

**Advance Oxidation of MDEA Using Fenton Reagent**

by

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

JANUARY 2009

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## CERTIFICATION OF APPROVAL

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A project dissertation submitted to the  
Chemical Engineering Programme  
Universiti Teknologi PETRONAS  
In partial fulfilment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
(CHEMICAL ENGINEERING)

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## CERTIFICATION OF ORIGINALITY

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



VICKNESH THANABAL

## ABSTRACT

Methyl Diethanolamine is widely used as a decarbonizer and Sweating agent in chemical, oil refinery, Gas synthesis, Natural gas & gas. After a few cycle operations, the MDEA becomes severely contaminated and loses its effectiveness and considered spent. This required replacement with the new MDEA. The spent MDEA may be sent to reclaimer for recovery. This is economically non profitable to the company because this required plant shut down that made the whole process to stop. Currently choose to clean the dehydration system at considerable cost, which produces large amounts of waste contain MDEA is more preferred method financial wise. Due to the problem, we need to find an optimize condition base on

1. Concentration of  $H_2O_2$  and  $FeSO_4$
2. Initial concentration of MDEA

in order to reduce its COD level and enable it for further treat in the biology treatment compartment. For this first experiment our task was to find the optimum ratio of hydrogen peroxide ( $H_2O_2$ ) solution and iron catalyst need to be used to get an optimum operating condition of decreasing the COD level.

## **ACKNOWLEDGEMENT**

My greatest thank you goes to God for taking care of me while I was undergoing my experiments, and helped me overcome any problem that arises. Also would like to express my gratitude and appreciation to my parents, and my siblings for the moral support and blessing that they gave all this while, it has been a great help.

A special note of thanks and appreciation goes to my very own FYP supervisor, AP Dr. Saikat maitra. He has been a great and unexceptional tutor and a good mentor who never fails to guide and share his vast knowledge and experiences with me at all times throughout the completion of this project. He has taught me patiently, and gave me full support to successfully complete this project.

I am also grateful to all other lab technicians. They had given me constant guidance and assistance to me in the lab especially during my difficulties with the equipment. Besides that, I would also express my gratitude to my friends and colleagues for the moral support and also the guidance for all this while. A simply 'thank you' is not enough to express my gratitude to all for their warm hospitality, guidance and support. Without all of you, I won't be able to achieve what I have now.

Last, but certainly not least, I would like to apologize if any party was inadvertently excluded from being mentioned above and would like to thank all parties that were involved in making this project a success.

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# CHAPTER 1

## INTRODUCTION

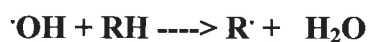
### 1.1 Background of Study

#### 1.1.1 Advance Oxidation

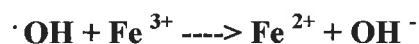
Advanced oxidation process (AOP) is one of the methods of treatment for the contaminated surface and ground water. The main reason behind this process is to break down the toxic and biorefractory organic pollutants found in industrial wastewater and in landfill into a smaller structure which is less harm to the environment. The idea behind this process is by the generation of very high oxidizing agents such as hydroxyl radicals to attack the long chain molecular structure and break it into smaller structure. They are few other method beside Advanced Oxidation Process for the AOP treatment methods include the use of ozone, UV, ozone in combination with UV ,ozone plus hydrogen peroxide, hydrogen peroxide and UV, Fenton's reagent and photo catalysis.

#### 1.1.2 Fenton's reagent

Fenton's reagent is known as one of the most effective and most often used substance in oxidation process and it also widely been used in the industry even today. Fenton's reagent is a combination of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution and iron catalyst which is used to oxidize contaminants of waste water. The process may be applied so that the polluted water can be biodegradability improvement by breaking the huge chemical structure into simpler form that later on can be treated in biological stream. This method also can be used to remove odor and color from the waste water. Reaction equation of Fenton's reagent



For complete mineralization high doses of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> are generally required because the regeneration of Fe<sup>2+</sup> ion is relatively slow



The procedure requires a range of pH which is between 3 to 4 for an optimize reaction. The reaction rates with Fenton's reagent are generally limited by the rate of ·OH generation (concentration of iron catalyst) and less so by the specific wastewater being treated. In this process we usually try to reduce the usage of iron catalyst because the reaction will form Iron (III) which a brown solid that need another treatment later on.

According to a journal written by Idil Arslan Alaton and Senem Teksoy (Acid dyebath effluent pre-treatment using Fenton's reagent: Process optimization, reaction kinetics and effects on acute toxicity; ELSEVIER) Fenton's reagent is the most effective and most commonly be used in the treatment of textile dyes and dyehouse effluent. According to the present study been made, a synthetic acid dybath effluent (SADB) bearing two azo and one anthraquinone dye together with two dye auxiliaries was subjected to pre-treatment with Fenton's reagent. Firstly, initial Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations as well as pH were optimized to achieve highest COD and colour removals during Fenton's treatment of SADB. In the second stage of the experiment work, kinetic studies were conducted to elucidate the effect of operating temperature (20°C < T < 60°C) on COD, colour adatement and H<sub>2</sub>O<sub>2</sub> consumption kinetics.

Obtained result indicates that 30% COD and practically complete colour removal (99%) could be achieve at T= 50°C. The kinetic studies revealed that a strong

correlation existed between COD removal and H<sub>2</sub>O<sub>2</sub> utilization rates. In the final part of the study, the acute toxicity of raw (untreated) and pre-treated SADB on heterotrophic biomass was investigated employing a modified (COD balanced), activated sludge inhibition test. The toxicity experiment demonstrated that the inhibitory effect of SADB toward sewage sludge could be completely eliminated when the effluent was pre-treated with Fenton's reagent.

The usage of the oxidation method is not only been applied in the textile dyes but also in other industry. In the pharmaceutical industry, there are four different types of manufacturing process which is fermentation, chemical synthesis, extraction and formulation. This process often generates moderate-to-high strength wastewater exerting seasonal and operational variations in effluent quality and quantity. Among the effluents originating from different operations in this industry, drug formulation effluent is characterized not only by low wastewater production rates but also extremely poor biodegradability and even toxicity caused by the active ingredient being formulated batch-wise. Particularly those effluents arising from the antibiotic formulation process contain high concentrations of refractory chemicals that lead to the complete inhibition of activated sludge treatment systems as well as to toxic effects on aquatic organisms in the water bodies receiving these effluents. Hence, chemical pre-treatment is often required prior to discharge into sewage system treatment system.

According to journal on "Photo-Fenton-like and photo-fenton-like oxidation of Procaine Penicillin G formulation effluent, (Arslan-Alaton, F.Gurses), Journal of Photochemistry and Photobiology A:Chemistry", numerous researchers have evaluated the treatment of refractory organic pollutants found in groundwater, surface water and industrial wastewater by so-called advanced oxidation process. Advance oxidation process is of great interest for the treatment of contaminated surface and ground-water and for the destruction of toxic and bio-refractory organic pollutants found in industry wastewater and in landfill leachate. Advanced oxidation processes rely on the generation of very reactive oxidizing agent that will produce free radicals such as the hydroxyl radical can initiate oxidative degradation reactions of refractory

synthetic and nature organic compounds and is capable of mineralizing them ultimately to CO<sub>2</sub> and H<sub>2</sub>O owing to their high oxidation potential which is +2.80 eV versus NHE in aqueous solution.

There are several oxidative process involving iron compounds and hydrogen peroxide to provide alternative way of hydroxyl radical generation. Direct photolysis of H<sub>2</sub>O<sub>2</sub> produce hydroxyl radical, however because of the fact that H<sub>2</sub>O<sub>2</sub> only weakly absorbs solar radiation, hydroxyl radical formation by this process is very slow. H<sub>2</sub>O<sub>2</sub> though, can serve as a hydroxyl radical source through pathways involving iron salts or oxides. The reaction of H<sub>2</sub>O<sub>2</sub> with Iron (III)/Ferric and Iron (II)/Ferrous in acidic aqueous solutions which are among the most common homogeneous system and potential sources of hydroxyl radicals generation.

Iron-catalyzed decomposition known as the Fenton's reaction provides an alternative way of oxidizing recalcitrant and toxic organic compounds present in the most industry wastewaters.

### 1.1.3 Amine

Amine is an organic compounds and a type of functional group that contain nitrogen as the key atom. Structurally amines resemble ammonia, wherein one or more hydrogen atoms are replaced by organic substituent such as alkyl and aryl groups.

Basically, there are three types of amines:

- **Primary amines** arise when one of three hydrogen atoms in ammonia is replaced by an organic substituent.
- **Secondary amines** have two organic substituents bound to N together with one hydrogen.
- **Tertiary amines** all three hydrogen atoms are replaced by organic substituents.

Note: the subscripts on the **R** groups are simply used to differentiate the organic substituents .

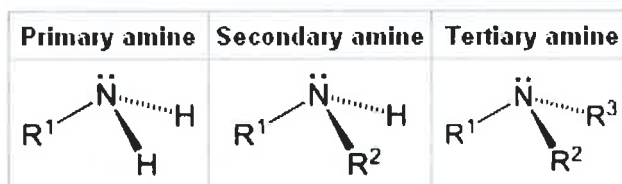
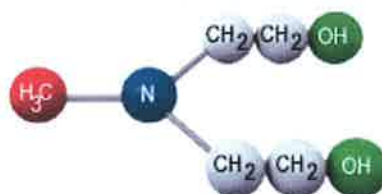


Figure 1: Types of Amine structure



MDEA: methyldiethanolamine

Figure 1: MDEA Molecule structure

## 1.2 Problem Statement

Treatment of Methyl Diethanolamine had been a big problem to company like DOA, BASF and PETRONAS because of the high chemical oxygen demand (COD) level that makes it possible to be treated through biological treatment packages. During the gas purification in the oil and gas industry, MDEA will be produce as a waste product. Due to the high range of COD concentration, it is impossible for it to be treated in the biological treatment compartment. Our task was to break down the MDEA component using Fenton's treatment to form carbon dioxide, water and NH<sub>3</sub>. In Malaysia, the two major company that produce MDEA as their waste component

was DAO and BASF industry. MDEA or known as Methyl Diethanolamine is a clear, colorless or pale yellow liquid. MDEA component can't directly be treated in the biological treatment compartment because biological treatment unit have a certain range of COD operating value. MDEA have higher COD value that excide the range of normal operating condition of the system.

### **1.3 Objectives and Scope of Study**

Methyl Diethanolamine is widely used as a decarbonizer and Sweating agent in chemical, oil refinery, Gas synthesis, Natural gas & gas. After a few cycle operations, the MDEA becomes severely contaminated and loses its effectiveness and considered spent. This required replacement with the new MDEA. The spent MDEA may be sent to reclaimer for recovery. This is economically non profitable to the company because this required plant shut down that made the whole process to stop. Currently choose to clean the dehydration system at considerable cost, which produces large amounts of waste contain MDEA is more preferred method financial wise. Due to the problem, we need to find an optimize condition base on

1. Concentration of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>
2. Initial concentration of MDEA

in order to reduce its COD level and enable it for further treat in the biology treatment compartment. For this first experiment our task was to find the optimum ratio of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution and iron catalyst need to be used to get an optimum operating condition of decreasing the COD level.

### **1.3.1 The relevance of the project**

MDEA or in scientific name known as Methyldiethanolamine are routinely used for the removal of carbon dioxide and hydrogen sulfide from natural gas in a packed or tray tower. Periodic cleaning of the tower is done by high speed water jet and the wastewater generated contains a significantly high concentration of the amine. This wastewater is toxic to bacteria and cannot be treated in a conventional treatment unit by biological oxidation. An alternative technique of treatment is advanced oxidation such as UV-H<sub>2</sub>O<sub>2</sub> or Fenton's reaction. In the present work, Fenton's reagent – a combination of ferrous sulfate and hydrogen peroxide – has been used to study the degradation of Methyldiethanolamine in wastewater. Degradation studies were carried out in a jacketed glass reactor. Samples were drawn from time to time and the COD was determined to follow the course of degradation. The rate of degradation declines above a pH of 4 because of decomposition of hydrogen peroxide. The concentration of ferrous sulfate, the amount of hydrogen peroxide and the initial concentration of MDEA are the important parameters that determine the rate of reaction. The effects of all these parameters have been studied. The reaction proceeds very fast at the beginning but the rate of degradation slows down at larger time.

## CHAPTER 2: LITERATURE REVIEW

### 2.1 Alkanolamine as Solvent

Most sour gas processing facilities separate hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) from raw gas through chemical absorption using alkanolamines (or "amines"). The prime alkanolamines are: monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA). The amine processes are cyclical involving both absorption and desorption steps-to reuse absorbents. Because these processes are closed loop, nonregenerable contaminants accumulate within the system and can cause reduced processing efficiencies and operational problems. Operational difficulties include: corrosion, foaming, solid deposition, losses of valuable amine and environmental problems. Gas plants that run with fresh solutions rarely experience any problems. Problems begin when contaminants build up in amine solutions. It is strongly recommended that gas plant solution quality is monitored and take preventive measures to keep solutions clean.

Alkanolamines in water solution are extensively used for scrubbing certain acidic gases. The most utilized alkanolamines for scrubbing acidic gases are monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA) and di-isopropanolamine (DIPA). The amines are regenerated in stripping tower for recycling back to the absorber. During shutdown and maintenance of these facilities, high concentrations of residual alkanolamine may be carried over into the wastewater, whereupon they can disturb the biological treatment system of the plant. Advanced oxidation processes (AOP's) have proved to be extremely effective in the degradation of high concentrations of organics which may be difficult to treat in a conventional biological oxidation unit. The more common AOP's use either H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> as the source materials for the generation of strongly oxidizing radicals such as hydroxyl



(HO<sup>•</sup>) and hydroperoxyl (HO<sub>2</sub><sup>•</sup>) in solution. Ultraviolet radiation or ferrous sulfate, separately or in combination, are used to initiate the process of generation of the oxidizing radicals. Fenton's reagent, a mixture of hydrogen peroxide and ferrous sulfate in aqueous solution, has proved to be more effective than UV-H<sub>2</sub>O<sub>2</sub> or UV-O<sub>3</sub> for most of the recalcitrant organics (Walling, C. 1975).

## 2.2 Natural Gas Processing

Natural gas is a major energy source in the world. It is one of the cleanest, safe, and most useful of all energy sources. World natural gas consumption rose by 3.1% in 2007 from 2834.4 billion cubic meters in 2006 to 2921.9 billion cubic meters. Malaysia, as one of the leading natural gas producers in the world, produced about 60.5 billion cubic meters of natural gas out of the total worldwide production 2940.0 cubic meters in 2007 (British Petroleum, 2008).

Raw natural gas typically consists primarily of methane (CH<sub>4</sub>), the shortest and lightest hydrocarbon molecule. It also contains varying amounts of ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>), normal butane (n-C<sub>4</sub>H<sub>10</sub>), isobutane (i-C<sub>4</sub>H<sub>10</sub>), pentanes and even higher molecular weight hydrocarbons. Other impurities such as acidic gases—carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and mercaptans such as methanethiol (CH<sub>3</sub>SH) and ethanethiol (C<sub>2</sub>H<sub>5</sub>SH)—and water vapor and also some nitrogen(N<sub>2</sub>) and helium(He) are present (Kohl and Nielsen, 1997) in natural gas.

It is well known that acidic gases in the presence of water are highly corrosive that can slowly damage the pipeline and equipment system. It also reduces the true heating value and eventually has effect on the price of natural gas. Concentration of acidic gases in the raw natural gas may vary from one source to another. Therefore, separation of acidic gas from raw natural gas is important to meet the natural gas standard in the market.

### 2.3 H<sub>2</sub>S and CO<sub>2</sub> Removal from Natural Gas

The primary gas purification processes generally belong to the following five categories (Kohl and Nielsen, 1997):

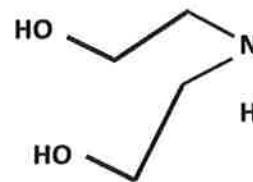
1. Absorption into a liquid
2. Adsorption on a solid
3. Permeation through a membrane
4. Chemical conversion to another compound
5. Condensation

Absorption is undoubtedly the single most important operation of gas purification processes. Aqueous alkanolamine is the most generally accepted and widely used solvent for capturing H<sub>2</sub>S and CO<sub>2</sub> from natural gas (Kohl and Nielsen, 1997). The amines that have proved to be of principal commercial interest for gas purification are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and di-isopropanolamine (DIPA).

Structural formula of alkanolamine contains two functional groups, which are the hydroxyl group and the amino group. The hydroxyl group will reduce the vapor pressure and increase the water solubility, while the amino group provides the necessary alkalinity in water solution to cause the absorption of acidic gas. The structural formula of the two model alkanolamines used in this work are shown below.

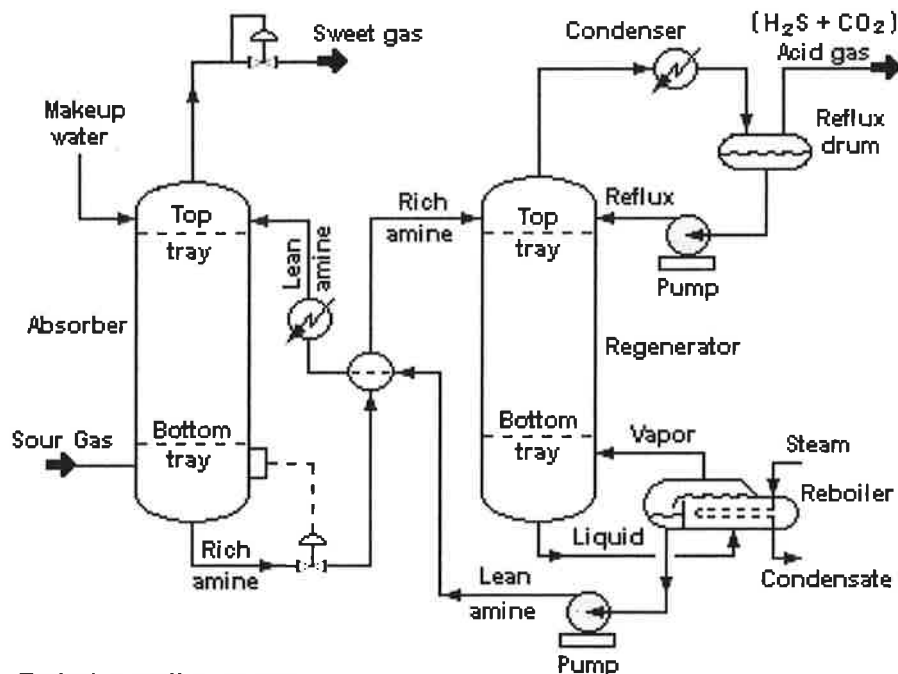


Monoethanolamine (MEA)



Diethanolamine (DEA)

Figure 2 Structural formula of Monoethanolamine (MEA) and Diethanolamine (DEA).



Typical operating ranges

Absorber : 35 to 50 °C and 5 to 205 atm of absolute pressure  
 Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure  
 at tower bottom

Figure 3 Flow diagram of a typical amine treating process (Wikipedia, the free encyclopedia)

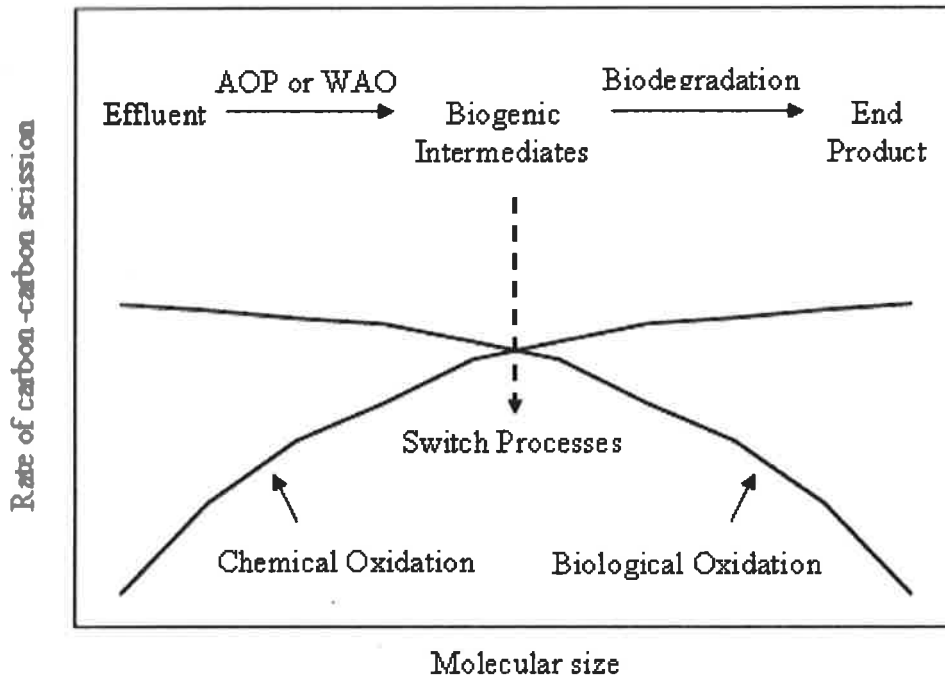
The basic flow arrangement of the alkanolamine acid gas absorption process is shown in Figure 1.2. Amine gas treating process includes an absorber unit and a regenerator unit as well as accessory equipment. In the absorber, the down flowing amine solution absorbs  $H_2S$  and  $CO_2$  from the up-flowing sour gas to produce a sweetened gas stream (i.e., an  $H_2S$ -free gas) as a product and an amine solution rich

in the absorbed acid gases. The resultant "rich" amine solution is then routed into the regenerator (a stripper with a reboiler) to produce regenerated or "lean" amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H<sub>2</sub>S and CO<sub>2</sub>. This H<sub>2</sub>S-rich stripped gas stream is then usually routed into a Claus process to convert it into elemental sulfur (Kohl and Nielsen, 1997). The CO<sub>2</sub> generated during desorption may be put to a number of uses including enhanced oil recovery (EOR).

#### **2. 4 The Hybrid Process: Advanced Oxidation followed by Biological Treatment**

Periodic cleaning of absorption and stripping towers in a natural gas processing plant will generate wastewater with a large portion of alkanolamine. High concentration of alkanolamine thus generated has low biodegradability or is often toxic to the bacteria and can not be treated in the conventional biological oxidation. An alternative technique is to partially degrade the amine by an advanced oxidation process (AOP's) such Fenton's reagent's ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ ) to generate smaller fragments of degradation products which are amenable to biological oxidation.

Coupling of chemical oxidation (AOP or wet air oxidation, WAO) as pre-treatment before biological oxidation as post-treatment is conceptually beneficial as it can lead to increased overall treatment efficiency (Mantzavinos, 2007; Jones, 1999; Koprivanac and Kusic, 2007). The concept is illustrated in Figure 2.3.



**Figure 4** The concept of coupling AOP-based pre-treatment with biological post-treatment (Mantzavinos, 2007).

## CHAPTER 3:

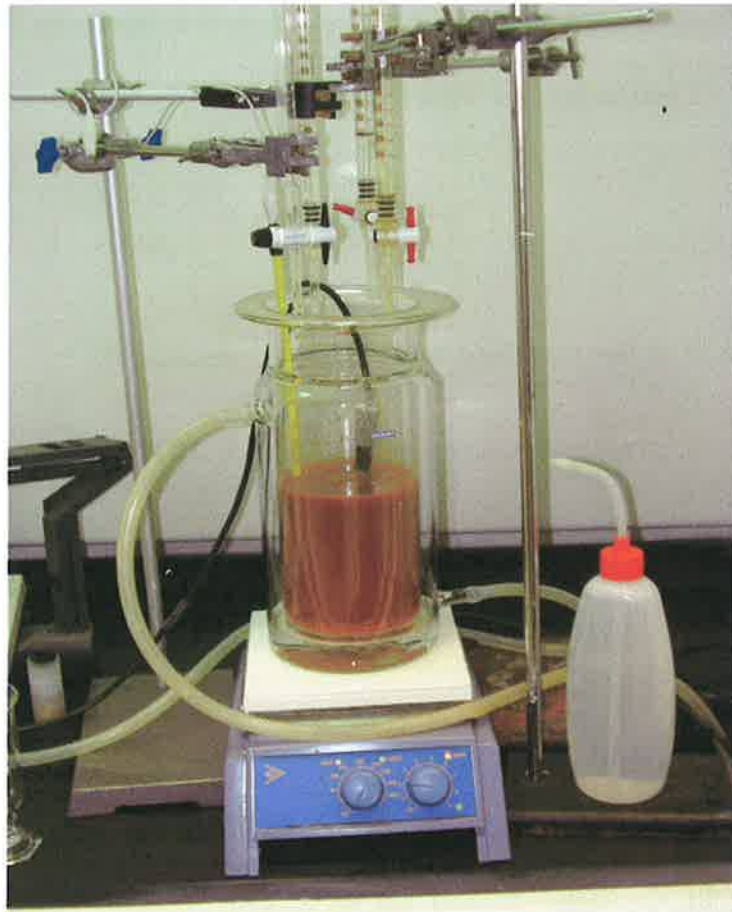
### METHODOLOGY

#### 3.1 Experimental set up

##### 3.1.1 Fenton's Oxidation Process

A stirred jacketed glass reactor was used to monitor the progress of Fenton's degradation reaction of the alkanolamine. A solution of the amine in desired concentration was prepared and  $H_2SO_4$  was added to it drop wise to adjust the pH to the desired value. The ferrous sulfate catalyst was added and the content was mixed well. This was followed by addition of requisite quantity of 30%  $H_2O_2$ . The reaction starts immediately and the temperature was maintained by circulating cooling water through the jacket. Samples of the liquid were withdrawn from time to time and the COD of the samples were measured following standard procedure using Hach 5000 spectrophotometer. Calibration of the Hach 5000 COD instrument was checked by measuring the COD of a 2.08mM potassium hydrogen phthalate.

Un-reacted  $H_2O_2$  present in a sample seriously interferes with COD measurement (Talinli and Anderson, 1992). Removal of the  $H_2O_2$  was done by warming a sample in a boiling water bath for 10 minutes after addition of 2 ml of 1(M) NaOH solution to 4 ml sample. The precipitated hydrated ferric oxide was removed by filtration using 0.45 $\mu$ m filter and the COD of the sample was measured. The change of volume of a sample at different stages was taken into account during COD calculation.



**Figure 5** Fenton's Process experimental set up

### **3.1.2 COD (Chemical Oxygen Demand) determination**

Chemical oxygen demand determination was performed using HACH analytical equipment Method 8000 that was approved by Standard Method for the Wastewater Analysis, USEPA. This parameter is very important to monitor the degradation of alkanolamine and the concentration of the test compound in bioreactor. Two ml of sample was oxidized using the standard chemical from HACH and digested at 150 °C for two hours on the DRB HACH digester. The COD reading was obtained by using

HACH DR 5000 spectrophotometer. The range of COD measurement is 0 – 1500 mg/L COD. Furthermore, COD removal at 30 minute was calculated by:

$$COD_{removal30} = \frac{COD_0 - COD_{30}}{COD_0} \times 100\%$$

where:  $COD_{removal30}$  = percentage of COD removal at 30 minute,

$COD_0$  = COD value at 0 minute, and

$COD_{30}$  = COD value at 30 minute

### 3.1.3 pH

The pH of the mixed liquor was measured using pH probe of HACH sens ion 1 pH meter. This pH meter was calibrated regularly. The pH of Fenton's process was used to monitor the oxidation process in the reactor, while pH of bioreactor to monitor the activity of microorganism in the bioreactor.



**Figure 6** List of solution according to time