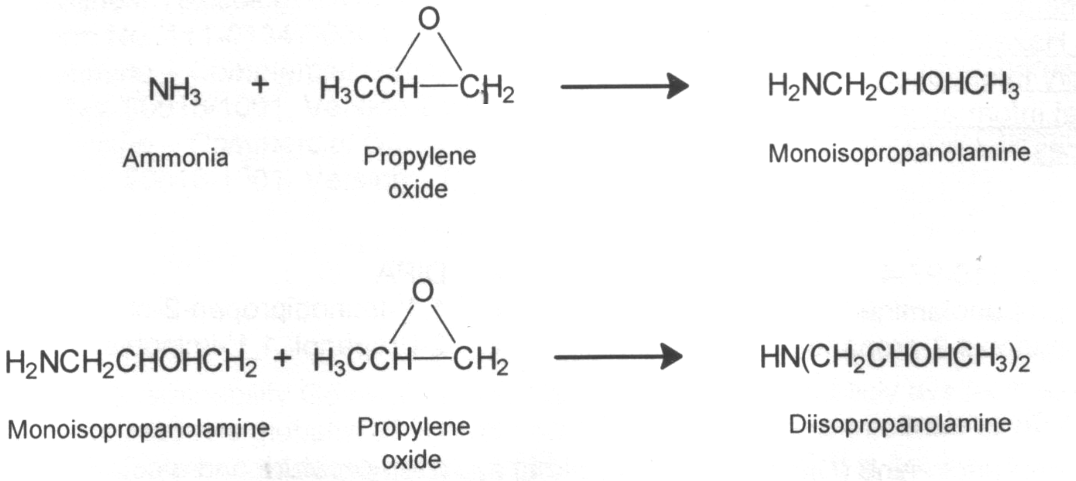


Figure 2.1: Synthesis of Diisopropanolamine

Source: Dow, 2008

2.5.2 Physical and Chemical Properties

DIPA exist as white solid at room temperature and start to melt at temperature 44°C to form colorless liquid. It is very soluble in water and has a mild ammonia-like odor. Detail physical and chemical properties of DIPA are summarized in Table 2.4.

Table 2.4: Physical and Chemical Properties of DIPA

Property	Unit	Value
CAS registry number	-	110-97-4
Molecular formula	-	$C_6H_{15}NO_2$
Molecular weight	g · mol-1	133.19
Melting point	° C	44
Boiling point	° C	249
Specific gravity		
20° C (DIPA) /4° C (Water)	-	1.004
40° C (DIPA) /4° C (Water)	-	0.992
Flashpoint	° C	126
Density at 25° C	$g \cdot cm^{-3}$	0.989
Vapour density (air=1)	$g \cdot L^{-1}$	4.6
Vapour pressure		
42° C	mm Hg	0.02
50° C	mm Hg	0.035
100° C	hPA	3
n-Octanol-water partition coefficient (Kow)	log	0.79
Organic carbon partition coefficient (Koc)	log	21.77
Henry's law constant	$atm \cdot m^{-3} \cdot mol^{-1}$	1.72×10^{-7}
Solubility in water		
25° C	g · L-1	870
Water soil partition coefficient (Kd)		
montmorillonite	L/kg	16-42
kaolinite	L/kg	3.5
humus-rich soil	L/kg	2.0
low carbon content surface soils	L/kg	0.73-4.0
till	L/kg	3.2
sandstone, shale/sandstone	L/kg	0.54-1.1
mean value for nine soils/sediments	L/kg	2.2
pKa	-log K	8.88
Viscosity		
30° C	centipoise	870
54° C	centipoise	86

2.5.3 Application of DIPA

Various industries have applied DIPA in their process either as solvent, raw material, corrosion protection, etc. Due to the physico-chemical properties of DIPA, it has been widely used in gas treating, cosmetic and personal care products, detergents, metalworking fluids, corrosion inhibitors, and cement applications.

2.5.3.1 Gas treating

In 1963, Shell has introduced Sulfinol process to tackle the high concentration of sour gases in natural gas; H_2S and CO_2 in the raw natural gas. The untreated natural gas is passed through a mixture of sulfolane, DIPA or methyldiethanolamine, and water. Sour gases are absorbed physically by sulfolane and chemically by DIPA thus producing sweet natural gas for commercial use.

2.5.3.2 Cosmetics and personal care products

DIPA salts are widely used as raw material for the manufacturing of creams, lotions, shampoos, soaps, and cosmetics due to its high foaming properties and low skin irritation. Furthermore, DIPA is chemically modified to be used as emulsifying agents for cosmetic lotions, bath preparations, and neutralizers in cosmetics. Due to it causticity, DIPA is used directly as acid neutralizer to provide a balanced pH, and also has suitable surfactant properties for hair sprays, hair wave lotions, skin lotions, and moisturizers.

2.5.3.3 Detergents and cleaners

DIPA is used extensively in soaps, cleaning products and detergents as an emulsifying and wetting agent, a foam stabilizer, and a rinse improver (Dow 1999). Alkanolamines (including DIPA) are also used in phosphate-free liquid detergents. In non-enzyme products, they contribute alkalinity, pH control, and enhancement of product stability. In enzyme products, alkanolamines contribute to the stability of the enzyme in water solutions.

2.5.3.4 Metal working fluids

Acidic additives and acidic decomposition products are major factors to the corrosion of metal surface, additionally with the presence of moisture. In this matter, DIPA acts as the neutralizer of acid components in lubricants and to prevent corrosion. It also works in reduction of friction in metal cutting operations, lubrication and foam suppression.

2.5.3.5 Corrosion Inhibitors

Alkanolamines including DIPA work as corrosion inhibitors of ferrous metals. The amines increase the pH thus making the proton reduction less favorable. Alkanolamines are added as corrosion inhibitors in coolant systems, lubricating oils, metal working fluids, hydraulic fluids and drilling systems.

2.5.3.6 Cement applications

DIPA is added in cement admixtures as an accelerator to reduce set time (Kirk-Othmer, 1999; Dow, 1999).

2.5.4 Toxicity and Effects of DIPA in Humans and Mammalians Species

2.5.4.1 Humans

Primary routes of DIPA exposure by human are through skin contacts and inhalation. In 1991, British Industrial Biological Research Association (BIBRA, *as cited by* CCME, 2006) reported their study on the effect of DIPA to human subject. According to the report, skin exposure of pure DIPA or 1% aqueous solution demonstrated variable skin irritation responses. When a sunscreen containing 1% of aqueous solution was applied to 24 human subjects for fifteen times application over 21 day period of study, they concluded that the substance had minimal irritation qualities. However, when 1% of

DIPA in a cream was tested in two other studies, sensitization reaction was observed with repeated application (CCME, 2006).

The material safety data sheet (Chemwatch, 2006) has summarized the potential health effect and toxicology information for DIPA. DIPA is a non-volatile chemical. However, if the vapor is inhaled, the person may feel discomfort to the upper respiratory tract. If the vapor concentration is high, the person may experience chest and nasal irritation with coughing, sneezing, headache and nausea. Exposure of DIPA to eyes is extremely discomforting and the person will experience pain and severe conjunctivitis. Immediate treatment is necessary and if the treatment is delayed, the person may have corneal injury and possible permanent impairment of vision. The study on effect of DIPA to human is limited to skin absorption only. A depth laboratory studies were conducted to animal subjects.

2.5.4.2 Mammalians species

Oral studies of DIPA to test animals were reported by DOW in 1954. From the test, higher dosed of DIPA showed observable effect to the lab rats where significant weight loss, reduction in body fats, organ sizes and weights, and changed of clinical biochemical parameters were observed. Thus, it was concluded that at the highest dose, rats suffered an acute inflammation and degeneration of kidney and urinary bladder (DOW, 1984). However, exposure of DIPA at lower doses showed no observable effect either by skin absorption or oral intake. Dow (1984) concluded that DIPA will be eliminated rapidly and completely in the urine.

CHAPTER 3

METHODOLOGY

3.1 Introduction

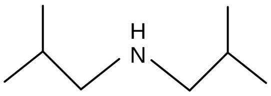
This chapter gives the detail on materials used, experimental and analytical procedure used during the project. The materials and equipments used are tabulated in the next section. Experimental procedure is explained in detail with a flowchart at the end of this chapter. Analysis of degradation products was then conducted by using high precision liquid chromatograph (HPLC).

3.2 Materials and Equipment

Materials

Two types of wastewater samples were used in the research; synthetic and real wastewater. Both samples contain certain amount of DIPA as the organic pollutant. Simulated wastewater was prepared based on the required concentration of DIPA by diluting concentrated DIPA. Meanwhile, real wastewater sample was obtained from a sour gas plant in Malaysia. The chemicals used in this research are summarized in Table 3.1. Meanwhile, Table 3.2 listed the equipments used for characterization and analysis of samples before and after Fenton oxidation.

Table 3.1: Chemicals used in the research work

Chemical Name	**Supplier**	**MW g.mol^{-1}**	**T_m °C**	**T_b °C**	**ρ (T = 25°C) kg.m^{-3}**
Diisopropanolamine (DIPA) 	Merck	133.19	44	249	0.989
Hydrogen Peroxide (H_2O_2) 30% by weight	Merck	34.00	-	-	1.11
Iron (II) Sulfate 7-hydrate ($FeSO_4.7H_2O$) 99.5 – 104.5%	HmBg Chemicals	278.20	-	-	1.04
Sulfuric Acid (H_2SO_4)	Systerm	98.08	-15	330	1.84
NaOH	R & M Chemical	40.00	65	-	1.04
Phosphoric Acid (H_3PO_4)	Merck	98.00	21	158	1.685

Equipments

Table 3.2: Equipments for characterizations and analysis

Parameters/ Characteristic	**Equipment**	**Supplier**
pH	SENSion 4	HACH
COD	DR5000 (method 8000)	HACH
BOD	BODtrak	HACH
TOC	DR5000 (method 10128)	HACH
TN	DR5000 (method 10072)	HACH
TSS/TVS	Oven Muffle furnace Weighing balance	Memmert Stuart Mettler Toledo
Oil and Grease	Oil and grease analyzer	NIC

3.3 Wastewater Preparation

3.3.1 Synthetic Wastewater Sample

Synthetic wastewater sample was prepared on daily basis before experiment. The concentration of synthetic sample was determined based on the required initial COD value. Calibration curve of COD versus volume of DIPA (Fig. A.1, Appendix A) was used to determine the exact volume of concentrated DIPA required. For example, to have a wastewater with 17,000 mg/L COD, the approximate volume of DIPA needed is 9.4 mL for 1 liter of solution.

3.3.2 Real Wastewater Sample

Pretreatment was however imminent for wastewater sample from the sour gas processing plant as it contains high oil and grease (O&G) and total suspended solid (TSS) content. In order to remove the O&G and TSS, a two step separation approach was done. Firstly, removal of O&G was carried out by using a 1-Liter separatory funnel. The funnel was filled up with wastewater and was left for 15 minutes to form two layers; oil floated at the top layer and dark water containing suspended solid settled at the bottom. Then, the water at the bottom layer was drained into tubes for centrifugation. The tubes were then placed in the centrifuge to remove suspended solid at 8,000 rpm for 15 minutes. Finally, the water was filtered by using vacuum pump to get a clear solution. Centrifugation and filtration is required to remove TSS because the solid is very fine and light where it will not settle even with an addition of coagulant. Figure 3.1 below show the wastewater sample before and after the pretreatment steps.

Figure 3.1: **Real wastewater before (left) and after (right) pre-treatment**

3.4 Experimental Procedure

3.4.1 Calculation

Before the experiment can be conducted, it is crucial to know the amount of reagents (H_2O_2 and $FeSO_4.7H_2O$) to be used. The amount of hydrogen peroxide is calculated based on the theoretical oxygen demand (ThOD) required.

$$\text{COD} = \alpha \text{ThOD} \tag{3.1}$$

ThOD is the calculated amount of oxygen which would be required to fully oxidize an organic compound. Meanwhile, α is a constant which assumed to be between 0.95 to 1 (Baker et al., 1999). In this calculation, α is assumed to be 1. Therefore, the amount of ThOD is equal to the COD of the wastewater (Baker et al., 1999). COD is the amount of specified oxidant that reacts with the sample under controlled conditions. Fig. A.1 in Appendix A shows the COD calibration curve for DIPA. The simulated wastewater was prepared based on the approximate initial COD required. Then, the COD value was used in the calculation to obtain the reagents amount. Theoretically, dissociation of one mole of H_2O_2 will produce one mole of oxygen radical as in reaction (3.2).

$$H_2O_2 \rightarrow H_2O + O^{\bullet} \qquad (3.2)$$

Then, the oxygen radical will react with the organic compound (represented by COD value). Based on the amount of initial COD and reaction (3.2), the amount of H_2O_2 required was calculated using equation (3.3) and (3.4). Equation (3.3) is derived base on the premise of equation (3.1). The calculation was detailed in the appendix section (Appendix B).

$$No. of\ \ mole\ of\ \ H_2O_2 = \frac{Initial\ \ COD\,(mg/L)}{Molar\ \ mass\ of\ \ oxygen\ \ radical\ \,(g/mol)} \qquad (3.3)$$

$$Vol. of\ \ H_2O_2\ (30\%) = \frac{No. of\ \ mole\,(mol)\ x\ Mol. weight\ \,(g/mol)}{Density\ (g/ml)\ x\ 0.3} \qquad (3.4)$$

From literature, wide range of optimum H_2O_2/Fe^{2+} was reported. Optimal molar ratio of 329 was reported by Morais and Zamora (2005) in the improvement of biodegradability of landfill leachates. Meanwhile, an investigation by Tang and Tassos (1995) reported a much smaller ratio of 1.9 to 3.7 for maximum degradation efficiency. A similar optimal ratio was also reported by Zhang *et al.* (2005) for landfill leachate with Fenton’s reagent (1.5). Another study by Sun *et al.* (2007) where degradation of azo dye Amido black 10B by Fenton’s oxidation process reported optimal molar ratio of H_2O_2/Fe^{2+} of 20. In 1997, Casero *et al.* studied the oxidation of aromatic amine by Fenton’s reagent and they reported a wider range of optimum molar ratio 5 to 40. Thus, as for initial study, molar ratio of 10 will be used and optimal molar ratio will be determined based on the degradation of target pollutant.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH \qquad (3.4)$$

From reaction (3.4), one mole of Fe^{2+} reacted with one mole of H_2O_2. Since molar ratio of 10 will be used for initial study, the mole of Fe^{2+} will be one tenth of H_2O_2.

$$Mass\ of\ Fe^{2+}\ required = No.\ of\ mole\ (mol)\ x\ Molar\ mass\ (g/mol) \qquad (3.5)$$

Since Fe^{2+} is only available in $FeSO_4.7H_2O$ form, the mass of $FeSO_4.7H_2O$ that contain desired amount of Fe^{2+} must be calculated.

3.4.2 Experimental Set-up

3.4.2.1 Fenton's oxidation process

The work flow of experimental procedure is shown in Fig. 3.2. A stirred jacketed glass reactor was used to monitor the progress of the reaction. The experimental setup for the research is shown in Fig. 3.3. The figure is based on the continuous dosing method.

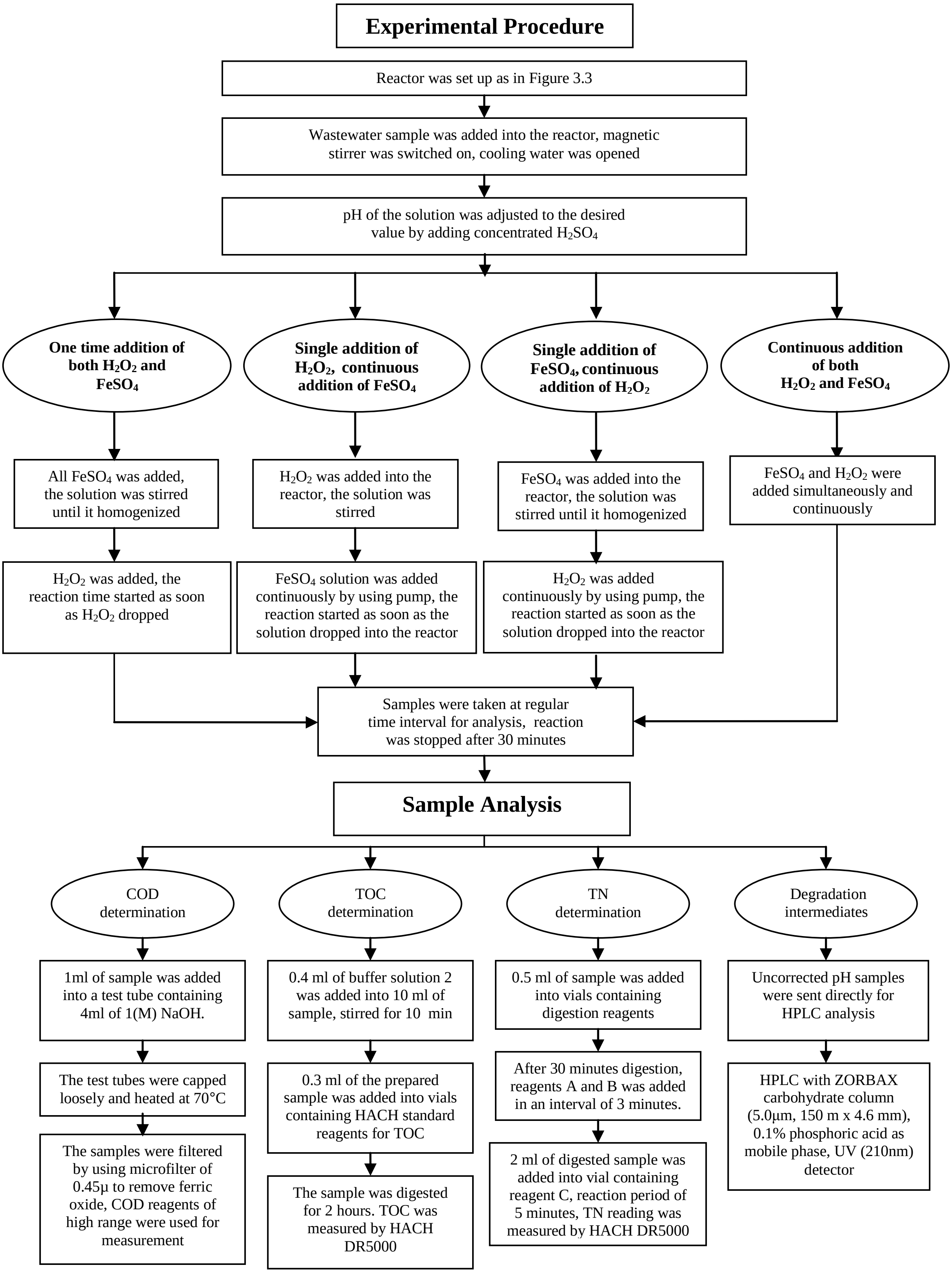


Figure 3.2: **Flowchart of the research work**

The synthetic sample was prepared based on the desired initial COD meanwhile the real sour gas plant wastewater was pretreated before use. The samples were placed in the jacketed glass reactor and pH was adjusted to the desired value by using concentrated H_2SO_4 and 1(M) NaOH. Reagents were added based on the mode of dosing that was studied:

- single addition of both reagents;
- single addition of Fe^{2+} ion, continuous addition of H_2O_2;
- single addition of H_2O_2, continuous addition of Fe^{2+} ion;
- continuous addition of both reagents.

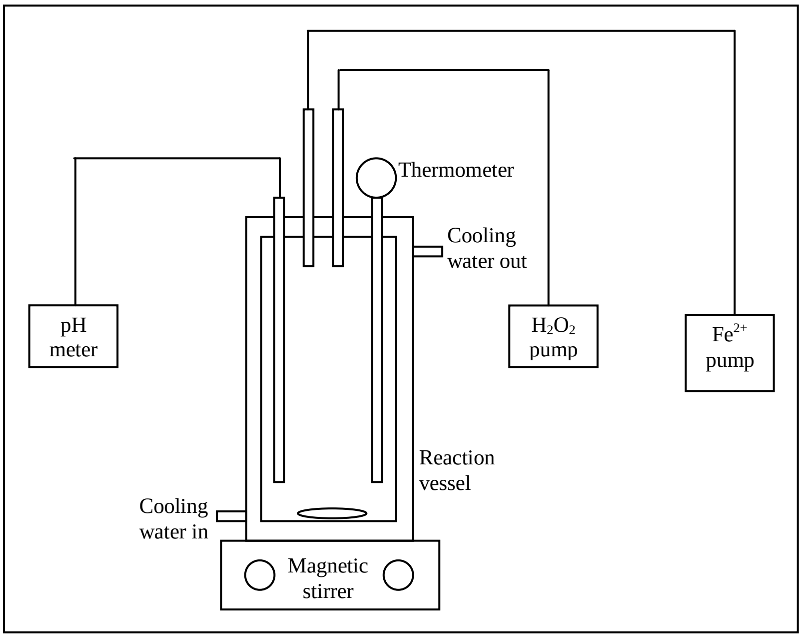


Figure 3.3: Schematic diagram of experimental setup

One mililiter of sample was taken and placed in a test tube containing 4 mL of 1(M) NaOH. This step was repeated for all samples. Unreacted hydrogen peroxide in the Fenton's oxidation interferes with COD measurement. Therefore, the alkaline was added into the samples to increase the pH to 10 so that hydrogen peroxide became unstable thus decompose into oxygen and water. Besides, precipitate of ferric hydroxide ($Fe(OH)_3$) can also be obtained at this pH (Walling and Goosen, 1973). The solution was then filtered by using syringe microfilter to remove the precipitate. In order to further ensure that no interference of H_2O_2 to the COD measurement taken place, the test tubes containing samples were heated in the hot water at 70ºC for 30 minutes to remove residual H_2O_2 (Lou and Lee, 1995; Jones, 1999; Kavitha and Palanivelu, 2005) as the peroxide is also unstable at temperature higher than 40ºC. After 30 minutes and there was no bubbles observed in the samples, the samples were left to cool off to room temperature.

3.4.2.2 Preparation of Fe^{2+} ion solution

The concentration of Fe^{2+} ion was calculated based on equation (3.5). Since the Fe^{2+} ion was available in the form of ferrous sulfate, the amount of ferrous sulfate that contains desired concentration of Fe^{2+} was weighed. Then, the ferrous sulfate was poured in a beaker containing magnetic stir bar. Deionized water was used to make the solution of Fe^{2+} ion to avoid any interference of other ions. The Fe^{2+} ion solution was stirred for 15 minutes or until the entire solid dissolved.

3.4.2.3 Reagents dosing methods

One time addition of both reagents

Sample was placed in the jacketed reactor. The pH of the solution was adjusted to the desired initial value by using concentrated sulfuric acid. Then, the ferrous sulfate powder that was previously weighed was added into the reactor and stirred with magnetic stirrer. The solution was stirred until the entire ferrous sulfate dissolved. Once all the catalyst dissolved and the pH was at the desired value, hydrogen peroxide was added into the reactor in one shot and reaction time was started. Samples were taken at regular interval to monitor the degradation process.

One time addition of Fe^{2+} ion, continuous addition of H_2O_2

Sample was placed in the jacketed reactor. The pH of the solution was adjusted to the desired initial value by using concentrated sulfuric acid. Then, the ferrous sulfate powder that was previously weighed was added into the reactor and stirred with magnetic stirrer. The solution was stirred until the entire ferrous sulfate dissolved. Once all the catalyst dissolved and the pH was at the desired value, hydrogen peroxide was added slowly and continuously by using pump into the reactor and reaction time was started. The flowrate of H_2O_2 depends on total volume of it required for degradation divided by 28 minutes as total reaction time would be 30 minutes. The two minutes reaction was allowed after reagents was fully added to make sure the last portion of reagents has ample time to react with organic compound. If the reaction time is prolonged, the flowrate will be lower. Samples were taken at regular interval to monitor the degradation process.

One time addition of H_2O_2, continuous addition of Fe^{2+} ion

Sample was placed in the jacketed reactor. The pH of the solution was adjusted to the desired initial value by using concentrated sulfuric acid. In the meantime, solution of Fe^{2+} ion was prepared as previously described. Once the pH was at the desired value, hydrogen peroxide was added into the reactor all in one shot. Then, solution of Fe^{2+} ion was added slowly and continuously by using pump and reaction time was started. The flowrate of Fe^{2+} ion solution depends on total volume prepared for the required concentration for degradation divided by 28 minutes. Samples were taken at regular interval to monitor the degradation process.

Continuous addition of Fe^{2+} ion and H_2O_2

Sample was placed in the jacketed reactor. The pH of the solution was adjusted to the desired initial value by using concentrated sulfuric acid. In the meantime, solution of Fe^{2+} ion was prepared as previously described. Once the pH was at the desired value, both hydrogen peroxide and solution of Fe^{2+} ion was added slowly and continuously by using two separate pump and reaction time was started. The flowrate of reagents depends on total volume of the required concentration for degradation divided by 28 minutes. Samples were taken at regular interval to monitor the degradation process.

3.4.3 Sample Analysis

3.4.3.1 Chemical oxygen demand (COD) determination

The degradation of samples was monitored based on the residual COD. Measurement of COD was carried using HACH analytical equipment Method 8000 that was approved by Standard Method for Wastewater Analysis, USEPA. 2 mL of the samples were oxidized by using standard chemicals from HACH. The vials containing the standard chemicals and samples were heated at 150°C for two hours by using HACH DRB200 digester. Once the digestion finished, the vials were allowed to cool down to room temperature for about 30 minutes. The COD reading was then obtained from HACH DR5000 spectrophotometer with the measurement range was 0 – 1,500 mg/L O_2. The degradation efficiency was calculated based on the percentage removal of COD from the samples (Eq. (3.6)).

$$COD_{removal(\%)} = \frac{COD_0 - COD_t}{COD_0} \, x \, 100 \tag{3.6}$$

where,

$COD_{removal(\%)}$ = percentage of COD removed

COD_0 = initial COD of the sample

COD_t = COD of the sample after t minutes reaction

3.4.3.2 *Total organic carbon (TOC) determination*

Measurement of TOC was conducted by using HACH analytical equipment Method 10128 that was approved by Standard Method for Wastewater Analysis, USEPA. The range for TOC measurement was 100 – 700 mg/L C. This analysis was conducted to compare the TOC profile with COD profile. The sample was firstly prepared by adding buffer solution of pH 2.0 and stirred for 10 minutes. Then, 0.3 mL of the prepared sample was digested by using standard reagents at 105°C for two hours on HACH DRB200 digester. Then, the TOC reading was obtained by HACH DR5000 spectrophotometer. The percentage of TOC reduction was calculated by:

$$TOC_{removal(\%)} = \frac{TOC_0 - TOC_t}{TOC_0} \, x \, 100 \tag{3.7}$$

where,

$TOC_{removal(\%)}$ = percentage of TOC removed

TOC_0 = initial TOC of the sample

TOC_t = TOC of the sample after t minutes reaction

3.4.3.3 *Total nitrogen (TN) determination*

TN was measured to compare the profile with TOC and COD profile of the sample. It was measured by HACH analytical equipment Method 10072 that was approved by Standard Method for Wastewater Analysis, USEPA. The range for TN measurement was 0 – 150 mg/L N. Half mililiter of sample was added into vial containing standard digestion reagents and heated for 30 minutes at 105°C. Once the digestion finished and the vial cooled to room temperature, reagent A powder pillow was added into the vial and it was allowed for a three-minute reaction period. After the timed expired, reagent B powder pillow was added, and the vial was shaken. Another two-minute reaction period started. As the time expired, 2 mL of the digested sample was taken and added into another vial (reagent C). After shaking, a five-minute reaction period began. Finally, the TN reading was obtained by using HACH DR5000 spectrophotometer. The percentage reduction of TN in the sample was calculated by:

$$TN_{removal(\%)} = \frac{TN_0 - TN_t}{TN_0} x 100 \tag{3.8}$$

where,

$TN_{removal(\%)}$ = percentage of TN removed

TN_0 = initial TN of the sample

TN_t = TN of the sample after t minutes reaction

3.4.3.4 *Determination of degradation intermediates*

Degradation intermediates were analyzed by using high precision liquid chromatography (HPLC) from Agilent model 1100. ZORBAX carbohydrate column (5.0 µm, 150 m x 4.6 mm) was used with 0.1% phosphoric acid as mobile phase and UV (210 nm) detector. The flow rate of the mobile phase was 0.5 mL/min. The unknown peaks of partially degraded sample were compared to the standard peaks based on the retention time. Standard acetic acid, formic acid, oxalic acid, and glycine were used for identification of the intermediates.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The following chapter details the results and findings for each factor that affect the degradation efficiency of DIPA in synthetic and industrial wastewater samples. Then, the degradation intermediates of DIPA were identified by HPLC. In general, the applicability of Fenton oxidation process to degrade DIPA has been proven. The degradation efficiency was quantified based on the percentage of COD reduction in the studied samples. Optimal parameters were investigated to minimize the cost and optimize the degradation of DIPA. Two types of samples were used whereas both contain DIPA, the target pollutant of this research.

4.2 Fenton Oxidation for Synthetic Waste of DIPA

Initial study for the applicability of Fenton's reagents to oxidize DIPA was conducted by using synthetic wastewater sample. This step was taken to ensure that the intermediates produced were due to the degradation of DIPA. Later, the intermediates formed were analyzed by HPLC to identify the compounds.

4.2.1 Effect of Initial pH

Fenton's oxidation is highly pH dependent process since pH controls the production rate of hydroxyl radicals and concentration of ferrous ions (Jian *et al.*, 2007;

Solozhenko *et al.*, 1995). Therefore, the optimal pH for the oxidation of DIPA was investigated by varying the pH of the solution while maintaining other experimental parameters. In 1975, Walling has reported the overall Fenton chemistry as in reaction (4.1) by accounting for the dissociation of water. Reaction (4.1) suggests that the acidic environment is needed in order to decompose hydrogen peroxide by the presence of H^+ in the equation.

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow Fe^{3+} + 2H_2O \qquad (4.1)$$

Previous study on the application of Fenton's oxidation to degrade various organic pollutants reported that the optimal pH range was between 2.5 to 4.5 (Lee and Shoda, 2007; Jian *et al.*, 2007; Badawy *et al.*, 2005; Azbar *et al.*, 2004; Neyens and Baeyens, 2003). Thus, a series of experiment were conducted at different pH values of 1, 2, 3, 4, and 5. Other parameters were kept constant with initial concentration of DIPA used was 5000 ppmv which equals to approximately 8,500 mg/L COD, the amount of ferrous sulfate and hydrogen peroxide used was 36 g/L and 33 mL/L respectively (where the molar ratio of H_2O_2/Fe^{2+} is 2) and the experiment was carried at ambient temperature and pressure. The reagents were added simultaneously at the beginning of the reaction.

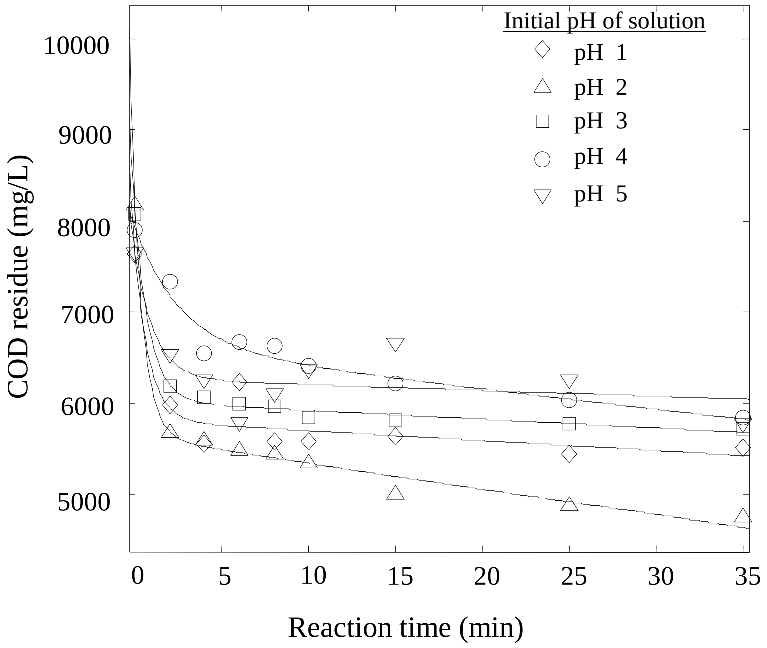


Figure 4.1: **Effect of initial pH to the degradation process**

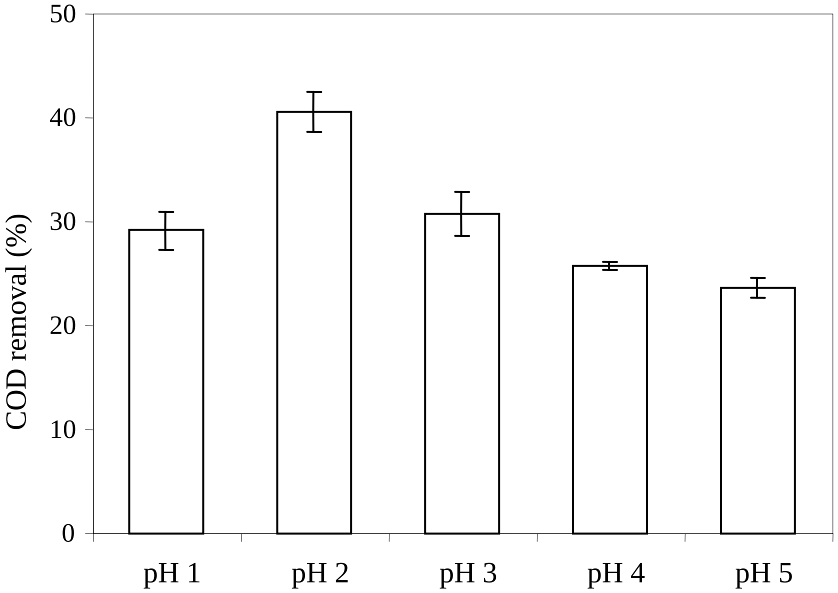


Figure 4.2: **Comparison of initial pH to the percentage of COD removal**

During the reaction, the initial pH of the sample decreased from the pH that was set initially. The formation of carboxylic acids such as acetic acid, oxalic acid and formic acid (Burbano *et al.*, 2005) may be the reason behind this which will be discussed later in this chapter.

From Fig. 4.1, the same trend of degradation profile can be observed at different pH. This is due to the fact that the reaction occurred very fast initially. As the reaction continued, the degradation started to stabilize. In this study, optimum degradation was achieved at pH 2 and it started to reduce at both lower and higher pH value (Fig. 4.2). The explanation behind this phenomena was that at low pH value (<2), the reaction was slowed down due to the high concentration of H^+ ion which reacted with hydrogen peroxide to form oxonium ion $[H_3O_2]^+$ (Kwon *et al.*, 1999) as in reaction (4.2). This oxonium ion makes hydrogen peroxide electrophilic which enhancing its stability thus reducing the reactivity with ferrous ions (Jian *et al.*, 2007). Furthermore, the formation of complex species $[Fe(H_2O_2)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ also slowed down the generation of $^{\bullet}OH$ radicals (Tekin *et al.*, 2006; Sun *et al.*, 2007).

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \qquad (4.2)$$

On the other hand, when high value of initial pH (>4) was used, the treatment efficiency decreased due to the formation of ferric-hydroxo complexes (Kuo, 1992) which deactivated the ferrous catalyst supplied to the system leading to the reduction of $^{\cdot}OH$ radicals generation. Besides, at this pH value, hydrogen peroxide as the oxidant decomposed into oxygen and water instead of hydroxyl radicals. The optimal pH value obtained from this set of experiment was then used in the following study.

In several studies of Fenton oxidation, they conducted the experiment in 30 minutes reaction (Rivas et al., 2001; Harimurti et al., 2009; Gotvajn and Zagorc-Koncan, 2005; Arslan-Alaton et al., 2008) Therefore, these experiments were started with reaction time of 35 minutes (5 minutes longer to observe any difference). From Fig. 4.1, the COD reduction started to level off at 5-minute reaction time except for the condition of pH 2 and pH 4. Even though the COD reduction continued for these pH values, the reduction was insignificant and did not contribute to the COD percentage removal. Therefore, for the next experiments, all reactions were stopped at 30 minutes of reaction since there was no observable difference.

4.2.2 Effect of Reagents' Dosing Method

In Fenton system, several reactions occurred simultaneously during the oxidation. Reaction (4.3) is the main reaction which produces $^{\cdot}OH$ radicals. Meanwhile, at the same time, reaction (4.4) and (4.5) (known as scavenging reactions) also occurred. These reactions may reduce the concentration of $^{\cdot}OH$ radicals in the reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH \qquad k_2 = 63 - 73\ M^{-1}S^{-1} \qquad (4.3)$$

$$^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} \qquad k_3 = 4.3 \times 10^{8}\ M^{-1}S^{-1} \qquad (4.4)$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + H_2O^{\bullet} \qquad k_4 = (1.2 - 4.5) \times 10^{7}\ M^{-1}S^{-1} \qquad (4.5)$$

Therefore, in order to minimize the side reactions while maximizing the treatment efficiency, an investigation was conducted to find the best way to add reagents into the system. Initial concentration of DIPA used was 5000 ppmv which equals to approximately 8,500 mg/L COD, the amount of ferrous sulfate and hydrogen peroxide used was 36 g/L and 33 mL/L respectively (where the H_2O_2/Fe^{2+} molar ratio is 2), the initial pH of the solution was 2 and the experiment was carried at ambient temperature and pressure. The reagents were added in four different ways as defined in Fig. 4.3.

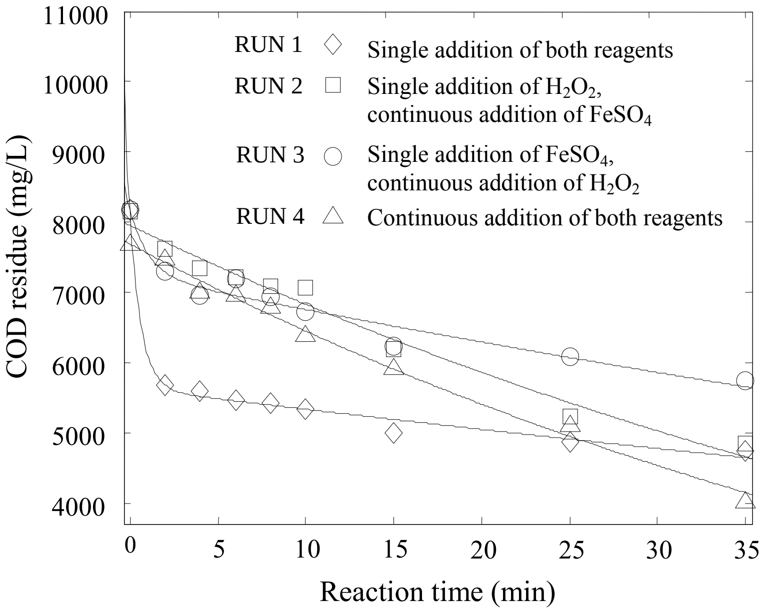


Figure 4.3: **Effect of reagents' dosing method to the degradation process**

In Run 1, the reagents were added in one shot at the beginning of the reaction. As shown in Fig. 4.3, the degradation was very fast during the first few minutes and then it started to stabilize till the completion of the reaction. A nearly similar degradation profile can be observed in Run 3. Meanwhile, in Run 2 and 4, the degradation kept going as the reagents were added continuously through the reaction.

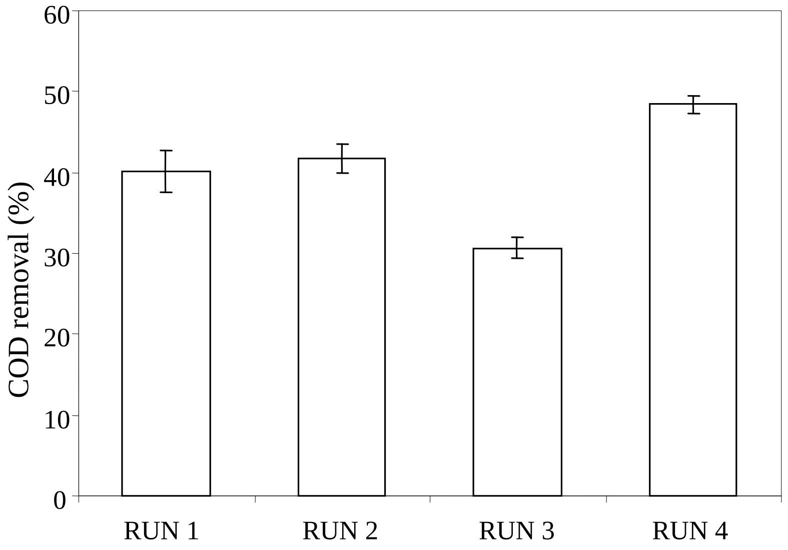


Figure 4.4: **Comparison between different ways of reagents' dosing method**

Fig. 4.4 summarizes the percentage COD removal for all runs. In Run 2 and 3, where one of the reagents was added at the beginning and the other reagent was added continuously, the degradation for Run 3 was the lowest. In this run, the ferrous catalyst presented in excess as it was added all at the beginning. From reactions (4.4) and (4.5), the reaction constant for the ferrous ion as scavenger was ten times higher than hydrogen peroxide. Therefore, when ferrous ions present in excess, it scavenged the generated OH radicals.

In Run 4, the concentrations of both reagents were controlled by adding both continuously. With this method, the possibility of reactions (4.4) and (4.5) to occur was reduced by supplying enough reagents to generate OH radicals only through reaction (4.3). As suggested by Casero *et al.* (1997) in their report, adding peroxide slowly would minimize the side reaction. By using this approach, conversion of hydroxyl radical ($HO^\bullet$) to the much less reactive hydroperoxyl ($HO_2^\bullet$) is diminished. Therefore, effectiveness of hydroxyl radical utilization is increased. Efficiency of continuous addition of hydrogen peroxide was also reported by Yalfani *et al.* (2009). They compared the efficiency of Fenton's reagent for the degradation of phenol with different mode of hydrogen peroxide addition. Continuous addition of hydrogen peroxide showed better removal compared to batchwise process. This report is inline with the kinetic modeling simulation developed by Duesterberg and Waite (2006).

They also reported a remarkable improvement of formic acid oxidation in continuous addition of reagent. Zhang *et al.* (2005) agreed that adding both reagents (H_2O_2 and Fe^{2+}) in multiple steps showed better degradation efficiency compared to single steps. From this observation, the highest COD removal was obtained in Run 4. Based on the result obtained in this set of experiments, the experiments for the next set were conducted by using continuous addition of both reagents.

Although it was stated earlier that the experiments will be stopped at 30 minutes of reaction, there was exception for this set of study. In order to determine the effect of reagents' mode of addition, the reaction was stopped at 35 minutes. For single addition of reagents, the COD reduction was level off after 2 minutes. On the other hand, in continuous addition of reagents, the COD reduction seems not to level off. However, the COD reduction was also insignificant to the COD percentage removal. The reagents were added completely into the reactor within 28 minutes of reaction. An extra of 7 minutes allowed the reaction of the reagents as well as OH radicals with the substrate (Kitis et al., 1999). It is to believe that the allowed reaction time was ample enough for the reaction because according to Kitis et al. (1999), reactions of Fenton's reagent were completed within 1 minute after the oxidant dosing due to the very fast consumption of ferrous ion by hydrogen peroxide upon dosing (< 1 minute). The formations of carboxylic acids which are refractory to OH radicals inhibit the COD reduction (Buxton et al., 1988).

4.2.3 Effect of Ferrous Ion Concentration

Ferrous ion is one of the main factors that directly affect the degradation of organic compounds in Fenton's oxidation. The right concentration of ferrous catalyst supplied to the system is very important because the production of OH radicals highly depends on it. The effect of ferrous sulfate concentration on COD removals was studied by changing the amount of ferrous sulfate added into the system while keeping other parameters constant. In this part, initial concentration of DIPA used was 5000 ppmv (approximately 8,500 mg/L COD), hydrogen peroxide used was 108 mL/L, the initial pH of the solution was 2 and the experiment was carried at ambient temperature and pressure. The reagents were added continuously for all experiments.

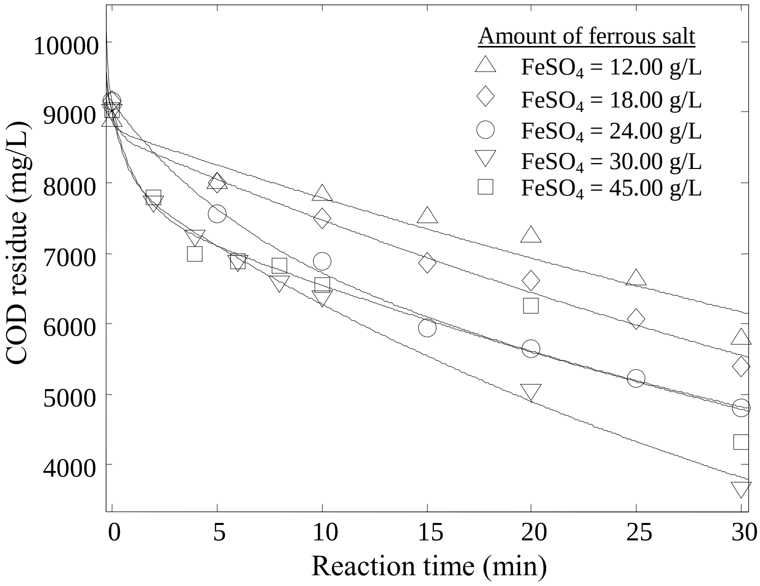


Figure 4.5: **Effect of ferrous sulfate concentration to the degradation**

Fig. 4.5 shows the degradation profile for all experiments in this set. The effect of ferrous ion concentration was summarized in Fig. 4.6 where five different amount of ferrous sulfate was used. At the lowest concentration (12.00 g/L of $FeSO_4$), the COD removal was at the lowest. Lowest amount of $FeSO_4$ means not enough ferrous ions were supplied to generate OH radicals. As the amount of $FeSO_4$ was increased, the COD removal increased.

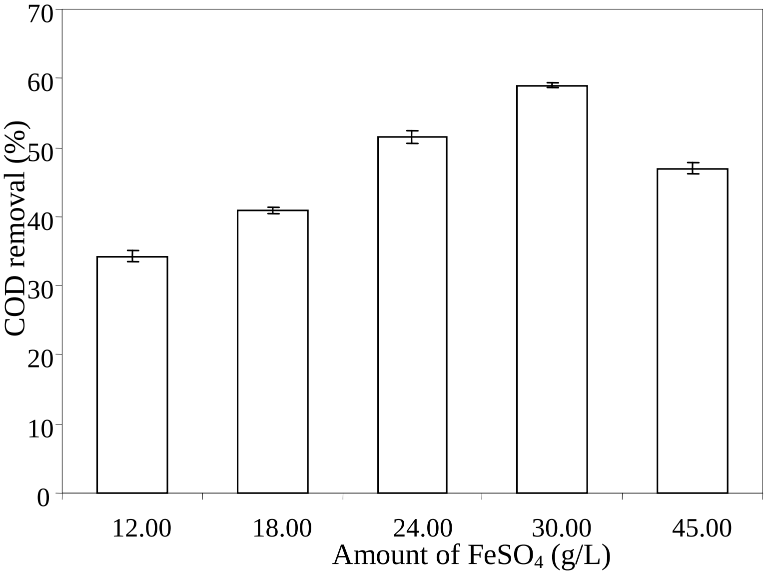


Figure 4.6: **Comparison of different ferrous sulfate concentration**

The removal of COD was at the highest (60 %) when 30.00 g/L $FeSO_4$ was added into the system. On the other hand, when the amount of $FeSO_4$ was increased further, the percentage removal of COD decreased. The explanation behind this observation was due to the scavenging effect of ferrous ion as in reaction (4.4). The $^{\bullet}OH$ radicals reacted with ferrous ions instead of attacking the organic compounds. Hence, the optimum amount of $FeSO_4$ for the degradation would be at 30.00 g/L.

4.2.4 Effect of Hydrogen Peroxide Concentration

Besides ferrous sulfate concentration, hydrogen peroxide amount is another main factor that directly affects the degradation of organic compounds by Fenton's oxidation. As previously described, hydrogen peroxide is the supplier of hydroxyl radicals that attack the organics. Thus, the optimal amount of hydrogen peroxide is very important to ensure the treatment is efficient. Effect of hydrogen peroxide to the degradation efficiency was studied by varying that amount in the experiment. The initial concentration of DIPA used was 5000 ppmv which equals to approximately 8,500 mg/L COD, ferrous sulfate used was 30.00 g/L, the initial pH of the solution was 2 and the experiment was carried at ambient temperature and pressure. The reagents were added continuously for all experiments. The results obtained were presented in Fig. 4.7 and 4.8.

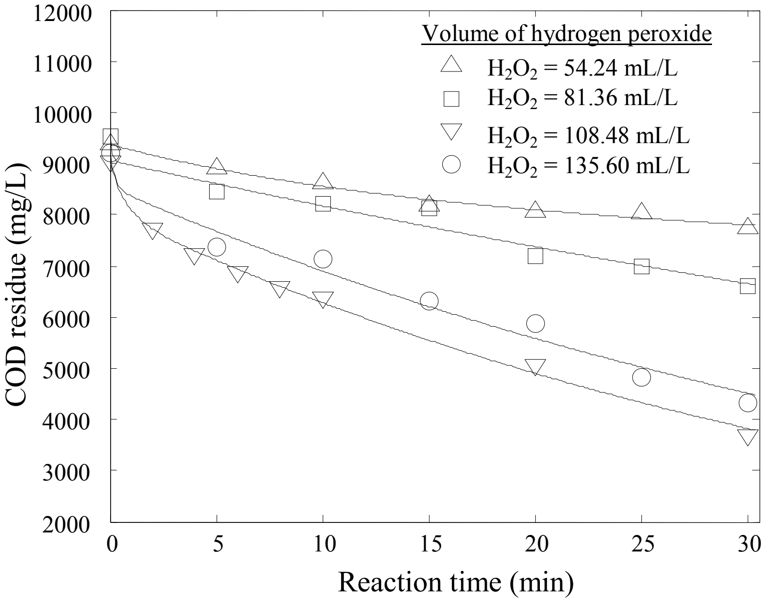


Figure 4.7: **Effect of hydrogen peroxide concentration to the degradation**

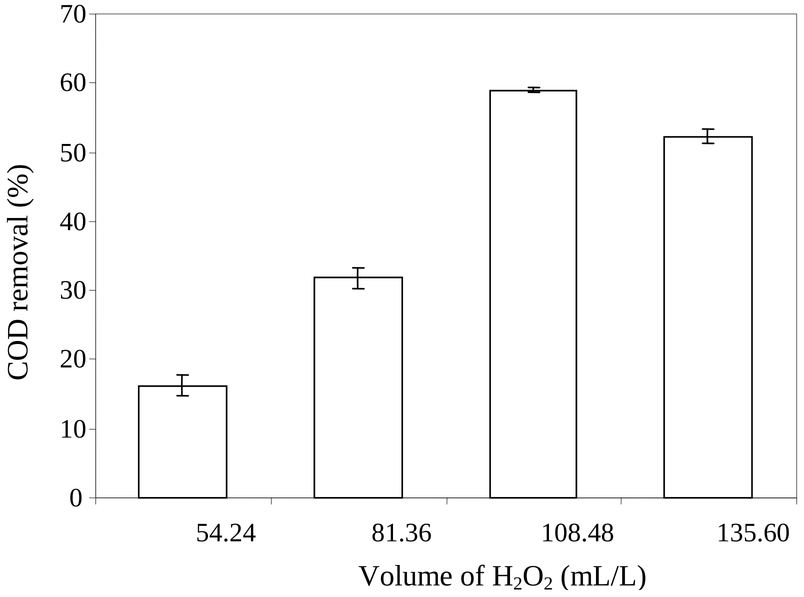


Figure 4.8: **Comparison of different hydrogen peroxide concentration**

The study on the effect of H_2O_2 concentration was started at the theoretical amount of peroxide required. Based one the calculation in Appendix B, for 8,500 mg/L of COD, 54.24 mL/L of H_2O_2 is required to completely mineralize DIPA to CO_2 and H_2O. Unfortunately, from Fig 4.7 and 4.8, even with that amount of peroxide, only 16 percent of COD removal was achieved. The COD percentage removal increased when the amount of peroxide used was doubled the theoretical amount. Sixty percent of COD removal was achieved with 108.48 mL/L. This result is in conclusion with the report by Zazo et al. (2009) where complete mineralization of phenol to CO_2 and H_2O requires hydrogen peroxide of 10 times the theoretical stoichiometric amount. In a report by Masomboon et al. (2009), only 35 percent of COD removal was achieved when theoretical amount of hydrogen peroxide was used. The supplied H_2O_2 may be used not only to degrade the target substrate, but also involve in scavenging reaction and reaction with the intermediates. The removal efficiency increased with the increasing of peroxide and highest removal was achieved at 4 times the theoretical amount. However, when doses of H_2O_2 were increased more than 108.48 mL/L, the COD removals started to decrease. The formation of much less powerful $^{\bullet}OH_2$ radicals which formed by the reaction between $^{\bullet}OH$ radicals and excess hydrogen peroxide was the reason behind this observation. Consequently, the COD percentage removal decreased.

4.2.5 Effect of Initial Concentration of DIPA

The amount of organic compounds in the wastewater plays a major role in the treatment efficiency by Fenton's oxidation. The effect of initial DIPA concentration on the COD percentage removal by Fenton's oxidation was studied by varying initial concentration of DIPA while maintaining the optimum ratio between DIPA, ferrous sulfate and hydrogen peroxide obtained from earlier study. The optimal molar ratio of H_2O_2/Fe^{2+} was 8 with initial concentration of DIPA at 5000 ppmv. Therefore, the amount of reagents were increased accordingly with the increased of DIPA concentration. Other experimental conditions were maintained as initial pH of 2 at ambient temperature and pressure. Both reagents were added continuously.

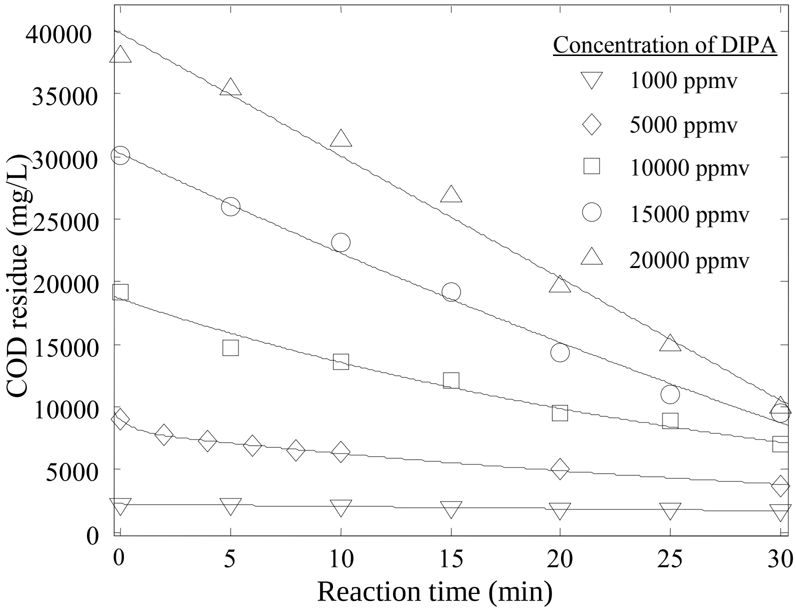


Figure 4.9: **Effect of initial concentration of DIPA to the degradation**

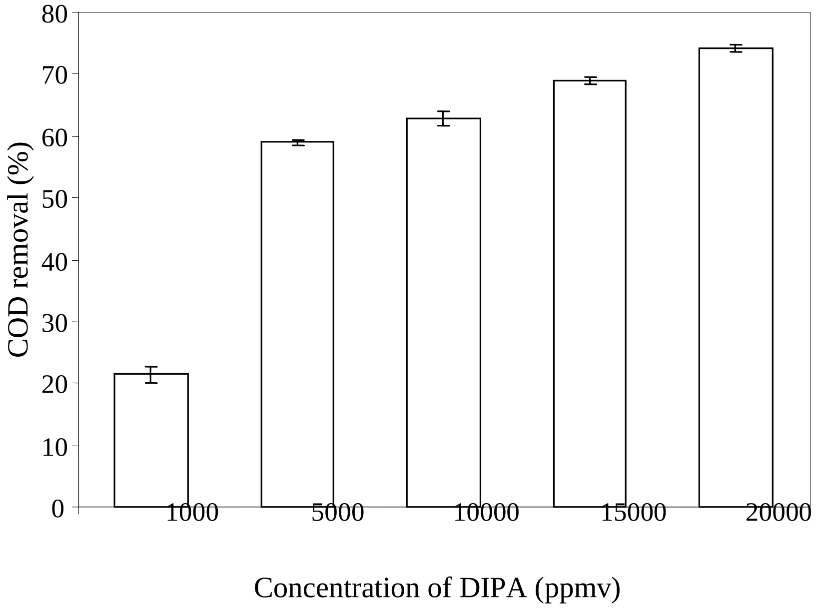


Figure 4.10: **Comparison between different concentrations of DIPA**

Fig. 4.9 and 4.10 show the residual COD and percentage COD removal respectively with respect to the variation of initial concentration of DIPA. The results indicate that increasing the initial DIPA concentration improved the COD removal. The COD reduction was significant at higher amine concentration with highest COD removal (74%) was achieved at the highest DIPA initial concentration. At high concentration, the amount of DIPA reacted with hydroxyl radicals increased which resulted in higher degradation of COD. Therefore, this results shows that Fenton’s oxidation is effective for high concentration of amine.

4.2.6 TOC and TN profile

DIPA ($C_6H_{15}NO_2$) contains carbon and nitrogen bonds which will break down during the degradation. The atoms will later form a smaller molecule compounds which either changes into gas or stay in the wastewater. Complete mineralization of organic compounds means the end products are CO_2 and H_2O. Incomplete mineralization means smaller organic compounds are formed. Chemical oxygen demand (COD) is the measurement of the amount of oxygen required for chemical oxidation of pollutant.

The amount of organic compounds is indirectly measured by COD. By knowing the initial COD of the wastewater, the amount of oxidant required in the oxidation process can be calculated. DIPA is an organic solvent produced from a combination of carbon, oxygen and nitrogen. The oxidation process is believed to be able to degrade this compound to several shorter substances which are more biodegradable. Total organic carbon (TOC) measures the amount of organic carbon bound in an organic compound. Meanwhile, total nitrogen (TN) measures all forms of nitrogen found in the water samples. By knowing the COD, TOC and TN profiles during the oxidation process, the fate of the organic compound can be determined. The percentage of degradation can also be calculated. Fig. 4.11 shows the COD profile of DIPA meanwhile the total organic carbon (TOC) and total nitrogen (TN) profile of DIPA during the degradation process is showed in Fig. 4.12.

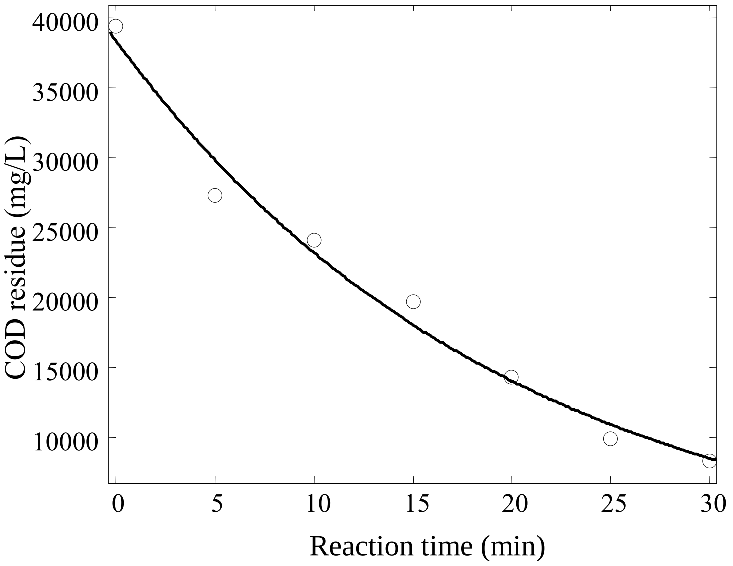


Figure 4.11: COD profile of DIPA during degradation by Fenton's oxidation

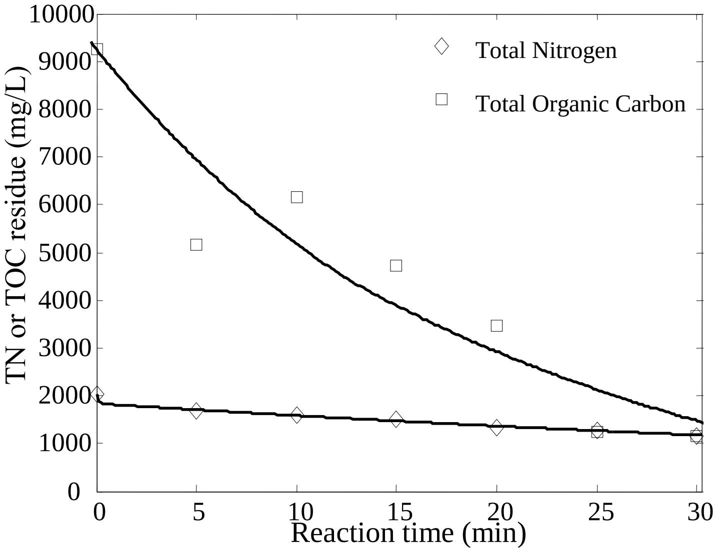


Figure 4.12: **TOC and TN profile of DIPA during degradation by Fenton's oxidation**

The Fenton's treatment of DIPA was carried at optimal conditions. High concentration of synthetic wastewater was used (20,000 ppmv of DIPA) which approximately equal to 39,000 mg/L COD. Theoretically, the initial TOC in the solution would be approximately 10,000 mg/L C. However, the measurement by spectrophotometer was 9,360 mg/L C which give a percentage difference of 6.4%. Similar result was obtained from the measurement of TN by which the actual value recorded was 2,040 mg/L N whereby theoretically the solution contains 2,079 mg/L N, a difference between two values of 1.88%. A small percentage difference in both TOC and TN may be due to measurement error.

The TOC profile in Fig. 4.12 shows nearly linear reduction of carbon in the solution (approximately 75% carbon loss). The carbon may be converted into CO_2 and released to the air during the degradation. Meanwhile, the residual carbon was converted to other smaller compounds such as carboxylic acids and other carbon based compounds. On the other hand, only 43% of TN loss during the degradation meanwhile another 57% remains in the solution but was converted to other nitrogen based compounds such as glycine, nitrate or nitrite. Nitrogen loss was lower compared to carbon loss due to the difference in bond strength between carbon-carbon (C-C) and carbon-nitrogen (C-N). The C-C bond strength is 145 kcal/mole while it is 184 kcal/mole for C-N bond (Brown *et al.*, 2000). Thus, the breakage of

C-C bond is easier compared to C-N. The nitrogen loss during the oxidation suggests the formation of nitrogen and ammonia gas (Guinea *et al*., 2009). However, since the volume of the reactor was small (1 Liter) and the experiment was carried in a fume hood, the smell of ammonia gas was not detected. A further research would be required in order to identify each of the intermediates and products formed.

4.2.7 Analysis of Degradation Intermediates

Formation of degradation intermediates during Fenton's oxidation is analyzed by using High Precision Liquid Chromatography (HPLC). For this analysis, an experiment was conducted at optimum condition of 20,000 ppmv of DIPA with initial pH value of 2, and Fenton's reagents amount is 120g/L of $FeSO_4$ and 433.92mL/L of H_2O_2 (H_2O_2/Fe^{2+} molar ratio of 8). Analysis of synthetic wastewater showed that degradation of DIPA was completed after Fenton oxidation (Fig. 4.13). The DIPA compound (r_t = 2.794 min) in the synthetic sample was fully degraded after the reaction. The intermediates formed during degradation are expected to be carboxylic acids. The reaction mechanism was suggested by Smit *et al.*(2002) as in Fig. 4.14.

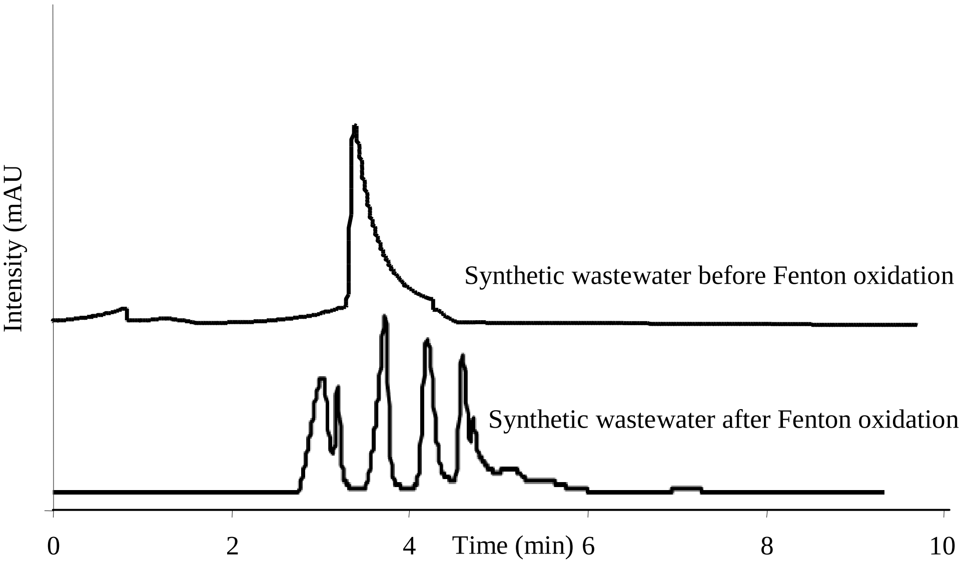


Figure 4.13 : **Analysis of synthetic wastewater before and after Fenton oxidation**

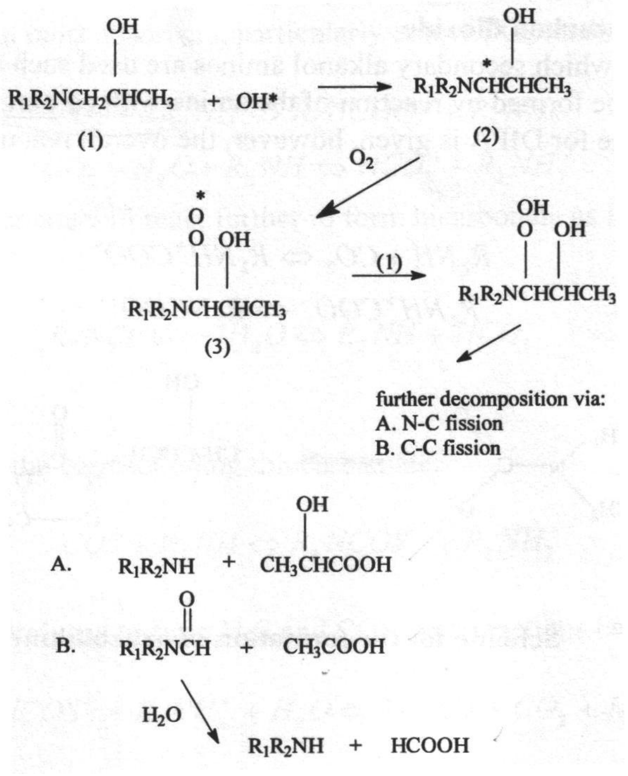


Figure 4.14: **Reaction mechanism of DIPA by oxidation (Smit *et al.*, 2002)**

Their research focused on the degradation of amine solvent in sour gas treatment unit where the oxygen presents in the feed gas of amine unit. Under high temperature and high concentration of oxygen, the formation of hydroxyl radicals may occur. The formation of acetic acid and formic acid was suggested from the C-C bond fission. These radicals also abstract α-hydrogen atom next to the nitrogen.

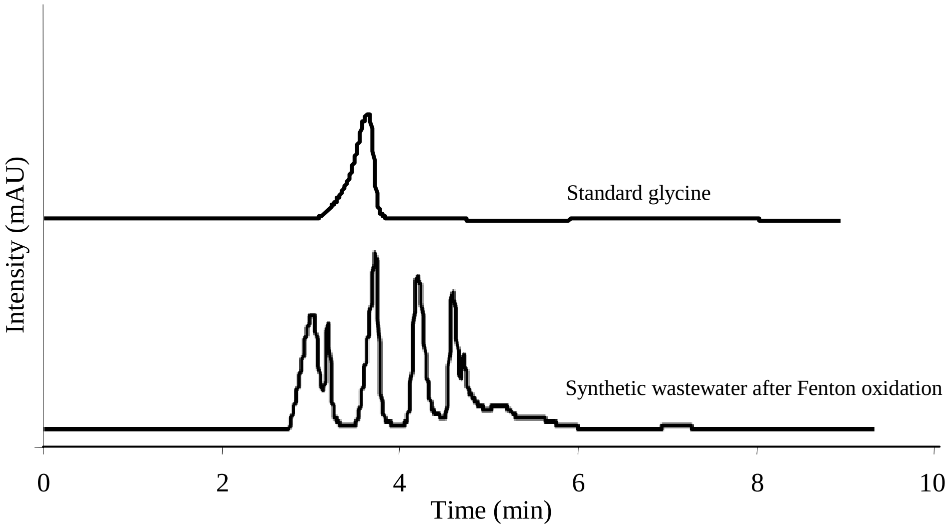


Figure 4.15: **Analysis of partially degraded DIPA by HPLC (glycine)**

Glycine is also expected from the partially degraded wastewater. Molecule structure of DIPA contains N-H bond which is predicted to be converted to glycine as one of the intermediates. From Fig. 4.15, the error between the known peak of standard glycine and the unknown peak is 3.1%.

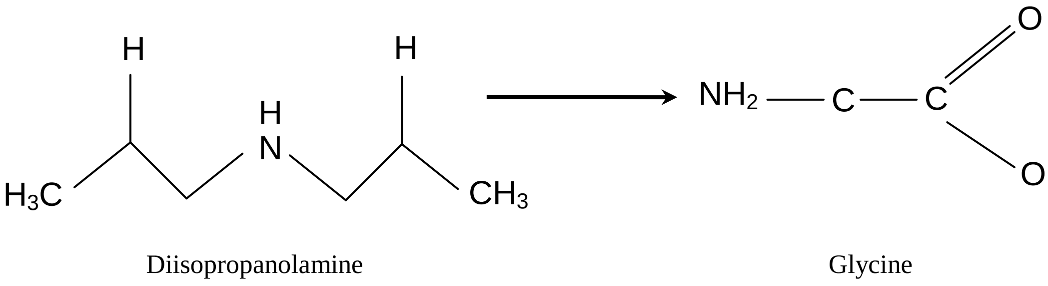


Figure 4.16: Formation of glycine as intermediate from DIPA

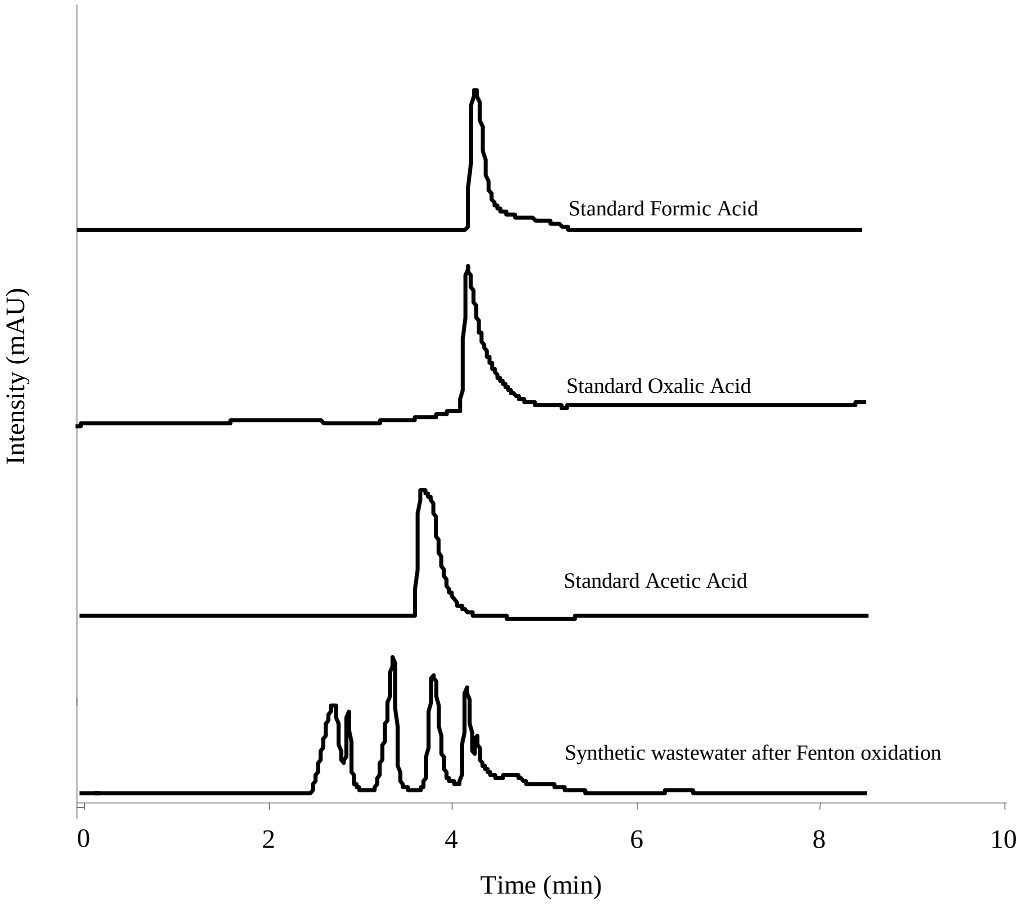


Figure 4.17: Analysis of partially degraded DIPA by HPLC (carboxylic acid)

The partially degraded sample was analyzed by HPLC to verify the formation of carboxylic acids as proposed by Smit *et al.* (2002). The retention time of standard acetic acid, formic acid and oxalic acid are compared to the retention time from the partially degraded sample. Fig. 4.17 shows the comparison of partially degraded sample with the standard acids. The retention time (r_t) of acetic acid (r_t = 3.692 min) is comparable with a peak from the sample (r_t = 3.567 min) with error of 3.39%. Meanwhile, another peak (r_t = 4.034 min) is more comparable to oxalic acid (r_t = 4.020 min) and formic acid (r_t = 4.078 min) with only 0.35% and 1.1% error respectively. These findings are parallel with the research reported by Kang *et al.* (1999) and Hess *et al.* (2003) where they reported the presence of oxalic acid during the degradation of dinitrophenol and nitro aromatic compounds by Fenton's oxidation. Other peaks may also be carboxylic acids based on the quite similar retention time. However, this can only be confirmed if the peaks are compared to the known peak of standard acids.

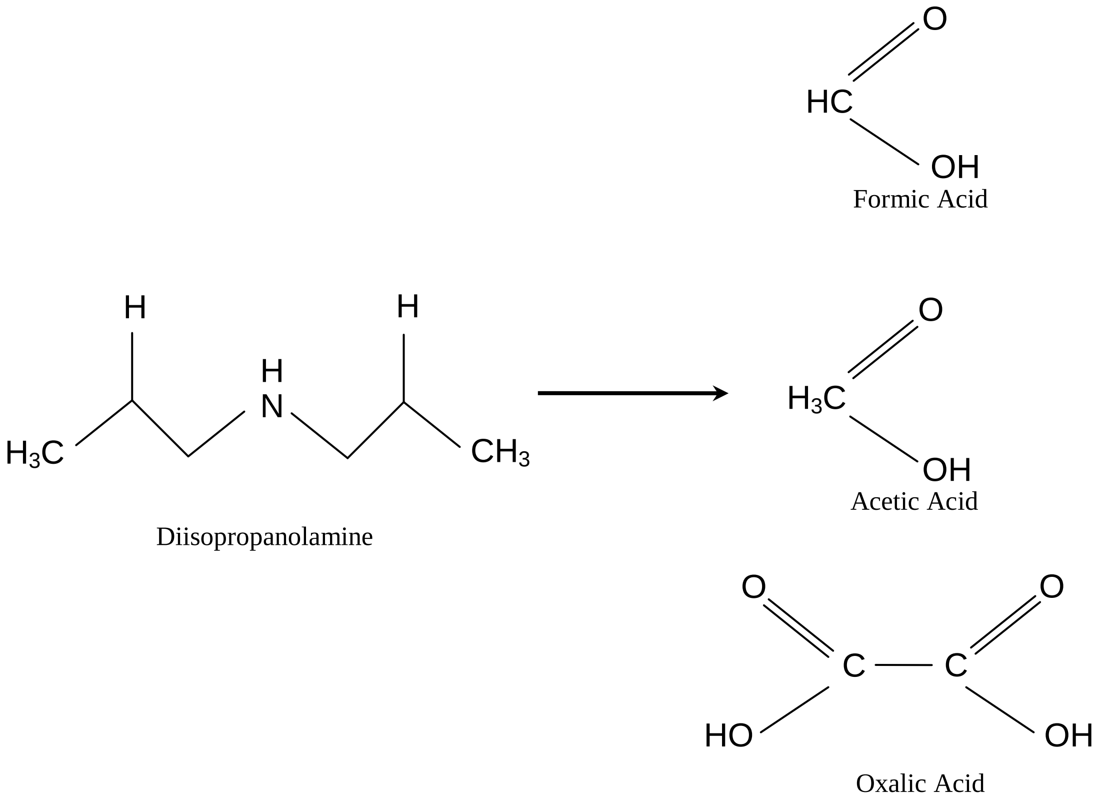


Figure 4.18: **Conversion of DIPA to carboxylic acids**

Chemical structure of the carboxylic acids produced during the degradation was showed in Fig. 4.18. The formation of short-chain carboxylic acids as intermediates was reported by many as a result of Fenton oxidation of organic compound. According to Chamarro *et al.* (2003), the biodegradability of a tested wastewater increased after Fenton oxidation and microorganisms able to degrade the Fenton oxidation's products only after initial organic compounds are depleted. The same founding was reported by several others (Gotvajn and Zagorc-Konca, 2005; Harimurti *et al.*, 2009; Rubalcaba *et al.*, 2007). The relationship between biodegradability and molecular structure was outlined by Eckenfelder and Musterman (1995). The most readily biodegradable groups are nontoxic aliphatic compound which contain carboxyl (R─COOH), ester (R─COO─R), or hydroxyl (R─OH) groups. Meanwhile, compound with dicarboxylic (HOOC─R─COOH) groups require longer acclimatization than those with a single carboxyl groups.

The carboxylic acids remain in the solution even after one hour of Fenton oxidation due to their low reactivity with OH radicals (Buxton et al., 1988). This observation is inline with the conclusion from a study by Burbano *et al.* (2002) where they investigated the degradation of MTBE intermediates with Fenton's reagent. Oturan *et al.* (2008) have studied degradation of carboxylic acid by electro-Fenton treatment. Formic acid was only fully degraded after 5 hours, 4 hours for oxalic acid and longer time required for acetic acid (8 hours).

4.3 Fenton's Oxidation for Industrial Wastewater Containing DIPA

Synthetic wastewater is different compared to the real wastewater from industry. Synthetic wastewater only consist of the target compound and water while real wastewater may consist more than one pollutant. Although Fenton's oxidation was proved to be effective to reduce large amount of COD, the same result may not be exactly the same to the real wastewater. This is due to the different characteristic between both wastewaters. This section will discuss in detail the applicability of Fenton's oxidation to treat real wastewater from a sour gas plant containing DIPA.

4.3.1 Characteristics of the Wastewater

Before the Fenton's oxidation was applied to the wastewater, the characteristic of the wastewater was determined. Table 4.1 summarized the important characteristics of the wastewater from a sour gas treatment plant.

Table 4.1: Characteristics of the wastewater from a sour gas plant

Characterization Study	**Unit**	**Amount**
pH	-	8.67
Chemical Oxygen Demand	mg/L	17, 028
5-day Biological Oxygen Demand	mg/L	909
Total Organic Carbon	mg/L	3,337
Total Suspended Solid	mg/L	4,517
Total Volatile Solid	mg/L	640
Total Nitrogen	mg/L	916
Oil and Grease	mg/L	622

Analysis of chemical oxygen demand (COD) and 5-day biological oxygen demand (BOD_5) were conducted to investigate the biodegradability of the sour gas plant effluent. From Table 4.1, the COD/BOD_5 ratio of the effluent is 18.7, which is very far from the ratios of 3 or lower where wastewater can be fully treated by biological process (Ng, 2006). For that reason, Fenton's oxidation process will be applied to treat this wastewater to improve its biodegradability.

Similar to the synthetic wastewater of DIPA, optimal conditions for the wastewater treatment were investigated. Then the BOD_5 of the treated wastewater was analyzed to see the effect of Fenton's oxidation to the biodegradability. In the Third Schedule of EQA (1974) for standard B, the discharge limit for COD, BOD, suspended solid, and oil and grease is 100 mg/L, 50 mg/L, 100 mg/L, and 10 mg/L, respectively. However, the said parameters in the wastewater were highly above the limit and must be treated before discharge. Besides, the presence of aliphatic amine

(DIPA) and several other unknown compounds make its COD value high and toxic to the environment (Fig. 4.19).

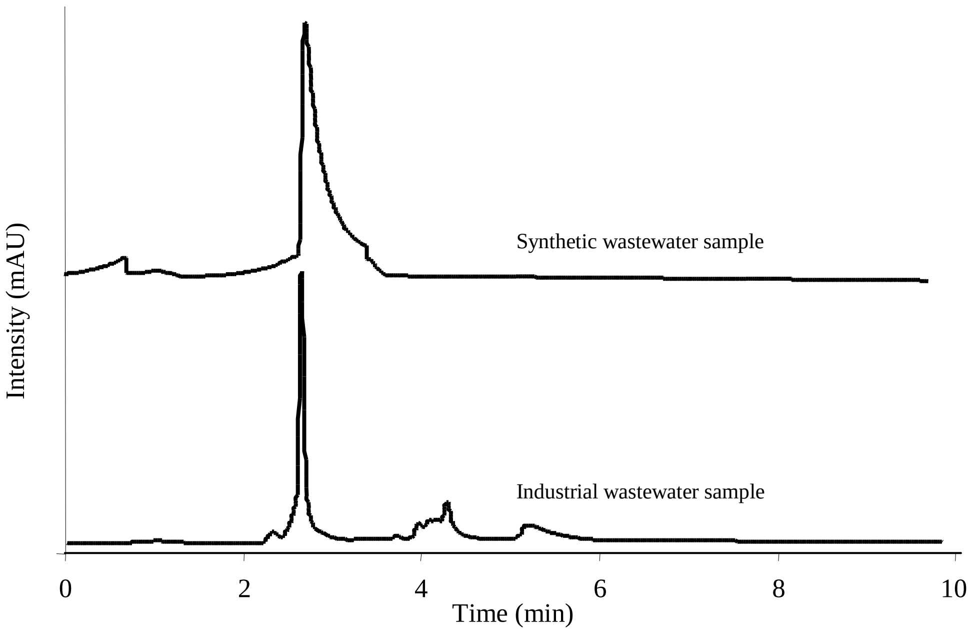


Figure 4.19: **HPLC analysis before of industrial wastewater before Fenton oxidation**

In Fig 4.19 above, the first graph is the synthetic wastewater sample which contains only DIPA as the pollutant. Meanwhile, the other graph represents the HPLC analysis of industrial wastewater sample. Single peak in graph of synthetic wastewater sample shows that only one pollutant present in the sample, while in the second graph, DIPA and several unidentified compounds present.

4.3.2 Effect of Wastewater Pretreatment

In Table 4.1, the wastewater has high oil and suspended solid content which may interfere during Fenton's oxidation. In order to investigate whether the presence of oil and suspended solid affect degradation efficiency or not, a set of experiments were conducted. Three different wastewater were used to study the effect; untreated wastewater (contains oil and suspended solid), partial treated wastewater (contains suspended solid only) and pretreated wastewater. For initial study, theoretical amount of hydrogen peroxide was used (216 mL/L). Molar ratio of H_2O_2/Fe^{2+} of 8 and initial pH of 2 was used as a continuation from the study using synthetic wastewater of DIPA. The experiments were conducted in ambient temperature and pressure. Reagents ($FeSO_4.7H_2O$ and H_2O_2) were added once at the beginning of the experiments.

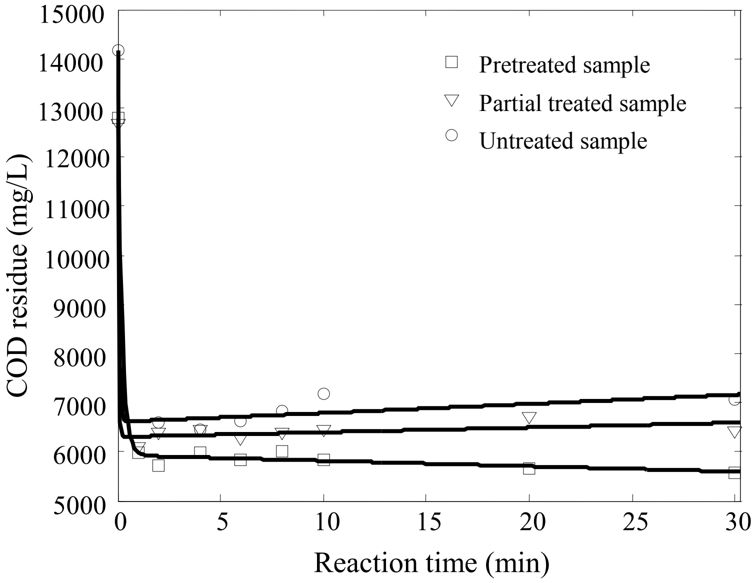


Figure 4.20: **Effect of wastewater pretreatment**

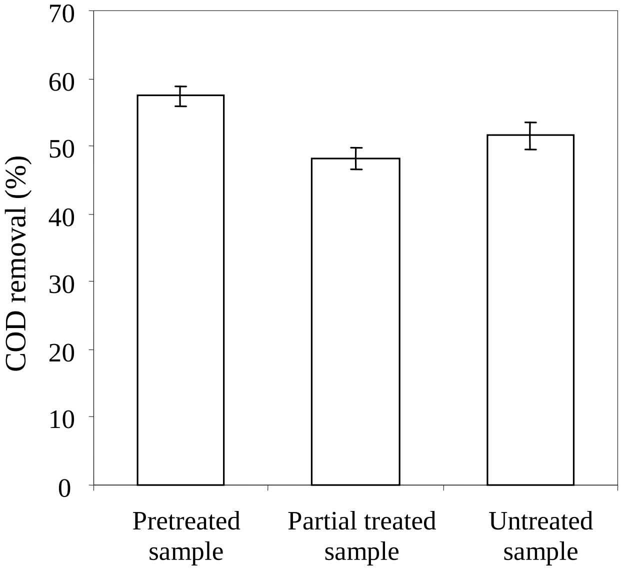


Figure 4.21: **Comparison between different types of wastewater**

Fig. 4.20 shows the effect of wastewater pretreatment before Fenton's oxidation to the degradation efficiency. The reagents were added in one aliquot at the beginning of the reaction. Therefore, the COD reduction was very significant in the first minute of the reaction. The formation of $^{\bullet}OH$ radicals and the reaction with organic substance was very rapid with second order rate constant of $10^7 – 10^{10}$ $M^{-1}S^{-1}$ (Casero *et al.,* 1997). As shown in Fig. 4.21, the pretreated sample gave higher COD reduction compared to the other samples. High amount of oil and suspended solid in the untreated and partial treated wastewater sample slightly reduce the effectiveness of Fenton's oxidation that only oxidized soluble organic compounds inside the wastewater. Even though the percentage removal has slight difference, the removal of these two pollutants is very important to adhere with the Environmental Quality Acts (1974) whereas stated in the acts the discharge limit for oil and suspended solid into inland waters is 10 and 100 mg/L respectively (EQA, 1974). Besides, the presence of oil and suspended solid during Fenton's system may cause plugging in the equipment and regular maintenance may be required to clean the equipment.

4.3.3 Effect of Different Molar Ratio

As discussed in the previous chapter, the molar ratio of reagents is very important to ensure the treatment is economically feasible. Besides, excess reagents will defer the degradation efficiency. Wide range of H_2O_2/Fe^{2+} molar ratio was reported in the literature. Apart from that, a study by Casero *et al.* (1997) on the degradation of amine by Fenton's reagent was used as the reference where they reported a range of optimum molar ratio 5 to 40. In view of the fact that the target substrate is an amine, a set of experiments were conducted at different molar ratio of 5, 10, 20 and 30. The experiments were conducted at initial pH of 2, theoretical amount of hydrogen peroxide was used (216 mL/L), and at ambient temperature and pressure. The amount of $FeSO_4.7H_2O$ was varied following the required molar ratio. Reagents ($FeSO_4.7H_2O$ and H_2O_2) were added once at the beginning of the experiments.

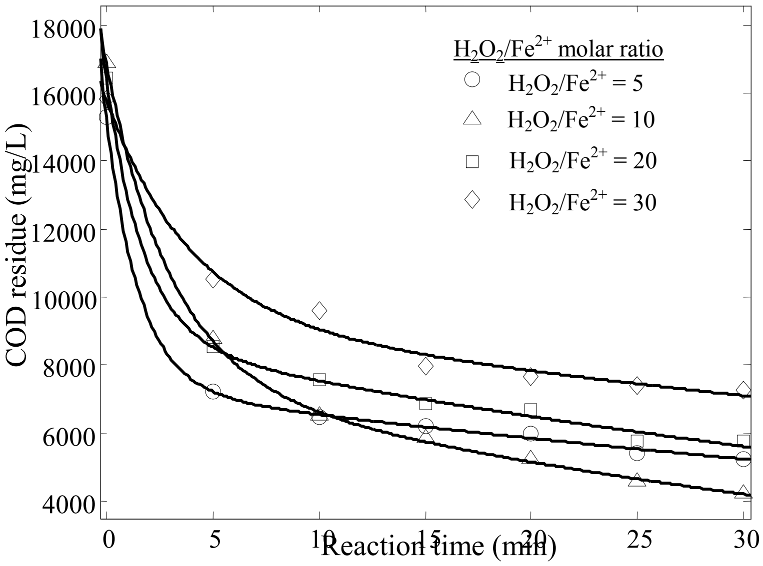


Figure 4.22: Effect of different H_2O_2/Fe^{2+} molar ratio

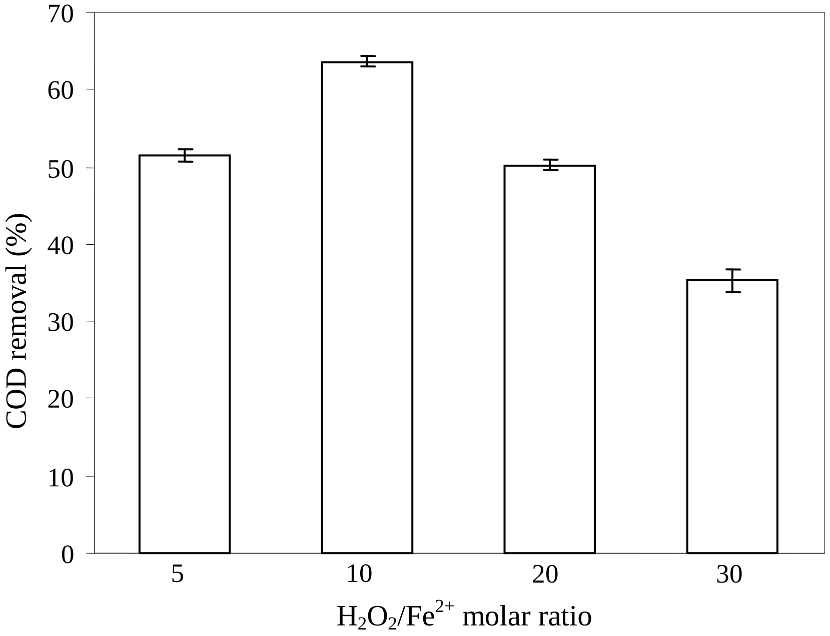


Figure 4.23: Comparison of different H_2O_2/Fe^{2+} molar ratio

The findings from the experiments were summarized in Fig. 4.22 and 4.23. As in Fig. 4.23, the highest COD percentage removal was obtained at molar ratio of 10 with 64 percent COD removal. When the ratio was reduced, the COD removal dropped to 50 percent. The similar result was achieved at molar ratio of 20 and the

COD removal dropped further with higher molar ratio of 30. At lower ratio, the amount of Fe^{2+} in the system was not sufficient to generate required amount of hydroxyl radicals for substrate oxidation. In contrast, at higher molar ratio (20 – 30), excess Fe^{2+} led to the scavenging reaction (4.4). The hydroxyl radicals react with ferrous ion instead of attacking the organic substrate. The optimum H_2O_2/Fe^{2+} molar ratio for the treatment of the wastewater was 10. Thus, this ratio was used in the following study.

4.3.4 Effect of Reagents' Dosing Methods

In the previous study where synthetic wastewater was used, four different dosing methods were compared. From the results, two highest COD percentage removal was achieved by one time and continuous addition of both reagents. So, these two dosing methods were compared in the treatment using real wastewater sample. The optimum H_2O_2/Fe^{2+} molar ratio of 10 was used. The experiments were conducted at initial pH of 2, hydrogen peroxide and ferrous sulfate used was 216 mL/L and 47.95 g/L, respectively. The process was carried out at ambient temperature and pressure.

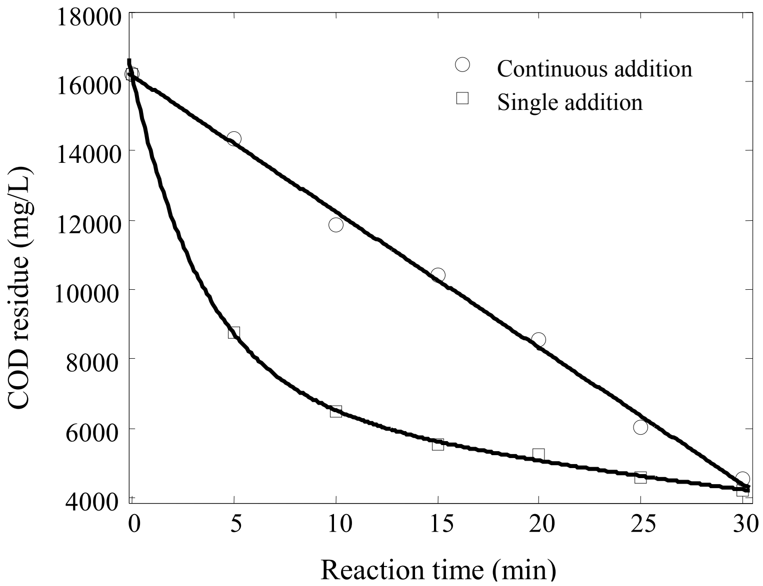


Figure 4.24: **Effect of reagents' dosing methods**

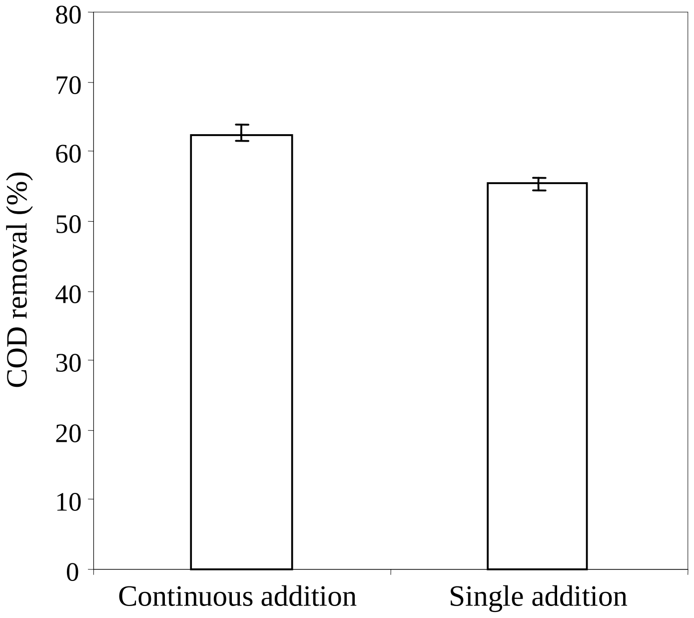


Figure 4.25: **Comparison of different dosing methods**

In Fig. 4.24, the COD residue after 30 minutes of treatment was almost equivalent. The different of COD percentage removal was only about 6 percent (Fig. 4.25). However, compared to one time addition of reagents, the pH and temperature were easier to maintain when reagents were added continuously. Besides, foaming problem was also minimized where the foaming was formed at 0.5 to 1.0 cm thickness only compared to one time addition where the foam formed extensively. Based on the observations and results obtained from this part, the next set of experiments was studied by using continuous addition of reagents.

4.3.5 Effect of Initial pH

Fenton’s oxidation for synthetic wastewater gave highest degradation at pH 2. However, it is not necessarily be the same for real wastewater. This is because the real wastewater contains more than one component which can be oxidized by Fenton’s reagent (Fig. 4.19). Thus, another set of experiments were carried out to find the optimum initial pH of the wastewater. Similar to the initial pH study for synthetic wastewater, a series of experiment were conducted at different pH values of 2, 3, 4, and 5. Hydrogen peroxide and ferrous sulfate used was 216 mL/L and

47.95 g/L, respectively. The process was carried out at ambient temperature and pressure. Both reagents were added continuously.

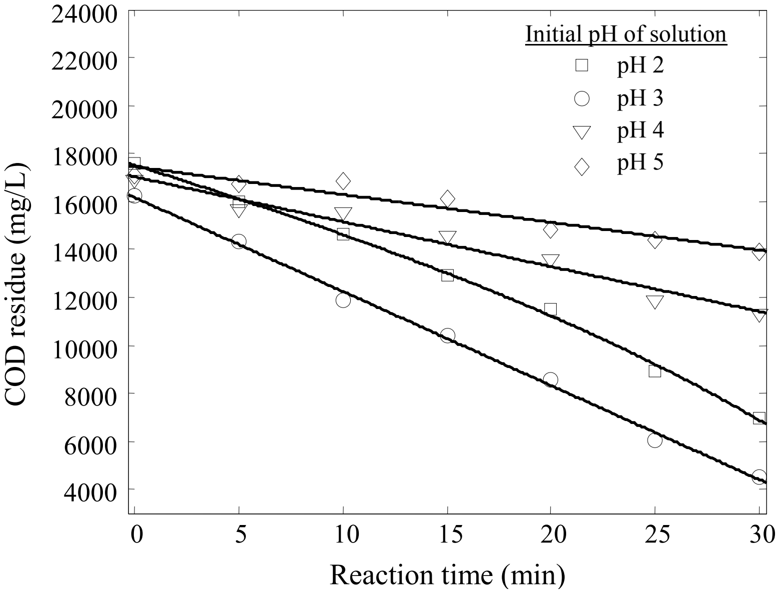


Figure 4.26: Effect of initial pH

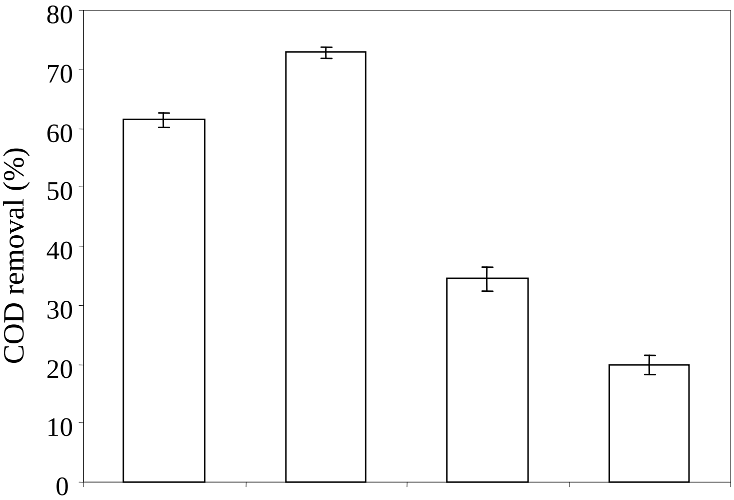


Figure 4.27: Comparison of different initial pH value

The effect of initial pH to the Fenton's oxidation efficiency was summarized in Fig. 4.26 and 4.27. The residual COD of the wastewater was at the lowest value with the treatment at pH of 3 (73% COD removal). At the highest pH value (5), only 20 percent of COD removal was achieved. This result showed that Fenton's oxidation highly affected by the initial pH of the wastewater. Fenton's oxidation is only effective in acidic environment as suggested by reaction (4.1). Consequently, the initial pH of 3 was used for the next study.

4.3.6 Effect of Hydrogen Peroxide Concentration

As the source of hydroxyl radicals (the essential component in the reactions), the correct concentration of hydrogen peroxide is vital either in treatment efficiency or from economic view. In the previous study on synthetic wastewater sample, the optimum concentration of hydrogen peroxide was found to be doubled the theoretical amount calculated. Therefore, for this moment, the obtained concentration of hydrogen peroxide was used with either increased or decreased 20 percent for each experiment (86 to 260 mL/L). Ferrous sulfate used was 47.95 g/L with initial pH of 3 at ambient conditions. The reagents were added continuously.

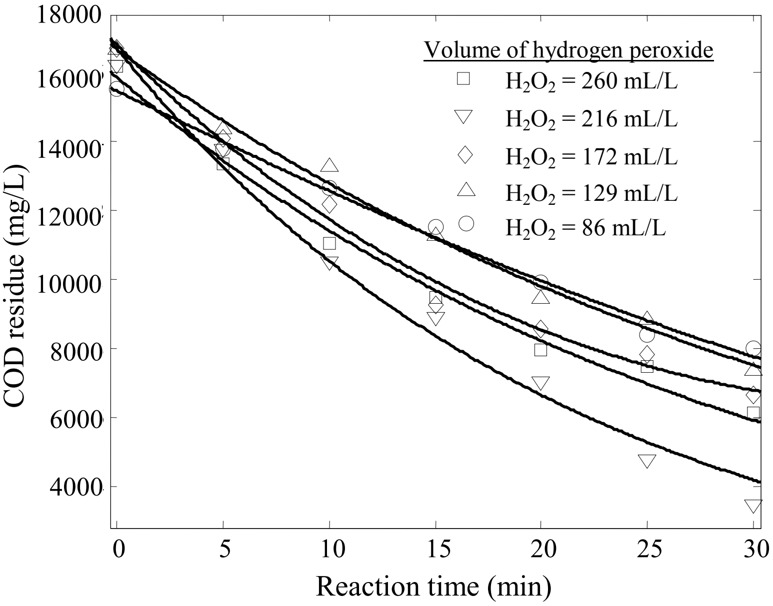


Figure 4.28: Effect of different concentration of hydrogen peroxide

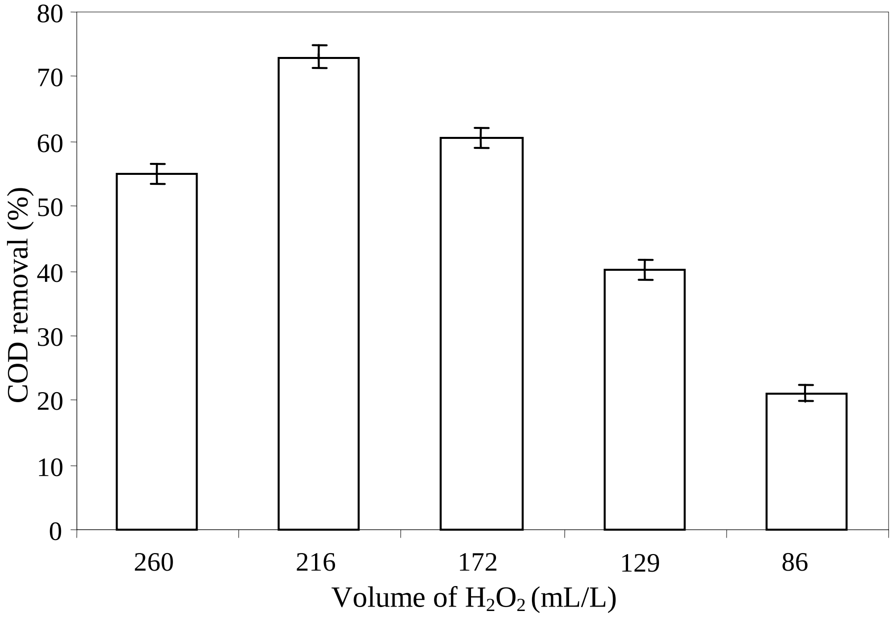


Figure 4.29: **Comparison of different volume of hydrogen peroxide**

Comparison of the degradation percentage in Fig. 4.29 showed that the highest COD removal was obtained at twice of theoretical concentration of hydrogen peroxide (216 mL/L). At higher concentration, the removal of COD decreased. The same findings were observed at the concentration lower than that where COD removal decreased when concentration of hydrogen peroxide was reduced. At higher concentration, this phenomenon happened due to the scavenging effect of hydrogen peroxide (reaction 4.5). For the meantime, insufficient hydroxyl radicals caused the degradation efficiency decreased at lower concentration of hydrogen peroxide. Due to that, two times of theoretical concentration of hydrogen peroxide (216 mL/L) is required in order to get the highest COD removal. This finding hereby confirmed that the optimal H_2O_2/Fe^{2+} molar ratio for the treatment of this wastewater is 10.

4.3.7 Effect of Reducing Reagents' Concentration

As gained in the previous study, the optimal H_2O_2/Fe^{2+} molar ratio is 10. However, the amount of reagents used was quite high. In this final part, the reagents' amount was reduced but the molar ratio was maintained at 10. In each experiment, the reagents were reduced 20 percent. Other conditions were at the optimum value (initial pH of 3, ambient temperature and pressure, continuous dosing of reagents).

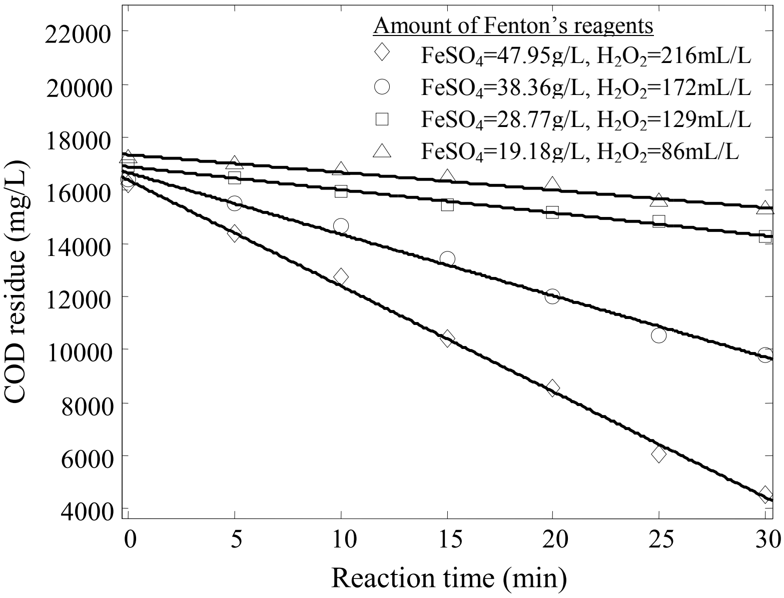


Figure 4.30: **Effect of reducing reagents' amount but maintaining molar ratio of 10**

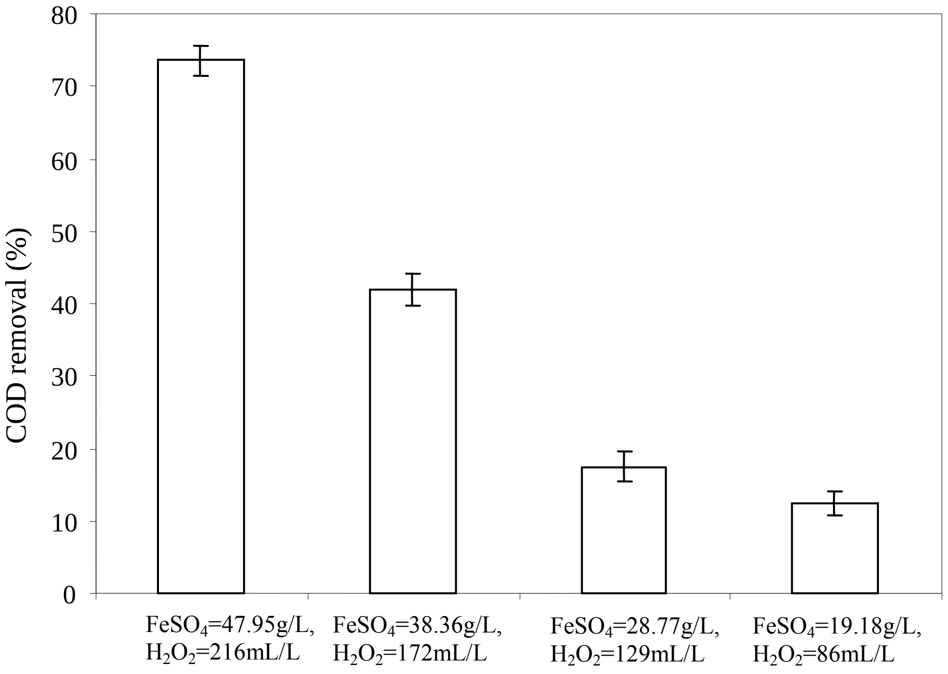


Figure 4.31: **Comparison of reducing reagents' amount with constant molar ratio of 10**

Reducing the reagents amount highly affected the treatment efficiency (Fig. 4.30 – 4.31). With only 20 percent of reagents reduced, approximately 30 percent of COD percentage removal decreased. Insufficient hydroxyl radicals for the reactions were the most possible reason behind this phenomenon.

CHAPTER 5

GENERAL DISCUSSIONS

5.1 Introduction

In previous chapter, the findings were discussed separately for each of the parameters studied. Therefore, this chapter will discuss in general the findings from the research works.

5.2 Fenton Oxidation of Diisopropalamine

This research works focused on the degradation of an aliphatic amine, diisopropanolamine (DIPA), by an advanced oxidation process. In this study, Fenton oxidation was selected as the treatment method due to its simplest theory and procedure yet favorably efficient. With the aim to investigate the applicability of Fenton oxidation to specifically degrade high concentration of DIPA, two types of wastewater samples were used; synthetic and industrial wastewater samples.

Acidic environment is very important for the Fenton oxidation to be effective, and the study revealed that highest COD removal was achieved when the initial pH of the solution was at 2 in synthetic wastewater. Meanwhile, application of Fenton oxidation to the sour gas plant wastewater showed highest COD removal in pH of 3. The difference observation between these two samples may be due to presence of more than one compound (excluding DIPA) in the real wastewater sample. However, these observations were in line with the reported findings in literature. In most literature, optimum pH was reported to be between 3 to 4 (Lee and Makoto, 2007; Sun *et al.*, 2006; Azbar *et al.*, 2004; Neyens and Baeyens, 2003; Lin *et al.,* 1999; Lin and Lo, 1997). On the other hand, Sedlak and Andren (1991) reported an optimum pH between 2 to 3 for the degradation of chlorobenzene by Fenton oxidation.

Fenton's reagents are basically consisting of H_2O_2 and Fe^{2+} ion. An excess concentration of either reagent will compromise the degradation efficiency. Optimal molar ratio of H_2O_2/Fe^{2+} is very crucial to optimize the COD reduction. The study conducted in this research on synthetic and real wastewater samples gave an optimal molar ratio of 8 and 10, respectively. These findings are parallel with a study by Guedes *et al.* (2003) who reported an optimal H_2O_2/Fe^{2+} molar ratio of 8 for the degradation of cork cooking wastewater. Meanwhile, an optimal molar ratio of 10 was reported in the degradation of several organic pollutants (Chamarro *et al.*, 2000). Although an attempt was made to reduce the amount of reagents while maintaining the molar ratio, the highest degradation was still obtained at the highest amount of reagents. These observations showed the strong effects of concentration of reagents (Fe^{2+} and H_2O_2) to the treatment efficiency.

During Fenton oxidation, several chemical reactions occur simultaneously. In order to reduce the occurrence of the side reactions, an investigation was conducted to study the way to add reagents effectively. It was observed that the highest degradation was achieved with continuous addition of both reagents. By adding reagents slowly and continuously, the possibilities of scavenging reactions to occur were reduced. At the same time, the degradation profile for continuous addition of reagents showed almost linear degradation. Contrarily, a very fast COD drop was observed in the first minute of the reaction when reagents were added all at one time, and then it started to stabilize until the reaction time was stopped.

Initial study was conducted by using low concentration of contaminant (approximately 8,500 mg/L COD for synthetic sample). Investigation of an optimum concentration of contaminant for degradation by Fenton oxidation showed that the treatment efficiency increased at high concentration of DIPA given that the ratio of

COD to reagents is kept constant. The same observation was reported by Canizares *et al.* (2009) where percentage of mineralization and COD elimination for the same compound was higher at high concentrations of pollutants. The same observations were noted when the study was carried out using real wastewater sample with different initial COD (dilution factors of 2, 3 and 4).

Prime objective of using Fenton oxidation is to achieve complete degradation of pollutants to harmless products. Unfortunately, in most cases, this objective is not achievable due to violent reaction when high concentration of hydrogen peroxide used. Therefore, Fenton oxidation is applied as pretreatment to improve biodegradability of the wastewater. In synthetic wastewater sample, COD/BOD_5 ratio before Fenton oxidation was 837 which were far from the biodegradable ratio of 3 or below (Ng, 2006). After 30 minutes of Fenton oxidation, the ratio was successfully decreased to 16 using optimum conditions and parameters. Albeit the ratio is still higher than the biodegradable ratio given by Ng (2006), 98 percent of the ratio is successfully reduced. Similar observation was noted in the treatment of the real wastewater sample. The COD/BOD_5 ratio before treatment was 18.7 and the ratio decreased to 9 after Fenton oxidation.

During these investigations, all experiments were conducted using constant sample volume of 500 mL. In real applications, the wastewater volume will be much higher and the treatment efficiency may not be the same. In order to verify whether this treatment method is applicable for large scale of wastewater, a set of experiments were conducted by using the real wastewater sample at four different sample volumes (500 mL, 750 mL, 1000 mL and 1250 mL). These experiments were carried out using optimum conditions that was previously determined. The findings were summarized in Fig. 5.1.

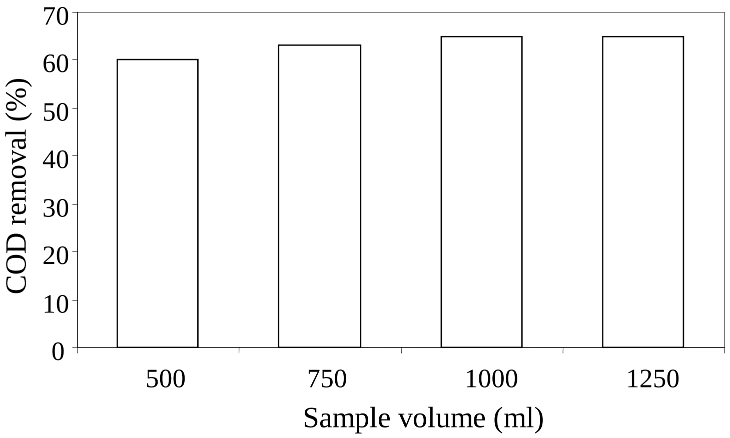


Figure 5.1: Scale up volume of sample

From the figure, only small difference in COD percentage removal (about 3 to 5 percent) was observed which can be neglected. Consequently, it can be concluded that increasing the reactor volume does not affect the treatment efficiency of wastewater by Fenton oxidation. Based on these findings, we can conclude that Fenton oxidation can be applied for the treatment of large scale of wastewater.

CHAPTER 6

CONCLUSIONS

The following conclusions can be drawn from the experimental work of the degradation of diisopropanolamine by Fenton's reagent.

1. Fenton's reagent is able to rapidly remove the COD of DIPA to a certain level after which the COD reduction become very slow. The percentage COD removal increases as the initial alkanolamines concentration increases provided the dosing ratios for Fenton's reagent are maintained. At the optimum condition and parameters, and maximum initial concentration of DIPA, 74 percent of COD elimination was achieved by Fenton oxidation in synthetic wastewater sample and 72 percent of the same in industrial wastewater sample.

2. The investigation on various parameters that affect Fenton oxidation showed that beside initial concentration of DIPA, pH and Fenton's reagent concentration also directly affect the degradation efficiency. In the synthetic wastewater sample, the optimum pH was found to be 2 and Fenton's reagent concentration was 216 mL/L H_2O_2 30% (by weight) to 59.9 g/L $FeSO_4.7H_2O$ (H_2O_2/Fe^{2+} molar ratio of 8) with 17,000 mg/L of initial COD. On the other hand, optimum pH for the real wastewater sample was 3 and Fenton's reagent concentration was 216 mL/L H_2O_2 30% (by weight) to 47.95 g/L $FeSO_4,7H_2O$ (H_2O_2/Fe^{2+} molar ratio of 10) with the same initial COD.

3. Organic acids (acetic, formic and oxalic) and glycine was identified as a reaction intermediate in Fenton's oxidation by using HPLC. Significant reduction of total organic carbon and total nitrogen also suggested the emission of gases during the oxidation. However, other degradation products could not be identified.

4. The biodegradability of synthetic and real wastewater sample were significantly increased. The COD/BOD_5 ratio for synthetic wastewater was successfully reduced up to 98 percent while 50 percent of the same was achieved for real wastewater sample.

CHAPTER 7

RECOMMENDATIONS

1. The main limitation of Fenton oxidation of DIPA is the incomplete COD removal due to some organic acid which are not degradable by hydroxyl radicals. Combination of Fenton oxidation with biological treatment may complete the COD removal.

2. Formation of ferric oxide in the form of sludge is a big problem in the Fenton's processes. The solid remains in the form of finely divided suspension that settles very slowly. Settling of hydrated ferric oxide itself may be taken up as a research problem. Application of a magnetic field may prove useful to enhance the rate of sedimentation.

3. For research purpose, a batch reactor acts as Fenton reactor. Fenton oxidation may work better in a plug flow reactor to simulate continuous addition of reagents since it was proved to be more effective. The study can be carried in a more suitable setup.

4. Although the rate model for Fenton's mineralization developed in this work is found to be applicable, a more versatile rate model should be develop to account for other compounds that exist in the real wastewater sample.

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APPENDIX A

COD CALIBRATION CURVE

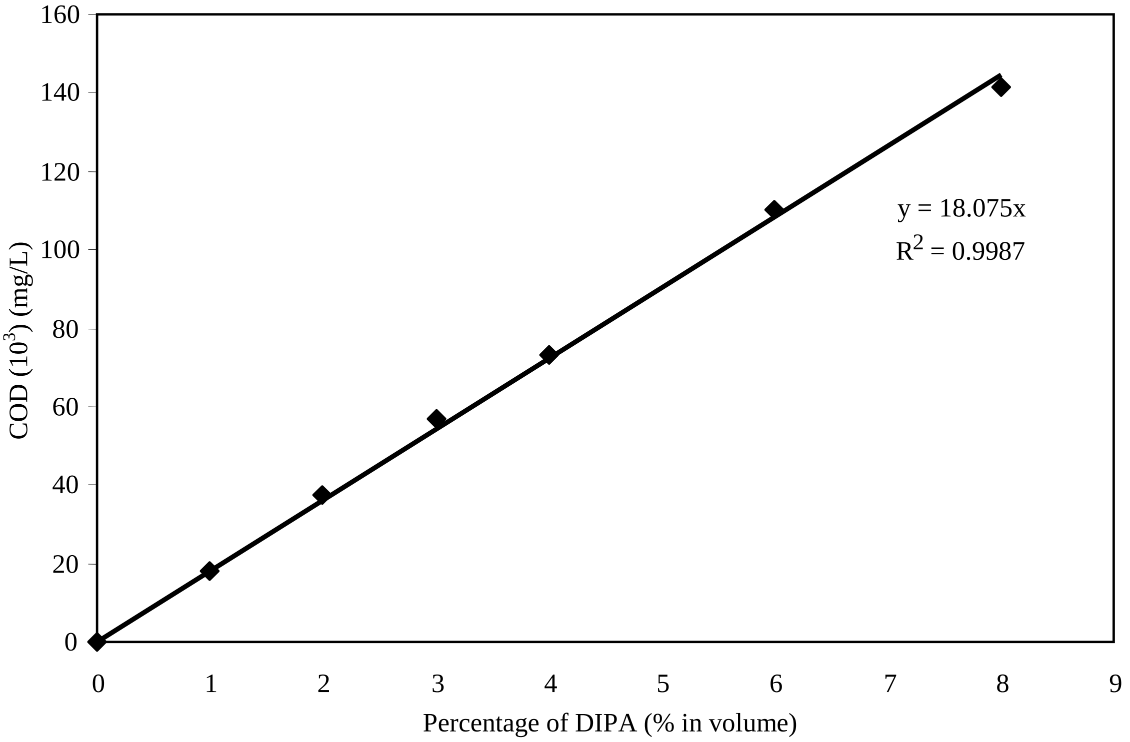

Figure A.1: **COD calibration curve for diisopropanolamine**

APPENDIX B

SAMPLE CALCULATIONS

Sample calculation to determine reagents' concentration

Theoretical oxygen demand (ThOD) is calculated based on equation (3.1)

$$COD = \alpha \, ThOD$$

where,

α is assumed to be 1.

Therefore, ThOD is equivalent to COD of wastewater. Theoretically, dissociation of one mole of H_2O_2 will produce one mole of oxygen radical. Then, the oxygen radical will react with the organic compound (represented by COD value). Thus, the number of mole of oxygen required will be equals to the number of moles of hydrogen peroxide used for degradation. Based on the amount of initial COD and reaction equation (3.2), the amount of H_2O_2 required calculated is

$$Number\ of\ mole\ of\ H_2O_2 = \frac{Initial\ COD\,(mg/L)}{Molar\ mass\ of\ oxygen\ radical\ (g/mol)}$$

$$= \frac{8{,}500\ mg/L}{16\ g/mol}\ x\ \frac{1\ g}{1{,}000\ mg}$$

$$= 0.5313\ mol/L$$

$$Vol.\,of\ \ H_2O_2\ (30\%) = \frac{No.\,of\ \ mole\,(mol)\ x\ Mol.\,weight\ \ (g/mol)}{Density\ (g/mL)\ x\ 0.3}$$

$$= \frac{0.5313\,mol/L\ x\ 34.01\,g/mol}{1.11\,g/mL\ x\ 0.3}$$

$$= 54.26\ mL/L$$

Then, amount of ferrous ion can be calculated based on the required H_2O_2/Fe^{2+} molar ratio. For this example, molar ratio is assumed to be 10.

Thus, number of mole for Fe^{2+} is

$$No.\,of\ \ mole\,of\ \ Fe^{2+}\ required = \frac{1}{10}\ x\ No.\,of\ \ mole\,of\ \ H_2O_2$$

$$= \frac{1}{10}\ x\ 0.5313\,mol$$

$$= 0.0531\,mol$$

$$Mass\,of\ \ Fe^{2+}\ required = No.\,of\ \ mole\,(mol)\ x\ Molar\ \ mass\,(g/mol)$$

$$= 0.0531\,mol/L\ x\ 55.845\ g/mol$$

$$= 2.9654\ g/L$$

However, Fe^{2+} is not present as ion. It is available as ferrous sulfate, $FeSO_4.7H_2O$. Therefore, the amount of this reagent is calculated to get the required concentration of Fe^{2+}.

$$Mass\ of\ \ FeSO_4.7H_2O\ \ = \frac{Mass\ of\ \ Fe^{2+}\ required\ (g/L)}{Molar\ mass\ Fe^{2+}\ (g/mol)}\ x\ Mol.\ weight\ \ FeSO_4.7H_2O\ (g/mol)$$

$$= \frac{2.9654\ g/L}{55.845\ g/mol}\ x\ 278.2\ g/mol$$

$$= 14.77\ g/L$$

APPENDIX C

PUBLICATIONS

Abdul Aziz Omar, Putri N Faizura Megat Khamaruddin and Raihan Mahirah Ramli, Fenton oxidation of a natural gas plant wastewater, *accepted for journal publication in Canadian Journal of Chemical Engineering & Technology 2010*

Putri N Faizura Megat Khamaruddin, Raihan Mahirah Ramli, A Aziz Omar and Binay K Dutta, Fenton's reagents dosing effect on treatment efficiency of Diisopropanolamine contaminated wastewater, *International Conference on Chemical Engineering and Applications* (2010) Singapore

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