Fenton Oxidation Of Amine Waste

By

NIK FAHIMEH YOUSEF

Dissertation Submitted in partial fulfillment of
The requirement for the Bachelor of Engineering (Hons)
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Universiti Teknologi Petronas
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

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CERTIFICATION OF APPROVAL

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Nik Fahimeh Yousef
2556

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Approved by :

____
(Mrs . Putri Nadzrul Faizura Megat Khamaruddin)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

MAY 2005

CERTIFICATION OF ORIGINALITY

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

(NIK FAHIMEH YOUSEF)

ABSTRACT

Amine carry over is a commonly-discussed problem in gas plant utilizing amine as a medium to obliterate acid gases from the incoming gas stream. Amine carry over will potentially end up in the effluent water thus, if improperly discharge will pollute the environment. Mixture of water with high amine concentration will resort to high chemical oxygen demand value, which is a direct and almost accurate measure of contaminants in water . The higher the COD value, the higher the concentration of contaminants in water. Mixture of amine with water is a tenacious and well mixed mixture, hence, to separate them is a challenge. This project is done to study the COD value reduction of amine waste using Fenton reagent. The parameters that are studied are the effect of Ferum as the catalyst and also the optimum Fe^{2+} : H_2O_2 which will give a higher COD value reduction.

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CHAPTER 1

1.1 BACKGROUND OF STUDY

1.1.1 Amine

Amines such as MDEA, DEA and DIPA are commonly used to eradiate acid gases from the incoming gas stream in liquefied natural gas (LNG) production. The carry over of amine into the effluent system of LNG plants is concerned matter. Despite other sources such as presence of salts and organic compounds, amine is also known to be one of the main contributors to increase the chemical oxygen demand (COD) of the effluent. (Md Isa et al., 2002)

The use of Fenton reagent to reduce the COD value of the amine waste in effluent water is a possible method.

1.1.2 Chemical Oxidation

Chemical oxidation will result in almost complete mineralization of organic pollutants and are effective for wider range of organics. One of chemical oxidation method is Fenton-like reaction. This oxidation with Fenton's reagent is based on ferrous ion and hydrogen peroxide.

Chemical oxidation by using Fenton's reagent is the chosen alternative to reduce the COD value of the mixture of amine and water.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

Amine carry over is a commonly-discussed problem in gas plant utilizing amine as a medium to obliterate acid gases from the incoming gas stream. Amine carry over will potentially end up in the effluent water thus, if improperly discharge will pollute the environment. Mixture of water with high amine concentration will resort to high chemical oxygen demand value, which is a direct and almost accurate measure of contaminants in water (Md Isa et al., 2002). The higher the COD value, the higher the concentration of contaminants in water. Mixture of amine with water is a tenacious and well mixed mixture, hence, to separate them is a challenge. The task of this project is to reduce the COD value of water containing amine waste by using Fenton's reagent.

1.2.2 Significant of the Project

Fenton reaction is an AOP process which can be used to degrade various organic matters in effluent system. The oxidation agent is H_2O_2 and Fe^{2+} will act as the catalyst for the process. The Fenton reagent which can be prepared in the laboratory is used to treat diluted amine waste is used as an alternative to reduce the COD value of the amine waste.

1.3 OBJECTIVES AND SCOPE OF STUDY

1.3.1 Objectives

The specific objectives of this project of Fenton Oxidation of amine waste are :

1. To reduce the COD value.
2. To determine the optimum Fe^{+2}: H_2O_2ratio.

1.3.2 Scope of Study

The carry over of amine into the effluent system of LNG plants is a concerned matter. The amine will have a high COD value which will be against the environmental laws.

The objective of this project is to reduce the COD value of the amine by oxidation method using Fenton reagent.

1.3.1 Feasibility of the Project within Scope and Time Frame

This final year research project is one semester project. Half of the semester was spent studying about the Amine itself and the other half performing laboratory works to reduce the COD value of amine waste. The COD reduction was studied only in terms of addition of Ferum as the catalyst in the Fenton reaction. Other parameters such as UV light , pH and temperature was not studied. The comparisons among the suggested processes for COD reduction of amine waste are based on literature review due to time constrain.

CHAPTER 2

LITERATURE REVIEW /THEORY

2.1 AMINE WASTE

2.1.1 Introduction To Amine

Amines are derivatives of ammonia in which one or more of the hydrogens has been replaced by an alkyl or aryl group. The nomenclature of amines is complicated by the fact that several different nomenclature systems exist, and there is no clear preference for one over the others. Furthermore, the terms primary (1°), secondary (2°) & tertiary (3°) are used to classify amines in a completely different manner than they were used for alcohols or alkyl halides. When applied to amines these terms refer to the number of alkyl (or aryl) substituents bonded to the nitrogen atom, whereas in other cases they refer to the nature of an alkyl group.

Amine , such as MDEA, DEA and DIPA is known to be one of the contributors to increase the chemical oxygen demand (COD) of the effluent. Therefore, its COD value needs to be decreased since it is harmful as mandated by the law. Advanced Oxidation Process (AOP) is believed to be the solution. The AOP type for this project is Fenton Reaction.

Amine sludges can contain a high sodium content. To eliminate sodium in amine process waste substitute potassium hydroxide for sodium hydroxide to maintain high pH in the process. Amine sludges have also been shown to have elevated levels of nickel and copper, probably as a result of corrosion while gas is being processed. The addition of potassium hydroxide to maintain pH during the process also helps minimize corrosion and the presence of these metals in the sludge. (Md Isa et. al. , 2003).

Like ammonia, most amines are Bronsted and Lewis bases, but their base strength can be changed enormously by substituents. It is common to compare basicities quantitatively by using the pK$_a$'s of their conjugate acids rather than their pK$_b$'s. Since pK$_a$ + pK$_b$ = 14, the higher the pK$_a$ the stronger the base, in contrast to the usual inverse relationship of pK$_a$ with acidity. Most simple alkyl amines have pK$_a$'s in the range 9.5 to 11.0, and their water solutions are basic (have a pH of 11 to 12, depending on concentration). (www. msu.edu/amine)

2.2 CHEMICAL OXYGEN DEMAND

The standard test for COD involves digesting the sample with strong sulphuric acid solution in the presence of chromium and silver salts. These potentially hazardous chemicals clearly need to be handled with extreme care. Recent health and safety concerns have made it necessary to find a means of carrying out this vitally important test whilst at the same time minimizing the risk to laboratory staff.

The chemical oxygen demand (COD) permits the way of measuring the amount of organic waste in wastewater or effluent water. The higher the COD value, the more the organic wastes are, hence, the higher the amount of dissolve oxygen needed by the bacteria to breakdown the organic waste in the effluent. Normally, oxygen is not a soluble gas in water and the dissolved oxygen concentration in wastewater in wastewater is very low. (Palitest , 2004)

2.3 ADVANCED OXIDATION PROCESS

Advanced chemical oxidation processes make use of (chemical) oxidants to reduce COD/BOD levels, and to remove both organic and oxidisable inorganic components. The processes can completely oxidise organic materials to carbon dioxide and water, although it is often not necessary to operate the processes to this level of treatment.

A wide variety of advanced oxidation processes are available:

- chemical oxidation processes using hydrogen peroxide, ozone, combined ozone & peroxide, hypochlorite, Fenton's reagent etc.
- ultra-violet enhanced oxidation such as UV/ozone, UV/hydrogen peroxide, UV/air
- wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant)

(Oxidation Systems, 2004)

Advanced oxidation processes are particularly appropriate for effluents containing refractory, toxic or non-biodegradable materials. The processes offer several advantages over biological or physical processes, including:

- unattended operation
- the absence of secondary wastes
- the ability to handle fluctuating flow rates and compositions

2.4 FENTON'S REAGENT

Introduction

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

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

This entry presents the general chemistry of Fenton's Reagent, and discusses the parameters which affect its performance.

General Overview

$$\mathbf{Fe^{2+} + H_2O_2 \text{ ----> } Fe^{3+} + OH^- + {}^{\cdot}OH}$$

$$\mathbf{Fe^{3+} + H_2O_2 \text{ ----> } Fe^{2+} + {}^{\cdot}OOH + H^+}$$

The procedure requires:

- adjusting the wastewater to pH 3-5;
- adding the iron catalyst (as a solution of FeSO4); and
- adding slowly the H_2O_2. If the pH is too high, the iron precipitates as $Fe(OH)_3$ and catalytically decomposes the H_2O_2 to oxygen -- potentially creating a hazardous situation.

Reaction rates with Fenton's Reagent are generally limited by the rate of $\cdot$ OH generation (i.e., concentration of iron catalyst) and less so by the specific wastewater being treated. Typical $Fe:H_2O_2$ ratios are 1:5-10 wt/wt, though iron levels < 25-50 mg/L can require excessive reaction times (10-24 hours). This is particularly true where the oxidation products (organic acids) sequester the iron and remove it from the catalytic cycle. Fenton's Reagent is most effective as a pretreatment tool, where COD's are > 500 mg/L. This is due to the loss in selectivity as pollutant levels decrease:

$$\mathbf{\cdot OH + H_2O_2 \text{----}{>} \cdot O_2H + H_2O}$$

$$\mathbf{\cdot OH + Fe^{3+} \text{----}{>} Fe^{2+} + OH^-}$$

In addition to free radical scavengers, the process is inhibited by (iron) chelants such as phosphates, EDTA, formaldehyde, and citric/oxalic acids. Because of the sensitivity of Fenton's Reagent to different wastewaters, it is recommended that the reaction always be characterized through laboratory treatability tests before proceeding to plant scale.

Discussion

Hydroxyl radical reactivity

The hydroxyl radical is one of the most reactive chemical species known, second only to elemental fluorine in its reactivity (see below).

Table 1 : Reactivity of chemical species

Reactive Species	Relative Oxidation Power (Cl_2=1.0)
Flourine	2.23
Hydroxyl radical	2.06
Atomic oxygen (singlet)	1.78
Hydrogen peroxide	1.31
Perhydroxyl radical	1.25
Permanganate	1.24
Hypobromous acid	1.17
Chlorine dioxide	1.15
Hypochlorous acid	1.10
Hypiodous acid	1.07
Chlorine	1.00
Bromine	0.80
Iodine	0.54

Source : Ind. Eng. Chem., Process Design & Development vol.7

The chemical reactions of the hydroxyl radical in water are of four types:

Addition: $^{\cdot}OH + C_6H_6 \text{ ----> } (OH)C_6H_6^{\cdot}$

where the hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product (cyclohexadienyl radical shown above).

Hydrogen Abstraction: $^{\cdot}OH + CH_3OH \text{ ----> } {}^{\cdot}CH_2OH + H_2O$

where an organic free radical and water are formed.

Electron Transfer: $^{\cdot}OH + [Fe(CN)_6]^{4-} \text{ ----> } [Fe(CN)_6]^{3-} + OH^{-}$

where ions of a higher valence state are formed, or an atom or free radical if a mononegative ion is oxidized.

Radical Interaction: $\cdot OH + \cdot OH \longrightarrow H_2O_2$

where the hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product.

In applying Fenton's Reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanisms (hydrogen abstraction and oxygen addition) predominate. Typical rates of reaction between the hydroxyl radical and organic materials are 10^9 - 10^{10} k (M^{-1} s^{-1}).

Effect of Iron Concentration

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

1. A minimal threshold concentration of 3-15 mg/L Fe which allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material;

2. A constant ratio of Fe:substrate above the minimal threshold, typically 1 part Fe per 10-50 parts substrate, which produces the desired end products. Note that the ratio of Fe:substrate may affect the distribution of reaction products; and

3. A supplemental aliquot of Fe which saturates the chelating properties in the wastewater, thereby availing unsequestered iron to catalyze the formation of hydroxyl radicals.

Iron dose may also be expressed as a ratio to H_2O_2 dose. Typical ranges are 1 part Fe per 5-25 parts H_2O_2 (wt/wt).

Effect of Iron Type (Ferrous or Ferric)

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction -- the catalytic cycle begins quickly if H_2O_2 and organic material are in abundance. However, if low doses of Fenton's Reagent are being used (e.g., < 10-25 mg/L H_2O_2), some research suggests ferrous iron may be preferred. Neither does it matter whether a chloride or sulfate salt of the iron is used, although with the former, chlorine may be generated at high rates of application.

It is also possible to recycle the iron following the reaction. This can be done by raising the pH, separating the iron flocculation , and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

Effect of H_2O_2 Concentration

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory for each waste to be treated. For example, in a typical application the following series

--Oxidized --Oxidized --Oxidized --Oxidized --Oxidized --
Substrate--Intermediate--Intermediate--Intermediate--Intermediate--Intermediate--CO_2
>"A" >"B" >"C" >"D" >"E" >

Each transformation in this series has its own reaction rate and, as the case of phenolics illustrates, there may occur build-up of an undesirable intermediate (quinones), which requires sufficient H_2O_2 to be added to push the reaction beyond that point. This is frequently seen when pretreating a complex organic wastewater for toxicity reduction. As the H_2O_2 dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, whereupon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity.

Effect of Temperature

The rate of reaction with Fenton's Reagent increases with increasing temperature, with the effect more pronounced at temperatures < 20 deg-C. However, as temperatures increase above 40-50 deg-C, the efficiency of H2O2 utilization declines. This is due to the accelerated decomposition of H2O2 into oxygen and water. As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between 20-40 deg-C.

Applications of Fenton's Reagent for pretreating high strength wastes may require controlled or sequential addition of H_2O_2 to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when H_2O_2 doses exceed 10-20 g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well.

Effect of pH

The effect of pH on reaction efficiency is illustrated below:

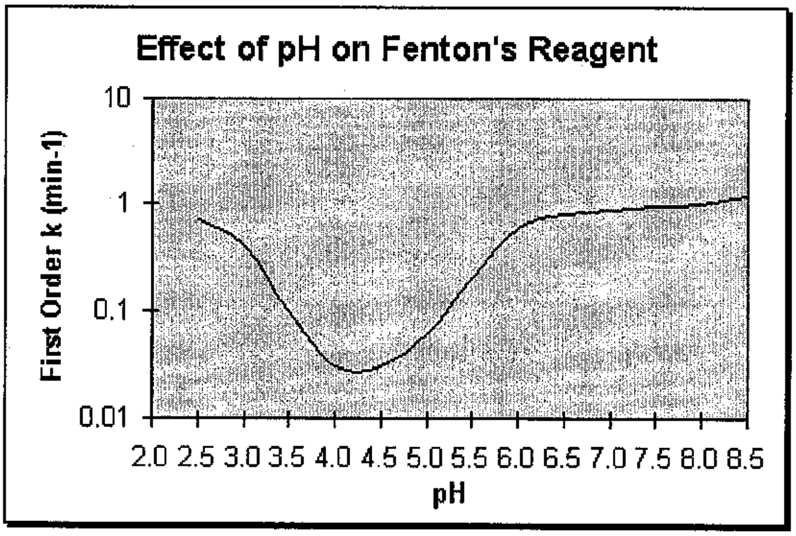

Figure 1 : Graph of Effect of pH on Fenton Reagent

Source : Ind. Eng. Chem., Process Design & Development vol.7

The optimal pH occurs between pH 3 and pH 6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. There have been some recent developments using nonradical scavenging sequestering agents (e.g., NTA and gallic acid) to extend the useful pH range to pH 8-9, but no commercial applications are known. The drop in efficiency on the acid side is less dramatic given the logarithmic function of pH, and is generally a concern only with high application rates.

A second aspect of pH deals with its shift as the reaction progresses. Provided an initial wastewater pH of 6.0, the following profile is typical of Fenton reactions.

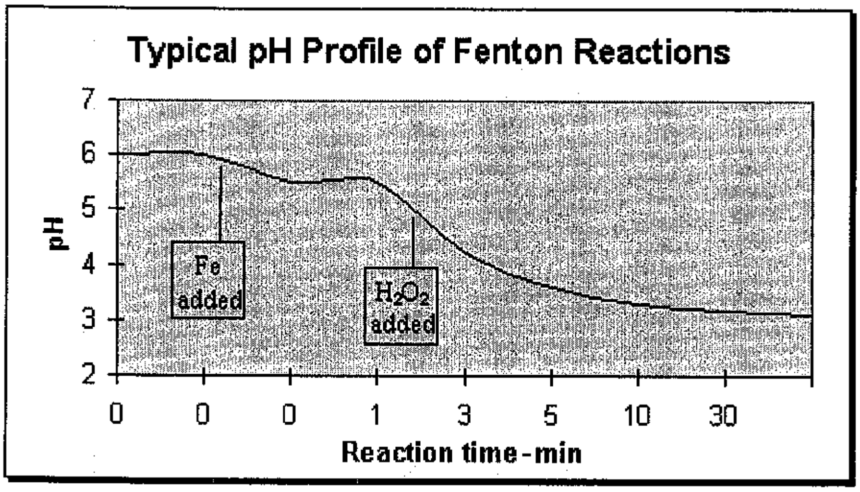

Figure 2 : Graph of Effect Of pH on Fenton Reagent

Source : <u>Ind. Eng. Chem., Process Design & Development</u> vol.7

The first inflection is caused by the addition of $FeSO_4$ catalyst which typically contains residual H_2SO_4. A second, more pronounced drop in pH occurs as the H_2O_2 is added, and continues gradually at a rate which is largely dependent on catalyst concentration. This drop in pH is attributed to the fragmenting of organic material into organic acids. This pH change is often monitored to ensure that the reaction is progressing as planned -- the absence of such a pH decrease may mean that the reaction is inhibited and that a potentially hazardous build-up of H_2O_2 is occurring within the reaction mixture.

Historically, Fenton's Reagent has been applied in batch mode. Today, however, it is being used in both continuous and sequential batch processes. A typical batch operation would consist of chemical storage and dosing modules (for H_2O_2, FeSO4, acid, and lime/NaOH); a primary reactor and (optional) holding tank; a solids dewatering device (optional); and miscellaneous temperature and pH controls. The materials of construction for the reactor and holding tank are typically Types 304 or 316 stainless steel, while those for the chemical storage systems may also be HDPE. Packaged Fenton's systems are available from some equipment providers, or US Peroxide can provide you with engineering guidance on custom designs and retrofits. (Bishop, D.F. et.al., 1968)

CHAPTER 3

METHODOLOGY /PROJECT WORK

3.1 PREPARATION OF AMINE WASTE SAMPLE AND FENTON REAGENT

3.1.1 Determining the amine waste initial COD value

To reduce the COD value of amine waste , the first step is to find the initial COD value of amine waste. Raw amine waste from the laboratory is used as the sample. Raw amine waste has a very high COD value. Since the COD vials (refer to Figure 3) used in the experiment have the range of 1500 only, the amine waste has to be diluted with water , because without dilution, the COD values cannot be determined.

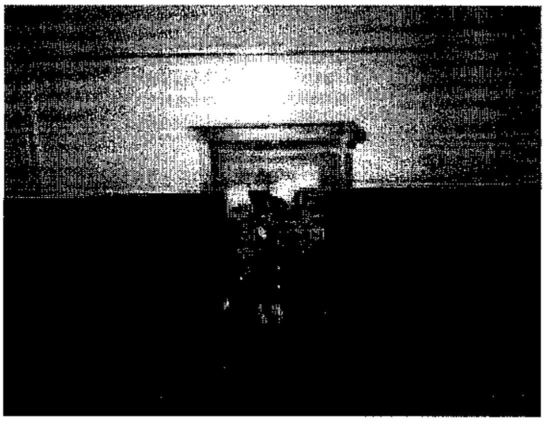

Figure 3 : COD vials

Amine waste is first diluted with 500 ml of distilled water . The amine waste used is about one ml for each dilution. Two ml of each sample is inserted into COD vials and then inserted into the thermoreactor (see Figure 4) for two hours. Then , the COD vials are taken for readings using the DR 2010 (see Figure 5) equipment which is a device to read the COD value of different ranges. The device is programmed to read the COD values of different ranges. The range has to inserted first so that the COD value can be determined. The equipment has to be zeroed first by using 2 ml of distilled water inserted into a COD vials as the zero reading.

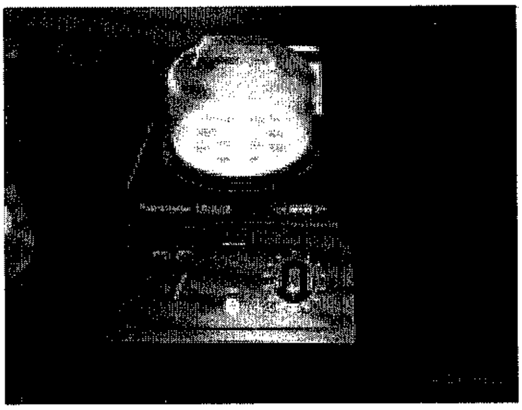

Figure 4 : Thermo reactor

Figure 5 : DR 2010

The dilution is done three times and each sample for each dilution are inserted into COD vials so that the COD reading can be determined. However , for the three reading, the average should be taken. The purpose of taking three readings is to determine whether the COD values obtained are reliable to be use d for the experiment. Therefore , for the 500 ml dilution of amine waste ;

1st reading – 217 mg/L

2nd reading- 228 mg/L

3rd reading –212 mg/L

3.1.2 Preparation of Fenton Reagent

The average of the values were taken as 219 mg/L. When the initial COD value is known, the amine waste can be treated with Fenton reagent. Therefore , the effect of Fe^{2+} : H_2O_2 can be studied by treating the amine waste with Fenton reagent. Fe^{2+} : H_2O_2 is a ferum to peroxide ratio that is going to treat amine waste. Ferum will act as the catalyst as amine waste is oxidized by hydrogen peroxide. Before starting , the Fe^{2+} : H_2O_2 going to be used has to be prepared. The amount of Ferum has to be determined first before preparing the hydrogen peroxide solution. The amount of Ferum depends on the initial COD value. Based on the initial COD value (219 mg /L), the amount of Fe^{2+} needed is calculated. Therefore , 500 x (219/20) = 5475 mg /L. Raw amine waste solution for each sample is determined as **50 ml** for all samples. Thus , the amount of ferum needed for each sample is 5475 mg/L x 0.05 L = **273.75 mg.**

After finding out the amount of ferum needed, the different ratios of Fe^{2+} : H_2O_2 can be prepared. Therefore, amount of H_2O_2 required for the ratio 0f 1:10 , 1: 20 , 1 : 30 and 1 : 40 can be prepared. To prepare the hydrogen peroxide , the strength of hydrogen peroxide should be known. The strength of H_2O_2 used is 30 % . Therefore , 30 % x 1110 mg/L.

This is because the hydrogen peroxide solution used is 30 % in strength and its density is 1110 mg /L . Amount of H_2O_2 required in mL :

For 1 :10 of Fe : H_2O_2

= 273. 75 x 10 / 333 mg/L = **8. 22 ml**

For 1 : 20 of Fe : H_2O_2

= 273.75 x 20 / 333 mg/L = **16.44 ml**

For 1 : 30 of Fe : H_2O_2

=273.75 x 30 / 333 mg/L = **24.63 ml**

For 1 : 40 of Fe : H_2O_2

=273.75 * 30 / 333 mg/L = **32. 88 ml**

The ratios of the Fe and H_2O_2 mixture that need to be prepared before the experiment is shown in table 2 :

Table 2 : Amount of Ferum and H_2O_2 needed to be prepared for each ratio

1.3 Ratio	Fe (mg)	Hydrogen Peroxide (ml)
1 : 10	273.75	8.22 ml
1 : 20	273.75	16. 44 ml
1 : 30	273.75	24. 63 ml
1 : 40	273.75	32. 88 ml

The ferum used is $FeSO_4$ in solid form. Therefore , stirring is required.

3.2 FENTON EXPERIMENT

3.2.1 Preparation Of amine waste samples

Amine waste is going to be treated with each ratio of Ferum and hydrogen peroxide. The reaction time will be two hours for each ratio. Each sample of amine waste is 50 ml inserted into 250 ml conical flask. Raw amine waste is used without dilution. For each ratio, three samples of amine waste is going to be treated so that average results can be obtained. Also , it is important to use three samples so that the results obtained can be reliable. Therefore , for each ratio of Ferum to hydrogen peroxide , three samples of amine waste are inserted into three different 250 ml conical flasks labeled 1, 2 and 3 .Each conical flask will contain 50 ml of amine waste. The samples need to have acidic condition which the pH should be 2-3, therefore sulphuric acid has to be added to the samples bit by bit and the pH should be observed so that it would be reduced to 2-3 . The pH reading can be determined using the pH meter (refer to Figure 6).

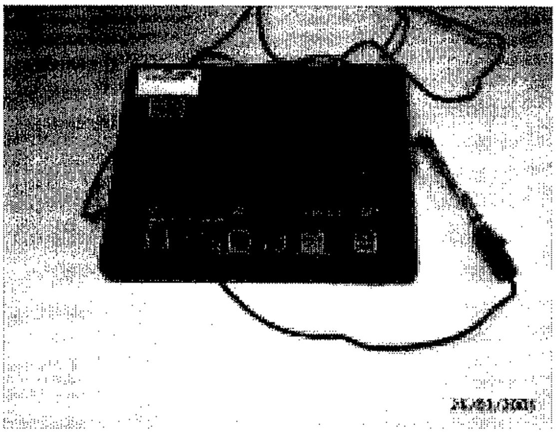

Figure 6 : pH meter

3.2.2 Startup Of Experiment

The water bath shaker (refer to Figure 7) is going to be used for the Fenton reaction to take place. The water bath shaker's temperature is set as 308 C and the shaker is set as 20 rpm. The conical flasks containing amine wastes are inserted into the water bath shaker. The clock is set so that the interval of 2 hours is supervised.

Figure 7 : Water bath shaker

3.2.3 Fenton Reaction

With all the conical flasks in the water bath shaker , the experiment can be started. For each ratio of ferum to hydrogen peroxide , ferum is added first then the respective amount of hydrogen are added bit by bit throughout the experiment. Every ten minutes , one ml of each sample is taken and diluted with 500 ml of distilled water. Then , two ml of each dilutions are inserted into COD vials to be taken for readings. The COD values can be read using the (refer to figure)

3.2.4Reaction Without Ferum as the catalyst

The experiment is repeated with new samples inserted into the water bath shaker.
The hydrogen peroxide amount for this part of experiment are the same amount used as in the ratios calculated before. However , ferum is not added into the conical flasks containing amine waste samples.

The acidic condition of the samples are still maintained with the pH of 2-3 . The purpose of this part of experiment is to study the COD reduction without the addition of ferum as the catalyst.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 CHARACTERISTICS OF AMINE WASTE

The amine waste used as the samples in this experiment were highly alkaline solutions. Strong acid such as Sulphuric acid was used to bring out the pH of the solution to reach 2-3 so that an acidic sample was produced for the Fenton reaction to take place. Acid was added bit by bit so that the pH would not drop below the desired pH range. Fenton reaction needs an acidic pH so that the reaction can occur. The color of amine waste was colourless without odor . As the ferum as the catalyst was added to the samples, the color changed into slightly greenish and when the samples were placed in the water bath shaker for the experiment to proceed , the samples turned dark and when the Fenton reaction was complete (after 120 minutes) the samples turned greenish again. The COD values of the samples were divided by 500 to simplify calculation and to show a better trend of COD value reduction versus time.

4.2 COD REDUCTION WITH THE ADDITION OF FERUM AS THE CATALYST

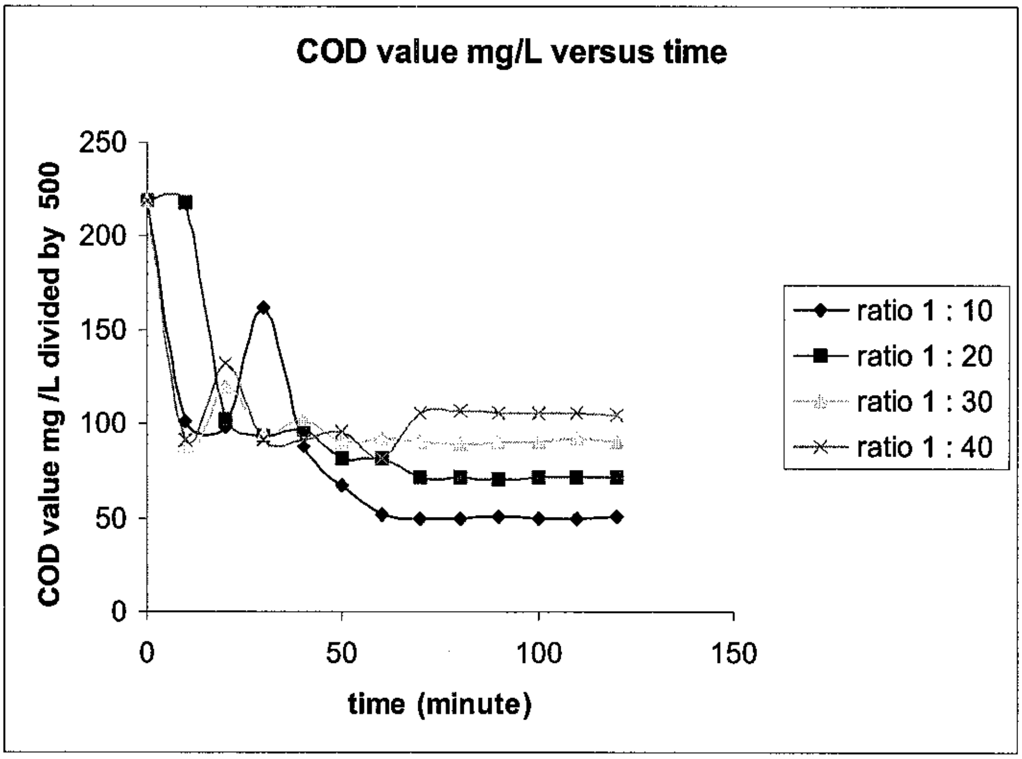

Figure 8 : Graph of COD value versus time with the addition Ferum as the catalyst

Graph shows COD value reduction of amine waste from initial value of 219 mg/L. The graph is plotted Ferum is used as the catalyst. The reaction time is 120 minutes where at 120 minutes , the COD reading become almost consistent.

The graph shows the average value of COD value versus time where the COD value reduction of amine waste was repeated three times and the COD readings obtained were in the same range according to minutes where the COD values taken. The results are shown in Table and Graphs in appendices. Therefore , here an average value of the graphs is presented to show the reduction trend.

The actual values obtained are times 500 because of the 500 dilution of amine waste with water before taking the COD reading. These values are very high and therefore, for the

purpose of calculation, the values are divided by 500 before hand.

As mandated by environmental laws, COD value of the range < 100 mg /l is allowed to be contained in effluent water. (Md Isa et. al., 2004) The purpose of Fenton reaction is to reduce this COD value to the allowable COD range. However, in the laboratory scale, the amount and the strength of the hydrogen peroxide is not sufficient to reduce the COD value up to desired range. Therefore , the COD value is divided by 500 to give the view of the reduction desired. However, in the industrial scale, stronger hydrogen peroxide is required. Therefore the COD value ratio of the laboratory compared to real industrial condition is assumed as 500 : 1 .

From the graphs above , they all seemed to give the same trend. After the 70 minutes time, the readings became linear. Therefore , the reaction time was about 70 minutes. The lowest COD recorded was 49 mg /L . It was observed with the 1 :10 ratio of Fe : H_2O_2.

Therefore the reduction is about

$[(219 - 49) / 219] * 100 \% = 77.6 \%$.

The optimum ratio obtained was in an acceptable range. The typical Fe : H_2O_2 range is about 1 : 10 – 1: 20 . (Application of a New Fenton Process without Sludge Production for the Treatment of Non Biodegradable Wastewater , Patrick Francoisse and Karl Heinz Gregor page 209)

4.3 COD VALUE REDUCITON OF AMINE WASTE WITHOUT THE ADDITION OF FERUM AS THE CATALYST

4.3.1 8.22 ml of Hydrogen Peroxide Used

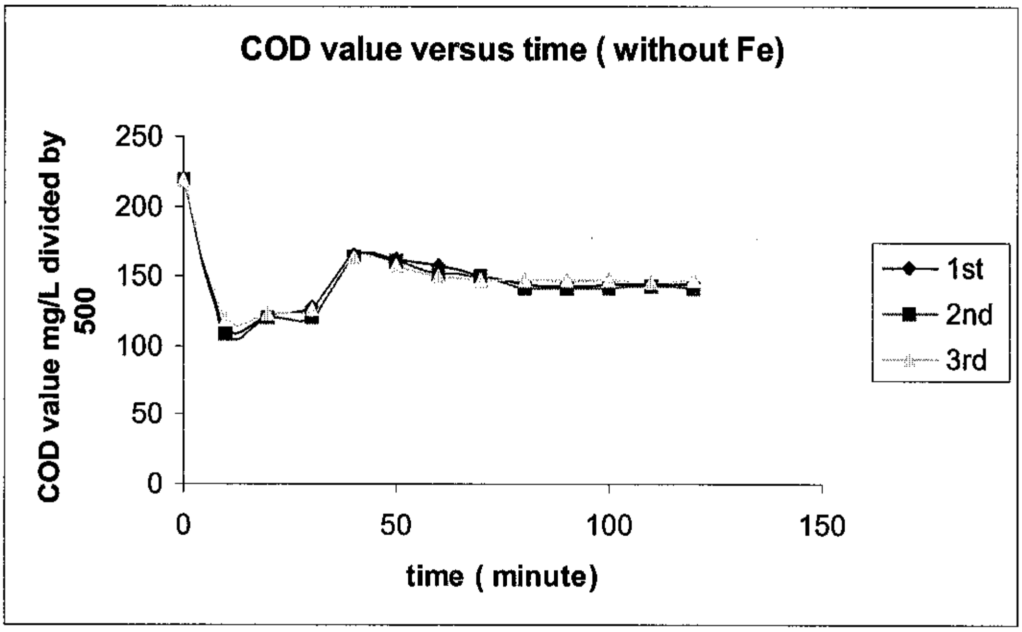

Figure 9 : Graph of COD value versus time with 8.22 ml of Hydrogen Peroxide used

Graph shows the COD value versus time of 8.22 ml of Hydrogen peroxide used as the oxidation agent. The amount of hydrogen peroxide used is equivalent to the amount of 1 :10 ratio of Fe_{2+} : H_2O_2 from the previous experiment without the addition of ferum as the catalyst. The amount hydrogen peroxide used in this part of the experiment reduced the COD value up to 147 mg/L from the initial value of 219 mg/L. The percent reduction was about [(219 – 147) / 219] = 32. 88 % . The experiment was repeated in 1st , 2nd and 3rd trial as shown in the graph. The COD value according to the minute taken were in the same range even if repeated three times. Therefore , the results were reliable.

4.3.2 16. 44 ml of Hydrogen Peroxide Used

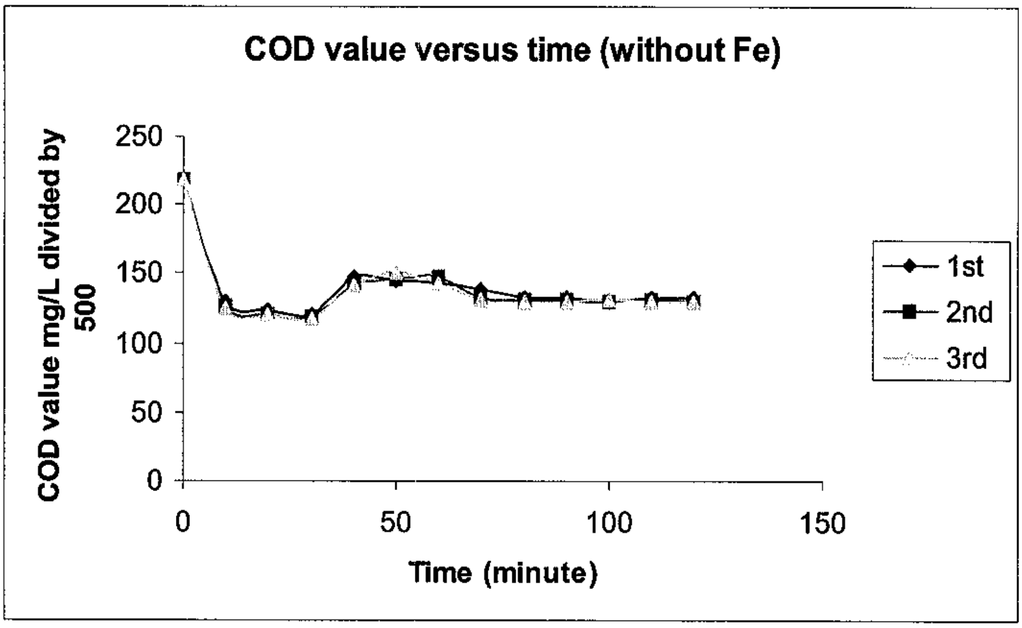

Figure 10 : Graph of COD value versus time with 16.44 ml of Hydrogen Peroxide used

From graph , the amount of hydrogen peroxide used is equivalent to the amount of hydrogen used where the ratio of Fe^{2+} : H_2O_2 was 1 : 20. The results are COD value versus time. The experiment is repeated three times in trial 1st , 2nd and 3rd. The values obtained were in the same range. The results can be viewed in (table) in appendices. From all the trials , the lowest COD value was 130 mg/L from the initial value of 219 mg /L. The percentage reduction is ; [(219 – 130) / 130] = 40. 64 % .

4.3.3 24. 63 ml of Hydrogen Peroxide Used

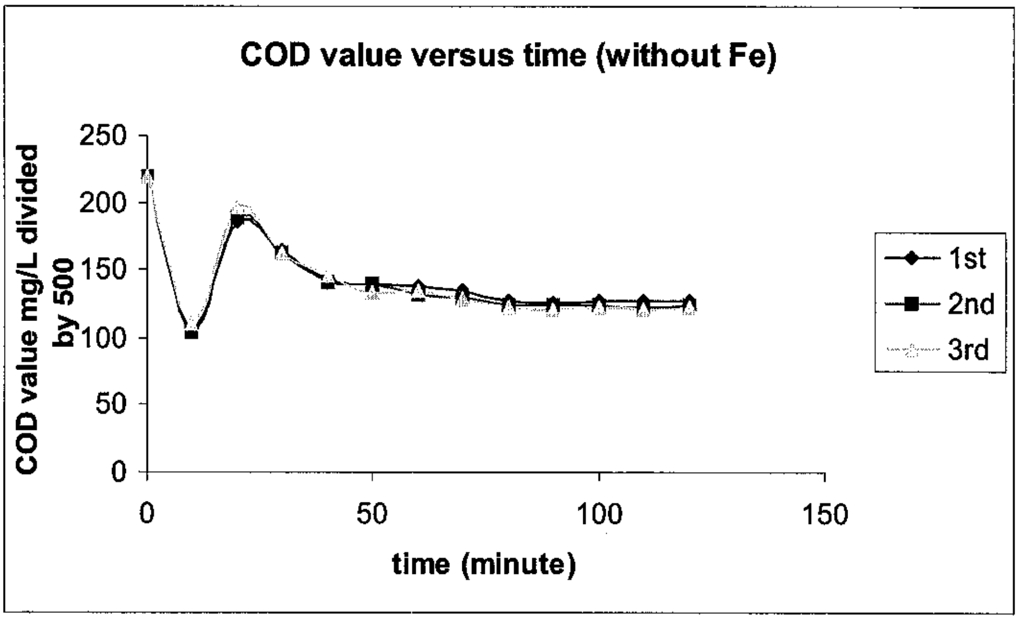

Figure 11 : Graph of COD value versus time with 24.63 ml of Hydrogen Peroxide used

From graph , the trend shows the COD value versus time. The amount of hydrogen peroxide used is equivalent to the amount of hydrogen peroxide used in 1 :30 ratio of Fe2+ : H_2O_2, without the addition of Ferum as the catalyst. The 1st , 2nd and 3rd experiment give results in the same range. (results are shown in table) . The lowest COD value obtained was 121 mg/L from the initial value of 219 mg/L . The percentage reduction is ; [(219 – 121) / (219)] = 44.75 % .

4.3.4 32.88 Of Hydrogen Peroxide Used

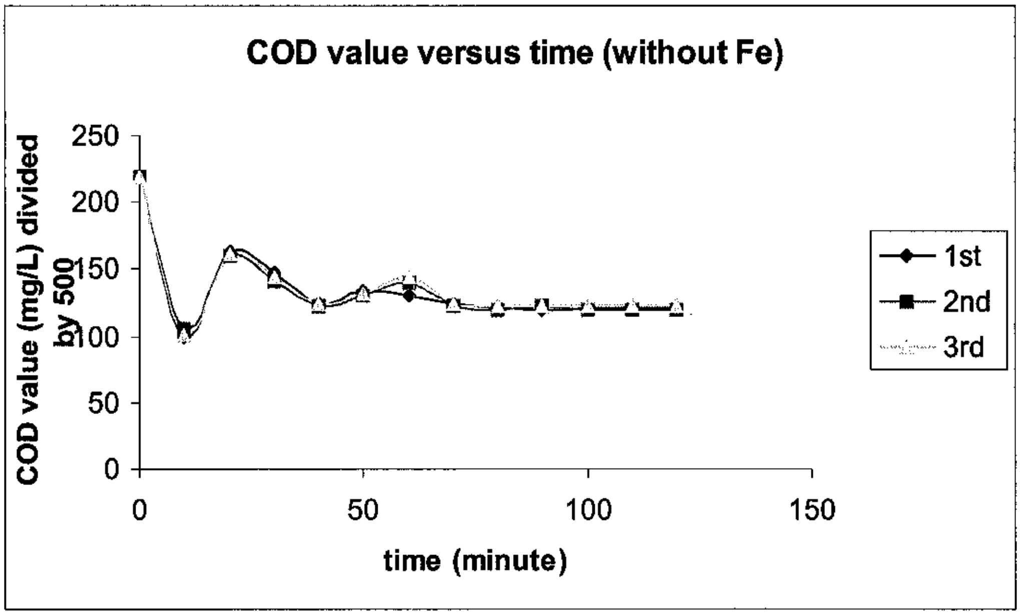

Figure : Graph of COD value versus time with 32.88 ml of Hydrogen Peroxide used.

From graph , the trend shows the COD value versus time. The amount of hydrogen peroxide used is equivalent to the amount of hydrogen peroxide used in the 1 : 40 ratio of Fe^{2+} : H_2O_2 , without the addition of Ferum as the catalyst. The 1st , 2nd and 3rd experiment give results in the same range. (results are shown in table) . The lowest COD value obtained was 119 mg/L from initial value of 219 mg/L. The percentage reduction is; [(219 – 119) /219] = 45.66 % .

For this experiment, without the addition of Fe as the catalyst, the reaction gave lower COD value reduction. The lowest COD value was 119 mg/L with the addition of 32.88 ml of H_2O_2.

The percentage reduction was ;

(219 – 119) / 219 = 45.66 %

This percentage reduction is far less if compared to the previous experiment where Fe was added. The experiment was repeated three times for each amount of H_2O_2 added to the amine solution. The purpose was to see if the first result was reliable of not. The results were reliable because even if the experiment was repeated three times, the results did not show much difference.

.From the graphs, the more H_2O_2 was added, the more COD value was reduced. However, the lowest value obtained was far greater than obtained from the previous where Fe was added. Besides that, the economics of the Fenton reaction depends on the cost of H_2O_2 used. Without the addition of Fe, a lot of H_2O_2 is needed for the same reduction of COD value. Therefore, it is not economical. However, following the addition of Fe requires the consideration of Fe sludge control.

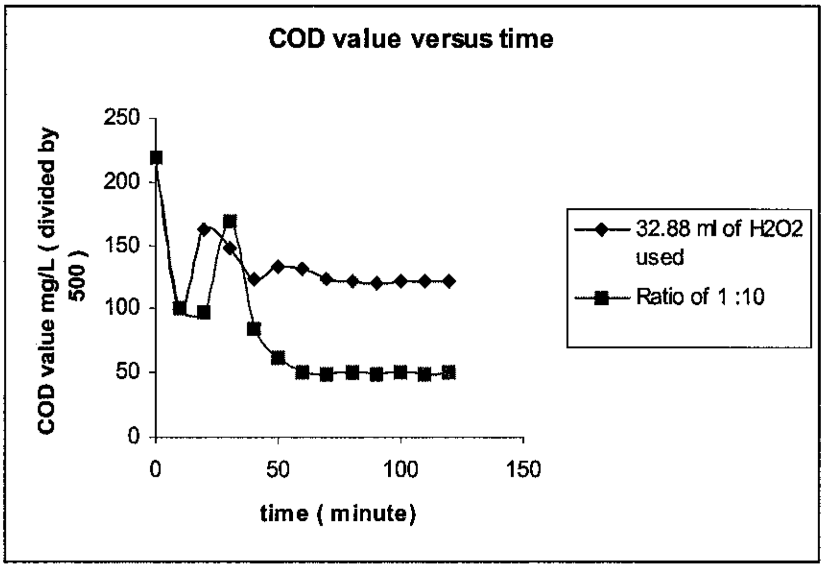

Figure 13 : Graph Of COD value reduction with/ without the addition of Ferum

Graph shows comparison that can be made when using Ferum as the catalyst . Ferum will help to reduce the COD further with less amount hydrogen peroxide used. The 1: 10 ratio of Fe_{2+} : H_2O_2 only contains 8.22 ml of hydrogen peroxide but has the potential of reducing the COD value much more that 32.88 ml of hydrogen peroxide which is used alone without the addition of Ferum as the catalyst

The experiment was done on a laboratory scale and the results obtained where in the laboratory range and capabilities. In industry , stronger hydrogen peroxide needs to be used to reduce the COD value up to <100 mg/l which is the allowable COD value range for effluent water as mandated by the environmental laws. (Md Isa et. al ., 2004)

This experiment did not cover other effects that might enhance the Fenton reaction. Other effects includes ; iron type used , temperature, pH and UV light. The results obtained did not have the effects of these parameters because they were kept constant. The only parameter used where the increasing concentration of hydrogen peroxide and the addition of Fe^{2+} . For more effective results all the parameters should have considered in the experiment and effect of each studied . However , from the observation , addition of Fe^{2+} enhanced the Fenton reaction.With increasing Hydrogen peroxide addition , the less the COD value became.

From theory , it does not matter whether Fe^{2+} or Fe^{3+} is used as the catalyst. However , with low dosage of Fenton Reagent used, some experts believe that ferrous iron is preferred. It also does not matter whether a chloride or sulphate salt of iron is used , although with chloride, chlorine may be generated with high rates of application.

Also , most commercial application of Fenton's Reagent occur at temperatures between 20 to 40 C.

The optimal pH for a photo –Fenton process occurs between pH 3 – pH 6. If the pH is too high, the iron precipitates as $Fe(OH)_3$ and catalyzes the H_2O_2 to oxygen, and will be very dangerous.

The pH used in the experiment was around 3 which is in the desirable range.

The UV light plays two different roles. First , it will produce more hydroxyl radicals and recover the Fe (II) needed in the Fenton reaction. The photo – Fenton may involve direct photolysis of Ferric Iron or photolysis of Fe (III) peroxy complexes. Secondly, it will drive ligand to metal charge transfer in the potentially complexes formed by Fe(III) and organics, which is a process well known for complexes formed between Fe (III) and carboxylic acid moiety. Large quantities of carboxylic acid are expected to be formed as degradation intermediates of the original organic substrate. The UV light parameter was not studied in this experiment .

Therefore , with the mentioned parameters kept constant , it will be beneficial to use Fe^{2+} as the catalyst so that less hydrogen peroxide will be used. However , for industrial application, the factors above should be considered so that COD value reduction will be more effective.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Fe^{2+} as the catalyst will results in a higher COD value reduction if compared to the increasing hydrogen peroxide addition without the catalyst present. For a beneficial purpose , the amount of hydrogen peroxide used can be optimized with the amount of catalyst addition. Therefore , less hydrogen peroxide is used. Other parameters such as iron type used , temperature, pH and UV light are kept constant throughout the experiment.

5.2 RECOMMENDATION

Treatment of effluent with using activated sludge is effective and not expensive. Industrial effluents contain organic pollutant that are toxic even to microorganisms and cannot be treated with biological methods. Therefore it is important to find a solution to pretreat the effluent water before it can be further treated with biological methods.

Although it is very effective to decrease COD, TOC , color and toxicity, Fenton Reaction has its own limitation which is the iron sludge production which contains contaminants that will seriously interfere with landfill or deposit. The development of Advanced Oxidation Process (AOP) has led to sophisticated technologies (UV, ozone , ultrasound , etc.) restricts the applicability pf these processes.

In 1992, a modified Fenton process has been presented that concentrates on sludge production control. It is named (FSR) **Fenton Sludge Recycling** process. In the meantime, this process has been developed on the pilot scale and run to treat highly loaded and refractory industrial wastewater. The FSR process involves ; oxidation of organic pollutants , precipitation and sludge separation and recycling or iron. This FSR process is very effective sludge control. Therefore, this process is a way for running the Fenton process without sludge production. (Francoisse et. al ., 1992)

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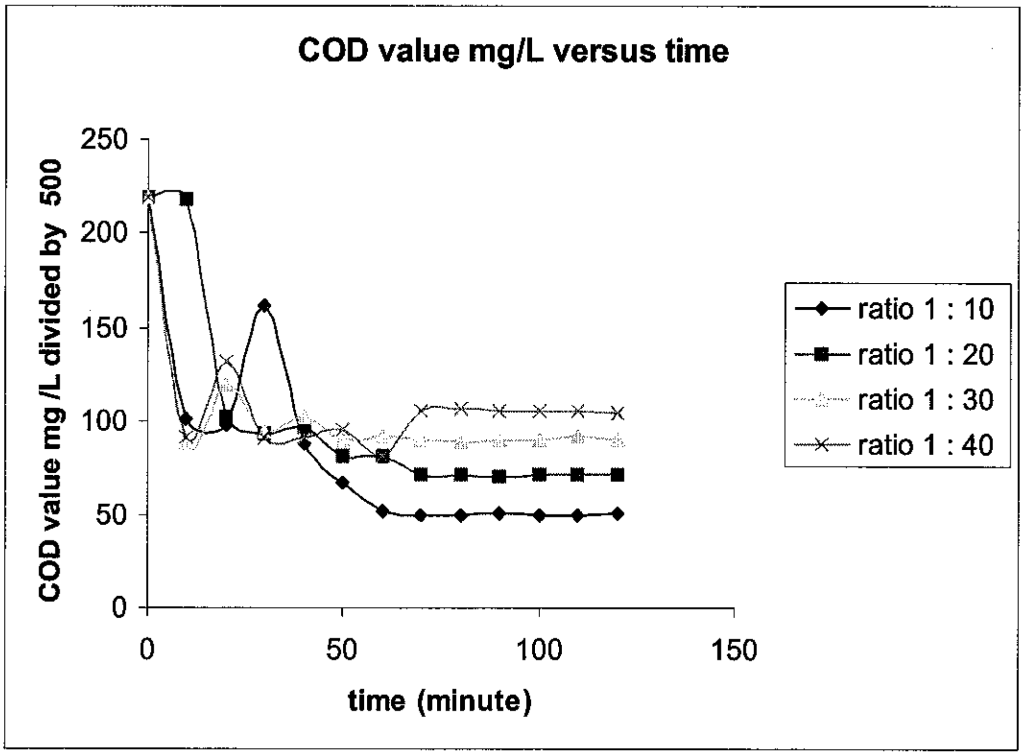
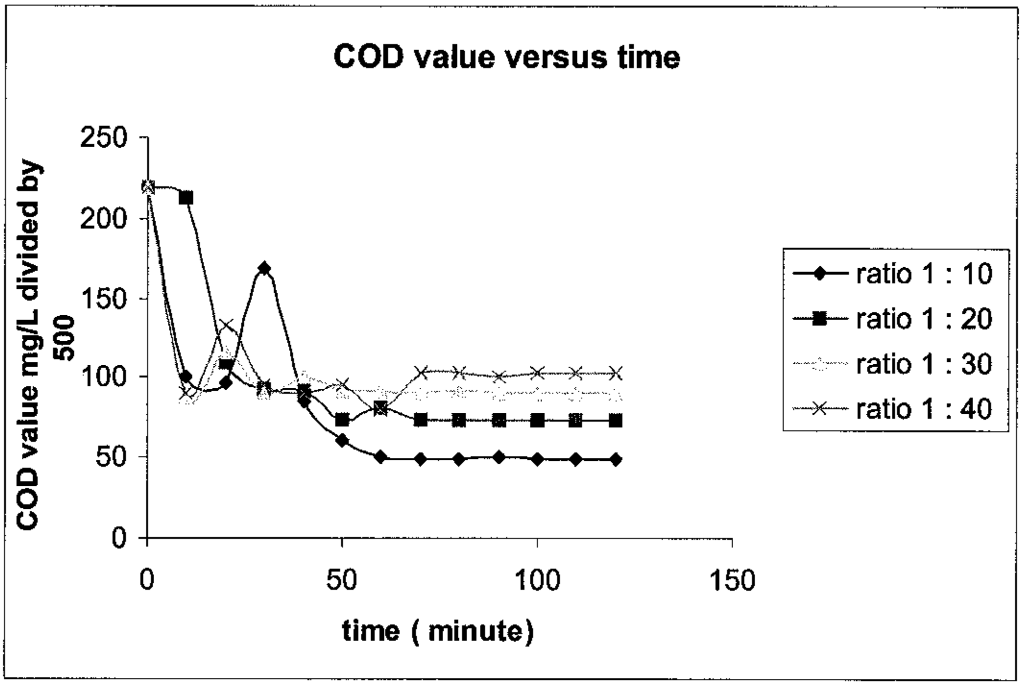
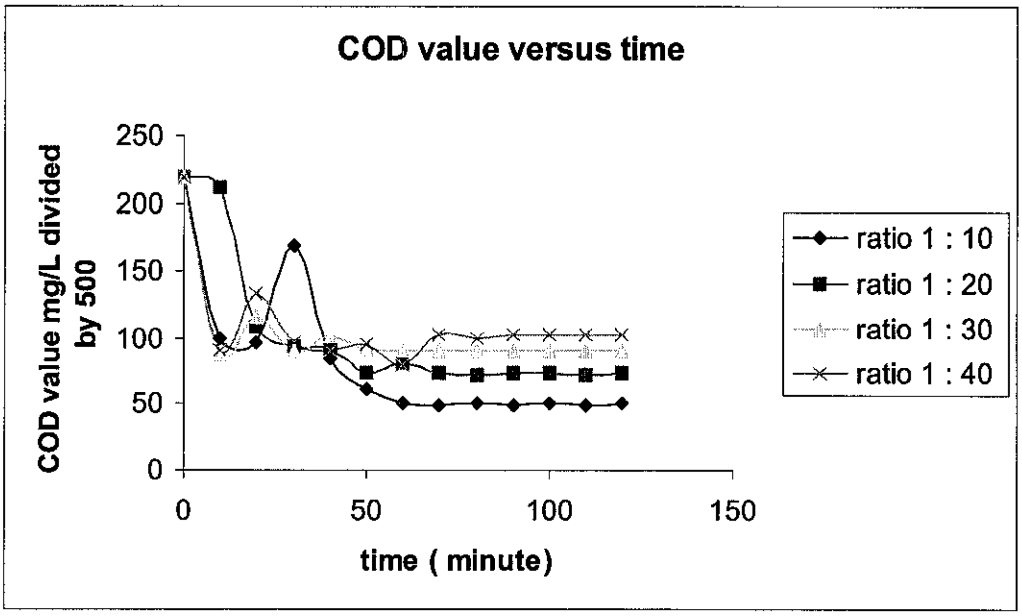
APPENDICES

- **APPENDIX A Graphs Of COD value versus time with the addition of Ferum as the catalyst**
- **APPENDIX B Tables of COD value with the addition of Ferum as the catalyst**
- **APPENDIX C Tables of COD value without the addition of Ferum as the catalyst**

APPENDIX A


COD value mg/L versus time
COD value mg /L divided by 500
250
200
150
100
50
0
0
50
100
150
time (minute)
ratio 1 : 10
ratio 1 : 20
ratio 1 : 30
ratio 1 : 40


COD value versus time
COD value mg/L divided by 500
250
200
150
100
50
0
0
50
100
150
time (minute)
ratio 1 : 10
ratio 1 : 20
ratio 1 : 30
ratio 1 : 40


COD value versus time
COD value mg/L divided by 500
250
200
150
100
50
0
0
50
100
150
time (minute)
ratio 1 : 10
ratio 1 : 20
ratio 1 : 30
ratio 1 : 40

APPENDIX B

COD reading mg/L divided by 500				
time (minute)/ratio	1 : 1 0	1:20	1:30	1:40
0	219	219	219	219
10	101	218	88	91
20	98	102	120	132
30	162	94	95	91
40	88	97	102	91
50	67	82	90	96
60	52	82	93	81
70	50	72	90	106
80	50	72	89	207
90	51	71	90	106
100	50	72	90	106
110	50	72	92	106
120	51	72	90	105

COD Readings mg/L divided by 500				
time (minute) / ratio	1:10	1:20	1:30	1:40
0	219	219	219	219
10	100	212	87	90
20	97	109	116	133
30	169	93	90	96
40	85	92	101	90
50	61	73	92	95
60	50	81	91	80
70	49	73	90	103
80	49	73	91	103

90	50	73	90	101
100	49	73	90	103
110	49	73	90	103
120	49	73	90	103

COD readings mg L divided by 500				
time (minute) /ratio	1:10	1:20	1:30	1:40
0	219	219	219	219
10	100	212	87	90
20	97	109	116	133
30	169	93	90	96
40	85	92	101	90
50	61	73	92	95
60	50	81	91	80
70	49	73	90	103
80	50	72	90	100
90	49	73	90	103
100	50	73	90	103
110	49	72	91	102
120	50	73	90	103

APPENDIX C

Table : 8.22 ml H_2O_2 Used

H_2O_2 in ml	COD value in mg/L divided by 500		
time(minute)	1st	2nd	3rd
0	219	219	219
10	113	108	119
20	122	121	124
30	128	121	127
40	165	163	164
50	162	161	158
60	158	152	150
70	150	151	148
80	144	142	147
90	143	141	147
100	144	142	147
110	144	143	146
120	144	142	147

Table : 16.44 ml of H_2O_2 Used

H_2O_2 in ml	COD value in mg/L divided by 500		
time(minute)	1st	2nd	3rd
0	219	219	219
10	129	127	125
20	123	121	120
30	120	119	118

40	148	141	142
50	145	146	150
60	143	147	143
70	139	132	131
80	132	131	130
90	132	131	130
100	131	130	131
110	132	131	130
120	132	130	130

Table : 24. 63 ml of H_2O_2 Used

H_2O_2 in ml		COD value in mg/L divided by 500	
time(minute)	1st	2nd	3rd
0	219	219	219
10	107	105	110
20	185	189	197
30	164	162	163
40	143	141	145
50	140	139	133
60	138	132	135
70	135	130	129
80	127	125	122
90	126	124	121
100	127	124	122
110	127	123	121
120	127	124	122

Table : 32.88 ml of H_2O_2 Used

H2O2 in ml	COD value in mg/L		
time(minute)	1st	2nd	3rd
0	219	219	219
10	100	105	101
20	163	160	162
30	147	142	145
40	124	122	125
50	133	130	132
60	131	139	144
70	124	122	125
80	121	119	123
90	120	122	123
100	121	120	122
110	121	119	123
120	121	119	122