Degradation of Diethanolamine (DEA) in solution using UV/H_2O_2

by

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Dissertation submitted in partial fulfilment of
the requirements for the
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CERTIFICATION OF APPROVAL

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In partial fulfilment of the requirement for the
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Approved by,

Jan 09, 2014
……………………………
(Prof Dr.T.Murugesan)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2014

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 excepts as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NUR MADIHAH BINTI YASER

ABSTRACT

In this project, the homogeneous advanced oxidation (AOP) process based on the generation of very reactive species such as hydroxyl radicals has been used for degrading Diethanolamine. With the presence of ultraviolet and hydrogen peroxide in this method, degradation of diethanolamine (DEA) in solution will be further studied. Other than that, the effects of initial hydrogen peroxide concentration, diethanolamine concentration, initial pH and temperature will be examined to determine the optimum condition for degrading diethanolamine. In most of petrochemical plant, amine-based CO_2 is used to capture carbon dioxide and hydrogen sulphide in the flue gas before it is released to the atmosphere. It is very important to remove carbon dioxide in the flue gas because releasing flue gas with carbon dioxide content to the atmosphere can increase greenhouse gases which then lead to serious environmental problem. An experiment in the laboratory will be conducted and the sample will be analysed by using total organic carbon (TOC) Shimadzu Model equipment to measure the total organic carbon after 4 hours degradation. The experiment conducted involved the effects of initial hydrogen peroxide concentration, initial diethanolamine concentration, initial pH and temperature to the DEA degradation by using UV/H_2O_2. Finally, optimization of DEA degradation is determined by using Portable_Statgraphics_Centurion 15.2.11.0 statistical software and also by doing experiment in laboratory.

ACKNOWLEDGEMENT

In the name of ALLAH the Most Merciful and The Most Compassionate,

First and foremost I would like to express my humble gratitude to Allah S.W.T, because of His blessings and guidance to me throughout my final year. I would also like to take this opportunity to express my sincerest gratitude to a number of people that have helped me throughout this project. Sincerely thank to Professor Dr.T.murugesan, who has been my supervisor and have supervised me throughput my project period. His ever willingness to teach and guide me has helped a lot in completing this project.

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ABBREVIATION AND NOMENCLATURE

AOP	Advamced Oxidation Process
CO_2	Carbon Dioxide
DEA	Diethanolamine
H_2O_2	Hydrogen Peroxide
HCl	Hydrochloric Acid
NaOH	Sodium Hydroxide
O_3	Ozonation
UV	Ultra Violet
RSM	Response Surface Methodology
TOC	Total Organic Carbon

CHAPTER 1

INTRODUCTION

1.1 Background Study

Nowadays, carbon dioxide, CO_2 is one of the main contributors that lead to greenhouse effect. CO_2 is mainly produced by the fossil fuel combustion for electricity generation, petrochemical industry an as well as emission from transportation (Arslan & Balcioğlu, 1999). In petrochemical industry, the raw natural gas that contained CO_2 need to be treated first before being used for further processing activities. This is because the presence of CO_2 in the gas stream will cause interference to the process and reduce the quality of the product (Barchas, 1992). Other than that, CO_2 also need to be removed from the fuel gas before releasing to the atmosphere is because to minimize the greenhouse effect and can generate profit to the company by selling the recovered CO_2 to the customers (M.N. Razali, 2010).

Based on the figure 1.1, emission of carbon dioxide released to the atmosphere has the largest percentage that cause global warming compared to other gases such as nitrous oxide, fluorinated gases and methane (Mariz, 1998).

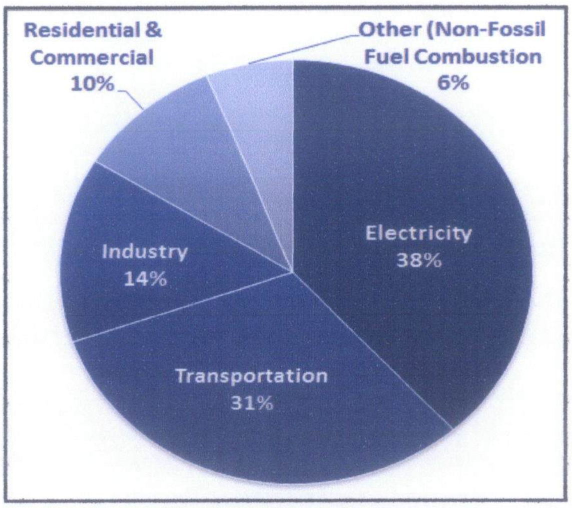


Figure 1: Percentage of Greenhouse Emission

According to a research that have been conducted in United States, the percentage of carbon dioxide also is keep increasing from year 1990 to 2010 as shown in figure 1. Therefore, it is very important to treat the flue gas in the chemical plant before it is being released.

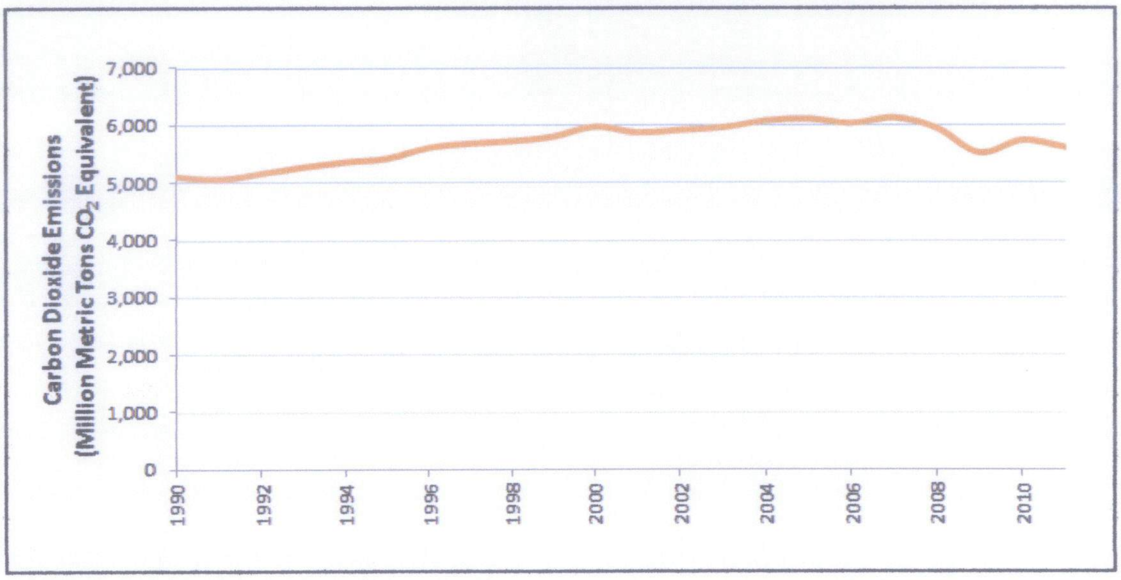


Figure 2: U.S Carbon Dioxide Gas Emission, 1990-2011

As shown in figure 2, the amount of carbon dioxide emitted to the atmosphere from industry field has contributed about 14% of greenhouse gases to the atmosphere which is the third largest contribution, while about 38% from electricity, 31% from transportation, 10% from residential and commercial and 6% from others sectors.

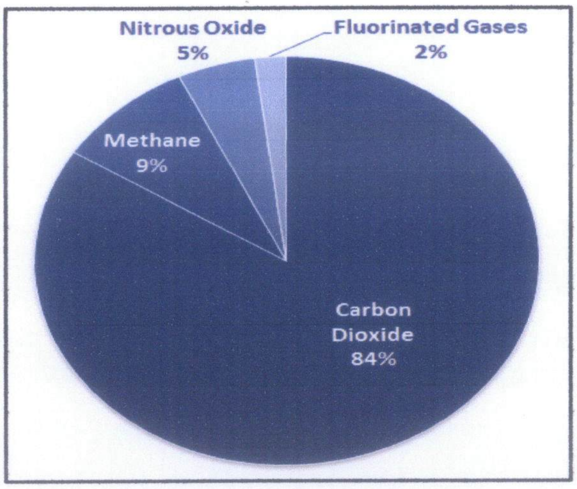


Figure 3: Sources of Greenhouse Gases Emission

However, other than being used as CO_2 scrubber, DEA also is widely used in cutting oils, soaps, shampoos, cleaners, polishers, cosmetics, pharmaceuticals and as an intermediate in the rubber chemical industry. Releasing untreated flue gas to the atmosphere is becoming an issue because it violates the Hazardous Air Pollutants under the Clean Air Act (Shah, Dai, & Mitch, 2013). When the DEA wastewater enters the Water Treatment Plant (WTP), it will upset WTP by increasing the Carbon Oxygen Demand (COD), oil concentration and solid suspended which then cause ineffectiveness of wastewater treatment. Therefore, if the concentration of amine in the effluent triggers the COD to exceed 200,000ppm level, the effluent will not be sent to the WTP (M.N. Razali, 2010).

In this project, Advance Oxidation Process (AOP) based on the Ultraviolet/Hydrogen Peroxide (UV/H_2O_2) system will be used for degrading DEA in solution. Among the Advanced Oxidation Process which involves ozonation O_3, combination of ozonation and hydrogen peroxide O_3/ H_2O_2, ultra violet UV, combination of ultraviolet and ozonation UV/ O_3, combination ultraviolet and hydrogen peroxide UV/H_2O_2, combination of ozonation, ultraviolet and hydrogen peroxide O_3/UV/H_2O_2, combination of Fenton's reagent and hydrogen peroxide Fe2+/H_2O_2 and phototocatlysis), it was found that degradation of phenol by using UV/ H_2O_2 showed the highest degradation rate, using Fenton is the fastest degradation and ozonation has lowered cost (Santiago Esplugas, 2002). Therefore, for degrading DEA, advanced oxidation process by using UV/ H_2O_2 was chosen to study the degradation of DEA together with the some parameters that may affect the degradation rate of DEA.

Other than that, AOP method based on ultraviolet/hydrogen peroxide has been successfully degrading most of the organic compounds present in the polluted water (Ghaly, Härtel, Mayer, & Haseneder, 2001). Therefore, in my current project, we will be studying the DEA degradation in solution by using hydrogen peroxide with the presence of ultraviolet. A photo-reactor model has been used in the experiment at laboratory scale which acts as reactor, UV lamp as the source of ultraviolet and with the presence of hydrogen peroxide. Four different parameters which are effect initial concentration of DEA, initial concentration of H_2O_2, temperature and initial pH on degradation of DEA will be studied in this project in order to determine the optimum condition for degrading DEA in solution.

After all the experiments have been completed, Response Surface Methodology (RSM) is used to model and analysis the response which is degradation percentage that has been influenced by several factors (Bezerra, Santelli, Oliveira, Villar, & Escaleira, 2008). The purpose of this method is to optimize the response. Other than that, the degradation percentage of analysed by the RSM is also be compared with the experiment value by using the value of each parameters.

1.2 Problem Statement

In previous research, other degradation of amine compound such as methanolamine (MEA) has been done by using AOP ultraviolet and hydrogen peroxide but not yet for diethanolamine (DEA). Therefore, in this study, degradation of amine will be experimented by varying the initial concentration of diethanolamine (DEA), initial concentration of H_2O_2, initial pH and temperature. Then, the optimum condition of DEA degradation will be determined by using both experiments and Response Surface Methodology (RSM) by Portable Statgraphics Centurion 15.2.11.0 (Bezerra et al., 2008). The main purpose of this study is to reduce environmental problems by reducing the emission of carbon dioxide to the atmosphere which has been one of the main contributors that lead to global warming and greenhouse effect (Jones, 1968). Therefore, this study is very important because for the sake of environment sustainability.

1.3 Objectives and Scope of Study

1) To study the degradation of Diethanolamine (DEA) by using UV/H_2O_2 method.
2) To investigate the effects of important process variables like initial amine concentration, initial H_2O_2 concentration, initial pH and temperature on degradation performance.
3) To optimize the degradation of Diethanolamine (DEA) using statistical approach.

Based on the objectives of this topic, the scope of study will be divided into three stages. For the first stage, the author will be focusing on the literature review about the previous study related to this topic. Secondly is conducting an experiment in the laboratory. The experiment will be conducted by varying few parameters such as initial amine concentration, initial H_2O_2 concentration, initial pH and effects of temperature on the degradation performance. There are about 36 experiments that need to be completed and each of the experiment takes 4 hours of irradiation time for each experiment. Finally, the last stage will be the finding of optimum condition that gives maximum rate of degradation of Diethanolamine (DEA) by using the experimental design based on the Response Surface Methodology, (RSM) by Portable Statgraphics Centurion 15.2.11. .

1.4 Relevancy of the Project

This project is relevant to the author because environments sustainability is one of the focus areas in the chemical engineering course. Other than that, in Universiti

Teknologi PETRONAS (UTP), Environment Engineering is one of the major courses in Chemical Engineering. Therefore, students have been taught to develop strategies and designs by applying chemical theories to reduce pollution for the sake of environmental sustainability. As a future engineer, the author has been assigned to do detailed research on degradation of DEA in solution using UV/ H_2O_2 Advanced Oxidation Process. This project is feasible as there are available chemicals stock in the chemical laboratory to be used in the experiment and as well as the equipment to analyse the sample. The equipment that will be used for this project is known as Total Organic Carbon (TOC) Shimadzu model. Early booking of glassware and equipment also have been made by the author to finish all the experiments within the time limit. About 36 experiments have been done in the chemical laboratory in order to complete this study. All the experiment have been successfully done and completed by the author in order the study those effects to the DEA degradation. Hence, it can be concluded that within these 4 months period of semester, the study is relevant and possible to be finished by the author.

1.5 The Feasibility of the Project

The project is feasible because it is within the scope and time frame. The author has planned to complete the research and literature review by the end of the first semester. Most of the materials and tools for conducting the experiment are already available in the chemical laboratory. Therefore, the author plans to conduct the experiment after mid-semester break and continue the experiment until the first five weeks of final year project II (FYP II). The experiment will be conducted to evaluate the effects of the various parameters while three weeks will be fully utilized to determine the optimum conditions for DEA degradation based on statistical approach. The equipment, Total Organic Carbon (TOC) Shimadzu Model used to analyse the sample is already available in the chemical laboratory. Therefore, after the author submit all the booking form, they are already can be used. Hence, it is feasible to complete this study.

CHAPTER 2

LITERATURE REVIEW

2.1 General Overview

Releasing untreated flue gas to the atmosphere is very dangerous to the human and as well to the environment. In petrochemical plants, the most commercial method used is amine-based CO_2 absorption in capturing CO_2 in the flue gas before it is released to the environment (M.N. Razali, 2010). During the CO_2 absorption process, the heavy hydrocarbon could be carried over to the absorber with the feed gas which then caused sudden foaming in the absorber. This problem is getting serious because the reaction between DEA and CO_2 also produce some salt which then increase the amount of suspended solids absorber and will also contribute to the foaming problem (Gjernes, Helgesen, & Maree, 2013). This phenomenon will decrease the absorption efficiency, increase amine losses and reduce the quality of the product gas and DEA (Casero, Sicilia, Rubio, & Pérez-Bendito, 1997). Therefore, it is not worth and appropriate to feed DEA back to stripper due to the difficulties in optimizing the absorption process, hence it has been removed as wastewater (M.N. Razali, 2010).

Numerous treatment methods and approaches have been employed to degrade DEA in solution and to minimize the high risk possessed by the untreated DEA solution. For example are amine-membrane techniques, molecular sieves and pressure and temperature swing adsorption (PTSA) using zeolites (Mores, Scenna, & Mussati, 2011). Each of those methods has their own advantages and disadvantages. For instance for absorption of CO_2 process, pure CO_2 is obtained and the recovered CO_2 can be used for other purposes while its drawbacks are it requires high amount of energy to regenerate the amine solvent, cause corrosion and excessive solvent degradation especially in gas stream containing O_2 (Mariz, 1998).

After desorption has been done, the DEA will recycle back to the absorber. This is because buying fresh DEA and handling it for waste disposal is very costly hence reduce the profit of the company(M.N. Razali, 2010). The photo-oxidation UV/ H_2O_2 reaction appears as a promising alternative for DEA degradation because of the system's simplicity and the generation of highly reactive hydroxyl radicals which can lead to full degradation of DEA (Goi & Trapido, 2002).

Figure 4: Diethanolamine (DEA) used in Experiment

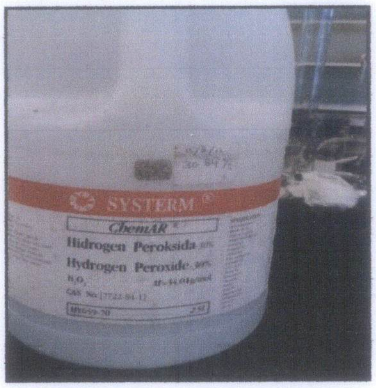


Figure 5: Hydrogen Peroxide used in the Experiment

Therefore, in this project further research will be done because research on Diethanolaimne (DEA) degradation using UV/ H_2O_2 method is not yet available in the literature. Studying about the degradation of DEA in solutiont is very important because it can cause a huge threat to the environment.

2.2 Diethanolamine (DEA)

Diethanolamine (DEA) is an organic chemical compound which has primary amine (due to amino group in molecule). DEA which has molecular formula $C_4H_{11}NO_2$ with molecular weight 105.14 g/mol and density 1.09 g/cm^3 is toxic, flammable, corrosive, colourless, acts as weak base and has viscous liquid with an odour similar to ammonia (M.N. Razali, 2010). DEA is produced by reacting ethylene oxide with ammonia as per equation below.

$$2C_2H_4O + NH_3 \longrightarrow C_4H_{11}NO_2 \qquad (1)$$

Figure 6 shows the molecular structure of DEA and table 1 show typical properties of DEA.

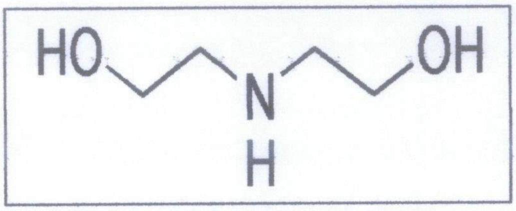


Figure 6: Molecule Structure of Diethanolamine (DEA)

Table 1: Typical Properties of Diethanolamine (DEA)

Formula	$HN(CH_2CH_2OH)_2$
Molecular formula	105.14 g/mol
Boiling Point at 760 mmHg, °C at 50mm Hg, °C at 10mm Hg, °C	268 182 150
Vapour pressure at 20°C, mm Hg	<0.01
Freezing point, °C (°F)	28.0 (82.4)
Flash point, °C (°F)	191(375)
Surface tension, dynes/cm at 30°C	48.5
Refractive index, n_D at °C	1.4747

There are some precautions that need to be taken when handling with the Diethanolamine (DEA) chemical. This is because diethanolamine (DEA) can cause some hazards to human and as well as to the environment. Inhale DEA may cause irritation of the respiratory tract, experience as nasal discomfort and discharge, chest pain and coughing. Other than that, DEA also can cause eye and skin irritation. The symptoms are they will experience excess blinking and tear production, excess redness and swelling of the conjunctiva. This can lead to corneal injury. Besides that, DEA also may harm people by skin contact and adsorption. Last but not least is swallowing DEA also may cause irritation to the mouth and throat, abdominal discomfort, vomiting and diarrhea. Therefore, in order to be safe, DEA chemical must be kept at the safe and suitable place, avoid breathing the vapour, wash thoroughly after handling and keep the container closed (Company, 2003).

2.3 Degradation of Diethanolamine (DEA)

Globally, our earth now is having serious environmental problems. One of them is global warming, due to increasing emission of carbon dioxide, methane, chlorofluorocarbon and nitrous oxide to the atmosphere. Among of those gases, CO_2 has contributed the largest percentage among other gases which is approximately 55% (Yeh & Bai, 1999). Therefore, the emission of CO_2 from the fossil fuel energy needs to be reduced in order to slow down the global warming effect. There are many methods that can be used to remove the CO_2 from flue gas such as chemical solvent absorption, chemical adsorption, cryogenic separation, membrane separation, biological fixations and O_2/CO_2 combustion process. However, among of those methods, chemical solvent absorption method has been applied in the removing CO_2 because based on many studies done, it is considered as a reliable and relatively low cost method (Yeh & Bai, 1999).

In most of the petrochemical plant, they used Monoethanolamine (MEA) or Diethanolamine (DEA) as the solvent to scrub CO_2 from the flue gas (Mores et al., 2011). The flue gas contains CO_2 enters the absorber and contacts with the DEA flowing counter currently with the flue gas. In the absorber, DEA which is a weak base will react with CO_2, a weak acid by forming a soluble salt, namely amine-carbamate (M.N. Razali, 2010).

$$C_4H_{11}NO_{2\,(l)} + CO_{2\,(g)} + H_2O_{\,(l)} \longleftrightarrow C_4H_{11}O_2NH^+_{\,(aq)} + HCO_3^-{}_{\,(aq)} \qquad (2)$$

After enters the absorber, the amine-carbamate compound will then enter the stripper. In stripper, amine-carbamate will dissociates into CO_2 and lean DEA and DEA will be recycled back into the absorber (Shah et al., 2013).

The author used UV/H_2O_2 advanced oxidation process treatment for degrading DEA in solution for her study. Parameters (initial concentration of DEA, initial concentration of H_2O_2, initial pH and temperature) which affect the degradation percentage also will be further studied in order to determine the optimum condition for DEA degradation. Therefore, in the experiment conducted, an amount volume of DEA will be added with an amount of hydrogen peroxide in the jacketed reactor with the presence ultraviolet lamp as the source of ultraviolet. Then, the experiment will be run for 4 hours and each 30minutes interval, 5 ml of sample will be taken out and will be analysed by using Total Organic Carbon equipment. Hence, the degradation percentage will be measured by the total organic carbon removal (%) for each parameter that being experimented.

2.4 Diethanolamine (DEA) Treatment Method

2.4.1 Conventional method

There are many treatments methods that are applicable in reducing the dangerous effects caused by degradation of DEA in solution (Santiago Esplugas, 2002). The treatment methods currently are divided into three groups which are biological method, chemical and physical.

Biological method

Biological treatment is considered very eco friendly because it manages to degrade organic contaminant in effluent at very low cost. However, the drawbacks of this biological method is that it needs a huge land area, less flexibility in its design and process and also get inhibited by toxicity of some chemicals (Bhattacharyya, 2005). Besides that, big amount of such disposal waste lead is not economical and environmental friendly because release untreated amines to the environment can cause harm to the ecosystem and public health ((Farid Benyahia, January 2010).

Chemical method

There are several included under chemical treatment method. For instance are photochemical, ozonation, using fentons reagent, sodium hypochlorite, cucurbituril and electrochemical destruction. Among those treatments, the author will use photochemical method where the DEA will degrade by UV treatment in the presence of H_2O_2. The degradation will occur when high concentration of hydroxyl radicals are produced where UV light activate chemicals, H_2O_2. The advantage of this method is no sludge is produced and reduced the foul odours.

Physical method

Physical treatment such as membrane filtration, activated carbon, wood chips, peat, fly ash and coal (mixture), using silica gel, in exchange, ion irradiation and electronic coagulation also have been using in degrading chemicals in effluents.

However, among those methods, chemical method by using amine based CO_2 absorption system is widely being used because the system can be used for dilute system and low CO_2 concentration, easy to use and can be retrofitted to any other plants (M.N. Razali, 2010). Currently, DEA is widely used in Flour Danial technology's Economic FG^{TM} and Econamine FG $Plus^{TM}$ (Mariz, 1998) and the ABB Lummus Global technology (Barchas, 1992) in removing carbon dioxide and hydrogen sulphide from flue gas (Harold, 2004).

2.5 Advanced Oxidation Process (AOP) & UV/H_2O_2 System

2.5.1 Advanced Oxidation Process (AOP)

AOP is one of the methods used to degrade most of the organic compound in the effluent. The reason why it is widely used nowadays is because of the inability of the biological process to treat highly contaminated and polluted water (Ghaly et al., 2001). Advanced Oxidation Process (AOP) is the process based on the generation of very reactive species such as hydroxyl radicals (OH.) that oxidize a broad range of organic pollutants quickly and nonselectively (O.legrini, 1993). Homogeneous AOP which are Fenton's reagent, light-assisted Fenton's oxidation, UV/ H_2O_2 treatment, ozonation at high pH etc. and heterogeneous AOP which is semiconductor-mediated photocatalysis have been thoroughly and comparatively evaluated for a variety of organic compounds and wastewaters in the past (Arslan & Balcioğlu, 1999). In addition, AOP is an excellent physical water treatment process because during the treatment process, it is able to remove the compound rather than changing it to another phase such as solid waste or sludge (Behnajady M., 2008).

2.5.2 UV/ H_2O_2 System

Figure 7 shows the schematic diagram of the laboratory-chemical installation for the experiment. The combination of UV/ H_2O_2 treatments can create a very fast and efficient for degradation. This is because if UV treatment alone is used, the range of contaminants UV can degrade by itself is very limited, thus slowing degradation and increase the time to degrade (Edward B.Rinker, 1996). For H_2O_2, it is very strong oxidizing agent where it is capable to destroy some halogenated and most non halogenated compounds in aqueous media (Sohrabi, 2008). The combination of UV/ H_2O_2 is one of the best known AOP's and their combination will form two free hydroxyl radicals, OH^- which is potent oxidizing agents. (Melanie Kito, December 1998).

$$H_2O_2 + hv \text{ ® } 2OH^- \quad (3)$$

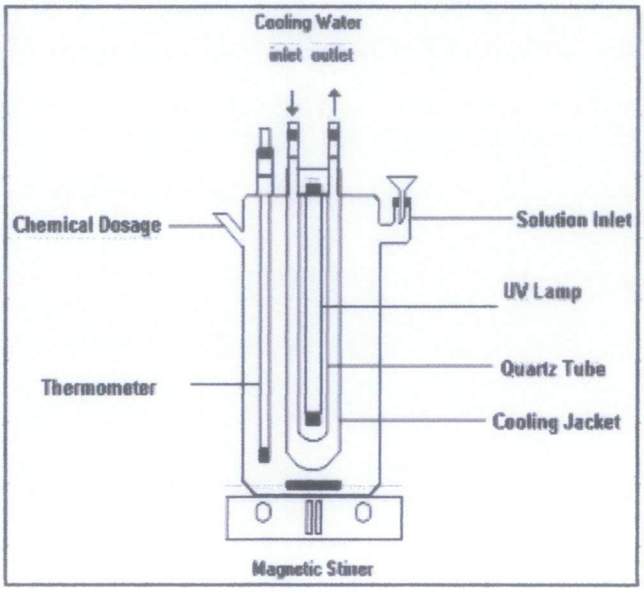


Figure 7: Schematic Diagram of the Laboratory Photo-Chemical Installation

The free hydroxyl radicals are not in the stable state because they are at excited state species since they are characterized by a one-electron deficiency. Therefore, because of its' instability, hydroxyl radicals, OH^- will tend to react with the first chemical that it comes in contact with and tend to completely oxidize dissolved organic contaminants in aqueous media (Peters, Hussain, Follmann, Melin, & Hägg, 2011).

$$H_2O_2 \text{ ® } HO_2^- + H^+ \qquad (4)$$

$$RH + OH\bullet \longrightarrow H_2O + R\bullet \qquad (5)$$

where R is the carbon chain.

From this reaction, carbon dioxide, water and salts will be produced as the product. Other than that, H_2O_2 is catalyzed with UV irradiation to create highly reactive radicals which react and cleave a wide variety of organics (Melanie Kito, December 1998).

2.6 Experimental Design

2.6.1 Introduction

In an experiment, one or more process variables are normally varied in order to examine the consequences the changes have one on one or more response variables. The (statistical) design of experiments (DOE) is an effective method to plan the experiments so that the results gained can be analyzed and a valid conclusion can be obtained. Experimental design's main aim is to improve the experiment works. Experimental design application is usually used to choose which experiment has to be conducted in order to have more data on the specific chemical process or products. Based on the results, it can be determined which parameters have a significant effect on the outcome process. Besides that, it is also aimed to know the number of experiments that have to be conducted in order to get enough information to do the analysis (Kurbus, 2003).

Therefore, it can be summarized that the main purpose of the experimental design (DOE) methodology is to decide the effect of the different parameters and their combination effect on the outcome of the process with less number of experiments (minimum effort). Statistical techniques like analysis of variance (ANOVA) need to be used to decide which factors and/or interactions are statistically significant for that particular process.

2.6.2 Screening of Process Parameters

There are few methods of experimental design which are includes full factorial, fractional factorial design, Box-Behnken, D-Optimal design and uniform design. The choice of the experiments has a specific effect on the system. The characteristics of the product named as a response. The factors that affecting the product are called independent variables while the product or the response is called dependent variables. So, experimental design can be defined as a set of carefully planned experiments.

In experimental design process, firstly the type of experimental design is determined. Then, the next step is to choose the initial factors and response and to select the experiment domain. Once screening process is done, insignificant factors are discarded. After determining which factors have minimal or insignificant on the response, the optimum setting of the significant parameters levels that produce the best response need to be performed.

2.6.3 Optimization

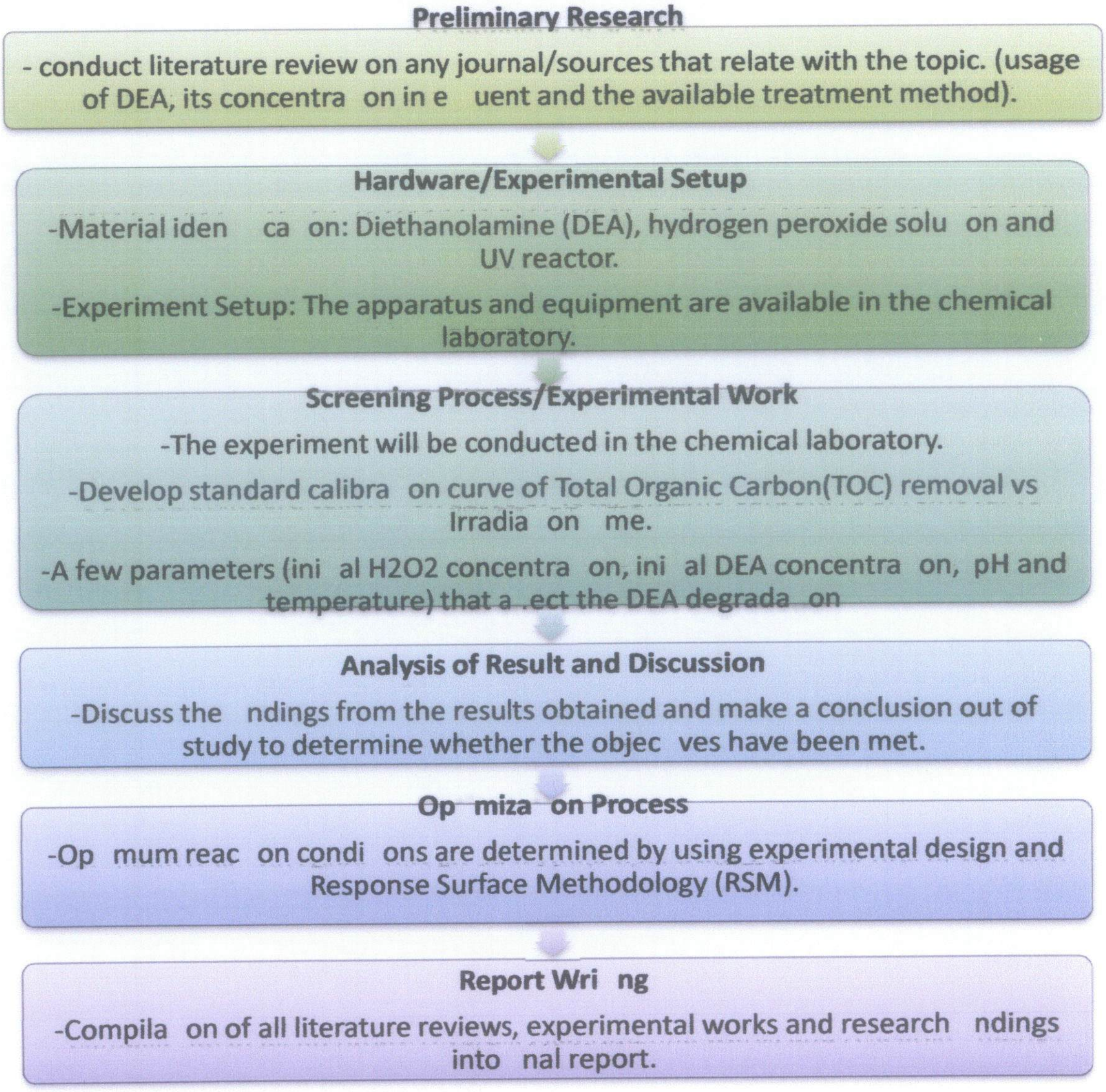
Response Surface Methodology (RSM) is utilized to find the optimum operating conditions and to examine the effect of important process parameters of Diethanoalamine (DEA) degradation (Catalkaya, 2006). Basically, RSM is the set of mathematical and statistical methods normally used to design experiments, build models, evaluate the effect of variables and determine the optimum condition of parameters to forecast the target responses. It is an important branch of experimental design and a critical tool in developing new processes, optimizing their performances and improving design and formulations of new products. RSM is used for the analysis of dependent variables as functions of independent variables. It is also used to find the optimum operating conditions or to determine a region for the factors at a certain operating specifications.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Project Flow

Figure 8 shows an arrangement of method has been done throughout the study.



Preliminary Research

- conduct literature review on any journal/sources that relate with the topic. (usage of DEA, its concentration in effluent and the available treatment method).

Hardware/Experimental Setup

-Material identification: Diethanolamine (DEA), hydrogen peroxide solution and UV reactor.

-Experiment Setup: The apparatus and equipment are available in the chemical laboratory.

Screening Process/Experimental Work

-The experiment will be conducted in the chemical laboratory.

-Develop standard calibration curve of Total Organic Carbon(TOC) removal vs Irradiation time.

-A few parameters (initial H2O2 concentration, initial DEA concentration, pH and temperature) that affect the DEA degradation

Analysis of Result and Discussion

-Discuss the findings from the results obtained and make a conclusion out of study to determine whether the objectives have been met.

Optimization Process

-Optimum reaction conditions are determined by using experimental design and Response Surface Methodology (RSM).

Report Writing

-Compilation of all literature reviews, experimental works and research findings into final report.

Figure 8: Chart Flow of Project

3.2 Laboratory Experiment

There are four main experiments that will be conducted in chemical laboratory.

a) Experiment 1 (Effect of initial H_2O_2 concentration)
Manipulated parameter: Initial H_2O_2 concentration
Constant parameters: Initial MEA, Initial pH, Temperature (25°C)

b) Experiment 2 (Effect of initial MEA concentration)
Manipulated parameter: Initial MEA concentration
Constant parameters: Initial H_2O_2 concentration (1500ppm), Initial pH, Temperature (25°C)

c) Experiment 3(Effect of initial pH)
Manipulated parameter: Initial pH (3-9)
Constant parameter: Initial H_2O_2 concentration (1500ppmM), Initial MEA concentration, Temperature (25°C)

d) Experiment 4: Effect of Temperature
Manipulated parameter: Temperature (30°C-50°C)
Constant parameter: Initial H_2O_2 concentration, Initial MEA concentration, Initial pH

3.3 Experiment Procedure and Analytical Method

3.3.1 Reagent

The main reagents used for the experimental work in this project are Diethanolamine (DEA) solutions, Hydrogen Peroxide H_2O_2 solution, sodium hydroxide NaOH, hydrochloric acid HCl and distilled water. The DEA, Hydrogen Peroxide (30%), NaoH and HCl were obtained from the chemical laboratory. Aqueous solutions of Diethanolamine, DEA were prepared by dissolving required quantity of the DEA, hydrogen peroxide and 400mL of distilled water in the volumetric flask as shown in figure 9. After that, the solution will be transferred into the reactor for reaction with UV/ H_2O_2.

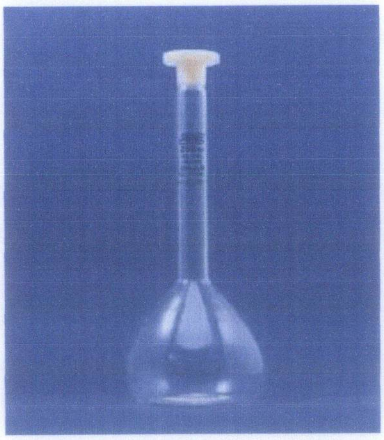
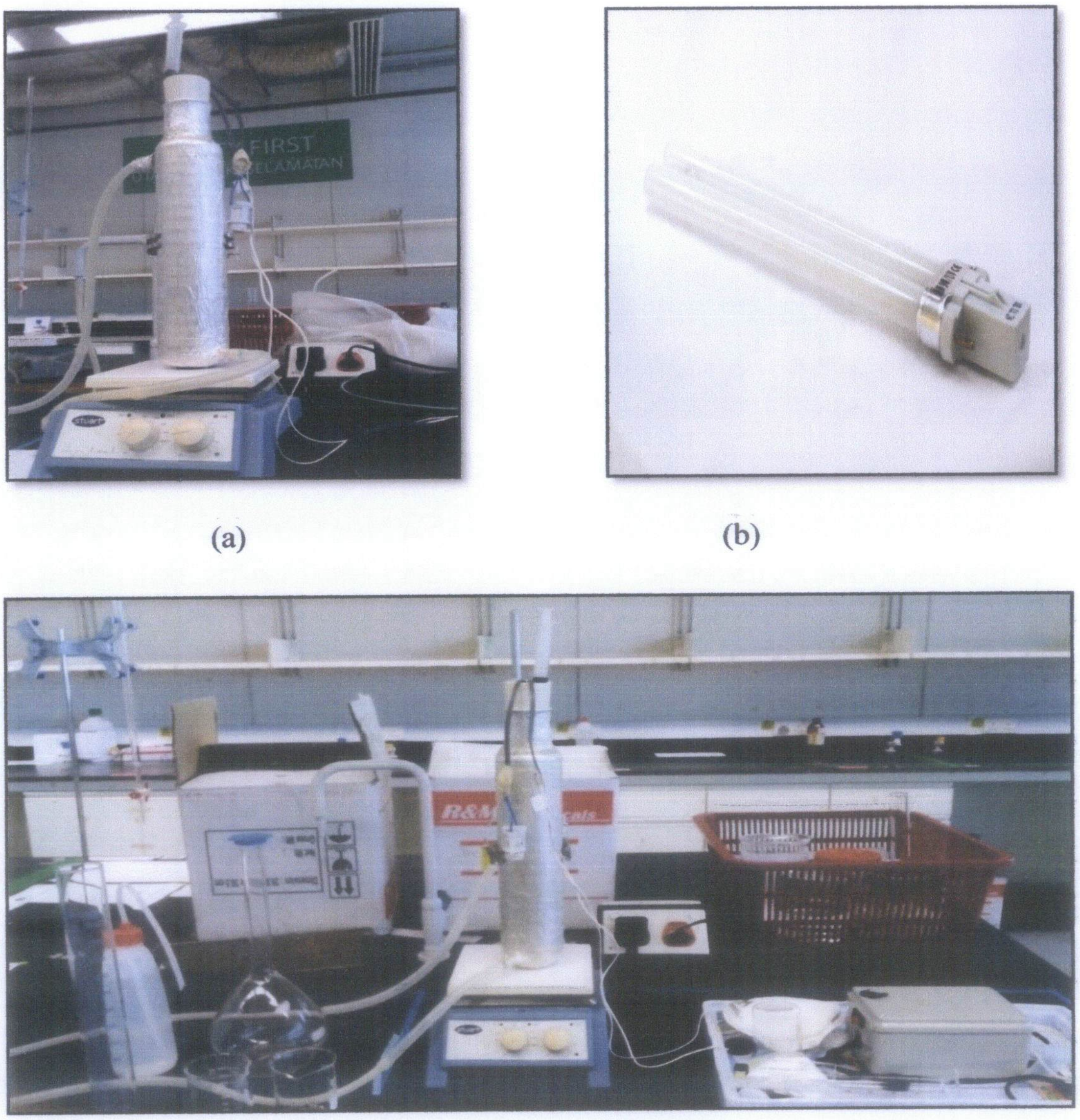


Figure 9: Prepared Sample Solution

3.3.2 Experiment

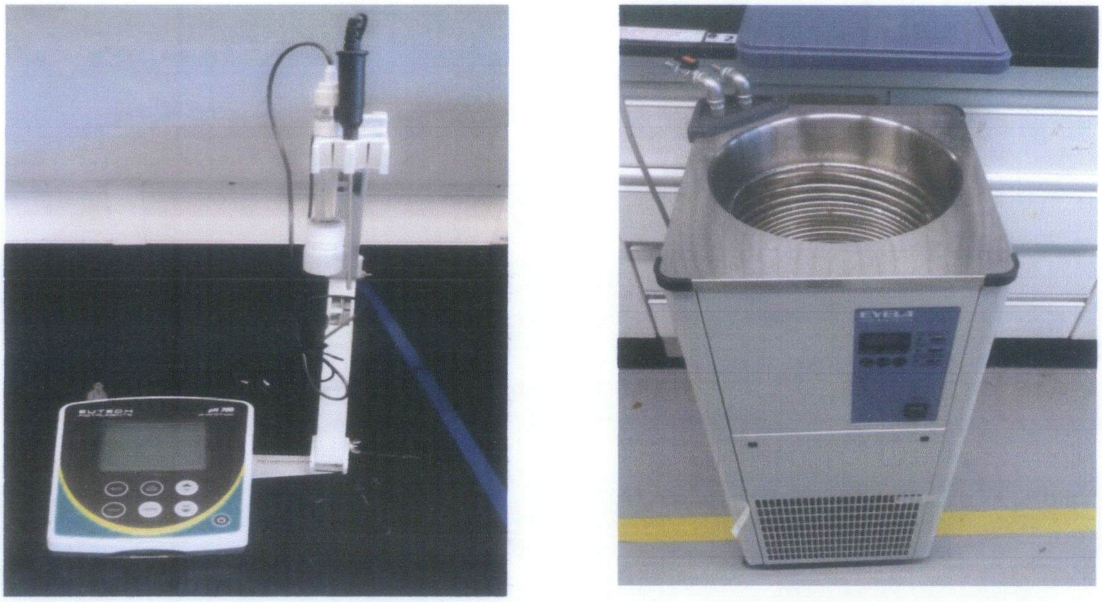
All experiments will be carried out in a 400 mL well stirred, jacketed, glass reactor. The outside of the reactor will be covered with an aluminium sheet. The reaction zone is a cylindrical borosilicate glass tube of 14 inch long with internal diameters of 2 inches. At the top, the reactor has inlets for feeding reactants and withdrawing samples. A magnetic stirrer is placed in the bottom to provide proper mixing. The radiation source is a UV lamp (8W, UV-C, manufactured by Philips, Holland) which was protected by a quartz tube as shown in figure 10.



(a) (b)

Figure 10: Experiment Setup in Laboratory a) Reactor Coated with Aluminium Foil b) UV Lamp Used for Radiation c) Full Experiment Setup

In each experiment, required quantity of the DEA solution with known concentration will be mixed with required amount of H_2O_2 used. At certain reaction intervals which is after 30 minutes, 5mL of sample will be withdrawn and analyzed with a Total Organic Carbon (TOC) Shimadzu for its TOC value while the pH will be adjusted by using sodium hydroxide (NaOH) and hydrochloric acid (HCl). Then, the temperature was maintained by circulating cooling water through the jacket reactor. All the apparatus are shown in figure 11.



(a) (b)

Figure 11:Equipment Used in Laboratory a)pH Meter to control the pH of the Solution b) Thermostatic Bath to control the Temperature of System

3.3.3 Analysis

The degradation of Diethanolamine (DEA) will be measured by using Total Organic Carbon (TOC), Shimadzu model as shown in figure 12. Total Organic Carbon is equipment used to measure the total organic carbon in the sample and it is equivalent to TOC=TC – TIC, where TC is Total Carbon while TIC is Total Inorganic Carbon. After 30minutes interval, 5ml of sample will be withdrawn from the reactor and is transferred to the bottle sample. After that, 25ml of distilled water is added into the bottle sample before it is being analysed by TOC.

Figure 12: Total Organic Carbon (TOC) Equipment Shimadzu Model

It consists of three stages for analysis by TOC. Firstly is acidification stage, followed by Oxidation Stage and lastly is Detection and Quantification stage (Reckhow, 2012). At the first stage, phosphoric acid has been added into the bottle sample and inert gas sparging to allow all the bicarbonate and carbonate ions convert to carbon dioxide. At second stage, photo-oxidation has been used because this method is the most reliable and has low maintenance of analyzing total organic carbon.

Graph of degradation efficiency versus each parameter (effect of initial H_2O_2 concentration, effect of initial DEA concentration, effect of initial pH and effect of temperature) are plotted to show how does those parameters affect the efficiency of degradation by measuring the total organic carbon removal after 4 hours experiment. The percentage of degradation efficiency is calculated by using the equation as follow:

$$\%\text{ degradation efficiency} = \frac{TOC\ Removal_f - TOC\ Removal_i}{TOC\ Removal_i}\ X\ 100 \qquad (6)$$

Where TOC Removal_f and TOC Removal_i is the values of TOC Removal after and before irradiation.

3.4 Statistical Design Experiment (Optimization)

A Box-Behnken design with three factors and three levels was used for fitting a second order response model. The value of R^2 will be used to determine the fit quality of the polynomial model equation (Ferreira et al., 2007). According to Box-Behnken design, three parameters which are initial H_2O_2 concentration (X1), initial pH (X2) and temperature of system (X3) were selected as independent variables because they are very important parameter in affecting the degradation of diethanolamine (DEA) using UV/H_2O_2. Then the Total Organic Carbon (TOC) removal is considered as the response (Y). The initial Diethanolamine (DEA) was kept constant at 1000ppm. Experimental range and levels of independent variables for the degradation of Diethanolamine(DEA) using UV/ H_2O_2 were presented in table 2 . For the optimization study, fifteen experiments were conducted.

Table 2: Experimental Region Investigated for Diethanolamine (DEA) Degradation

	Range Levels			
Independent Variable	Factors	1	0	-1
Initial H2O2 Concentration (ppm)	X1	1000	1500	2000
Initial pH	X2	3	5	7
Temperature (°C)	X3	30	40	50

3.5 Analysis by Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is used to model and analysis this process where the response (degradation efficiency) is influenced by several factors. The objective of this method is to optimize the response and it was represented by a linear polynomial model with interaction as follow:

$$Y = \beta + \sum_{i=1}^{k} \beta_i \ x_i + \sum_{i=1}^{k} \beta_{ii} \ x_i^2 + \sum_{ij} \sum \beta_{ij} \ x_i \, x_j + \varepsilon \qquad (7)$$

Where,

Y = Predicted Response

x_i = Coded Factors

β_0 = Constant Terms

β_i = the Linear Effect

β_{ii} = the Squared Effect

β_{ij} = the Interaction Effect

Experimental results were analyzed by using Portable Statgraphics Centurion 15.2.11.0 statistical software. This software is used to approximate the response of dependent response variable and to find the effects coefficients, standard deviation of coefficients and as well as other parameters of the model.

3.6 Project Activities

Activities	WEEK																													
	FYP (I) MAY 2013															FYP (II) SEPTEMBER 2013														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Confirmation of Project Title	▨	▨	▨	☆											SEMESTER BREAK															
Literature Review			▨	▨	▨	☆																								
Submission of Extended Proposal							☆																							
Proposal Defense								▨	☆																					
Preparation of chemicals and glassware										▨	▨	▨	▨	☆																
Submission of Interim Report														☆																
Experiment																▨	▨	▨	▨	▨	▨	▨	☆							
Submission of Progress Report																								☆						
Pre-SEDEX																										☆				
Submission of Draft Report																											☆			
Submission of Dissertation (Soft Bound)																											☆			
Submission of Technical Paper																												☆		
Oral Presentation																												☆		
Submission of Dissertation (Hard Bound)																														▨

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of UV Radiation in the presence of H_2O_2

Three experiments were carried out in order to see the Total Organic Carbon (TOC) Removal differences by using UV radiation only, H_2O_2 and combination both UV radiation plus H_2O_2. Each experiment was carried out for 4 hours. Figure 13 shows the TOC remove versus irradiation time graph for these three experiments. The green line indicates for reaction with the presence H_2O_2 only, red line with the presence of UV only while the blue line is with combination and presence both UV radiation plus H_2O_2. There was no significant loss of Organic Carbon and degradation of DEA for reaction with the presence with only UV radiation and H_2O_2 alone. However, when the sample is subjected to the presence of both UV radiation and H_2O_2, there is significant loss where the TOC remove is significantly decreased as time increased. The reduction of TOC remove can be linked with the generation of hydroxyl radicals, which is a strong oxidising agent.

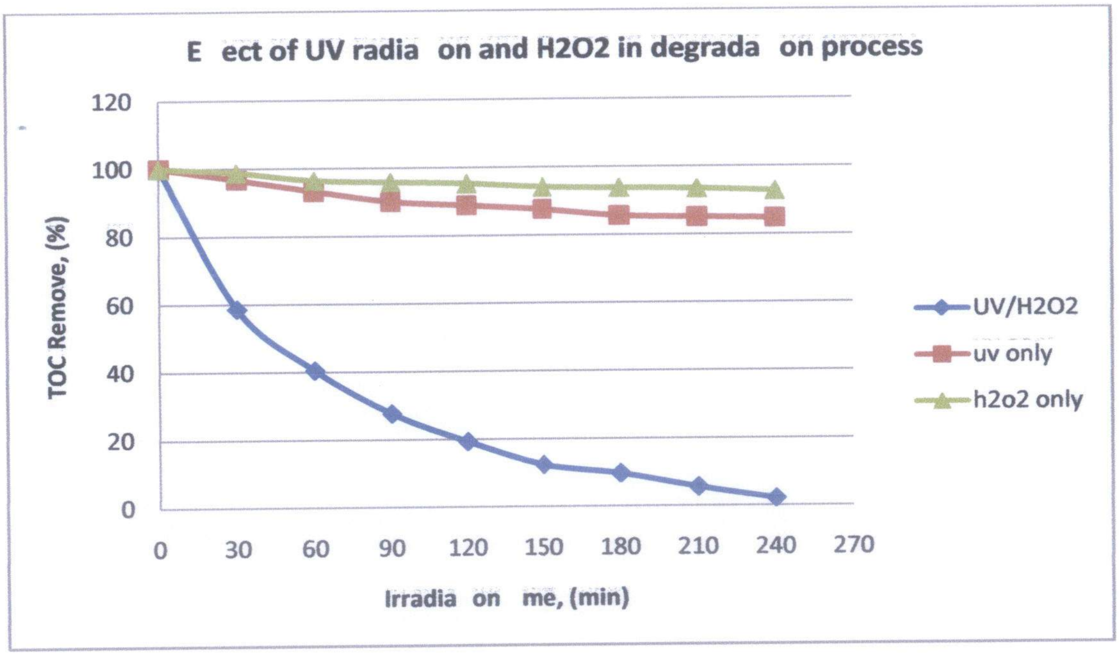


Figure 13: Effect of UV Radiation and Hydrogen Peroxide on Degradation of Diethanolamine (DEA) (DEA=1000ppm, H_2O_2=1500ppm, pH=5)

4.2 Effect of Initial H_2O_2 Concentration

The effect of initial H_2O_2 concentration on the degradation efficiency is investigated by adding different concentration of H_2O_2 which is between 500 ppm to 2000 ppm into the sample prepared. The results are shown in the figure 13 as follow, Total Organic Carbon (TOC) remove versus irradiation time.

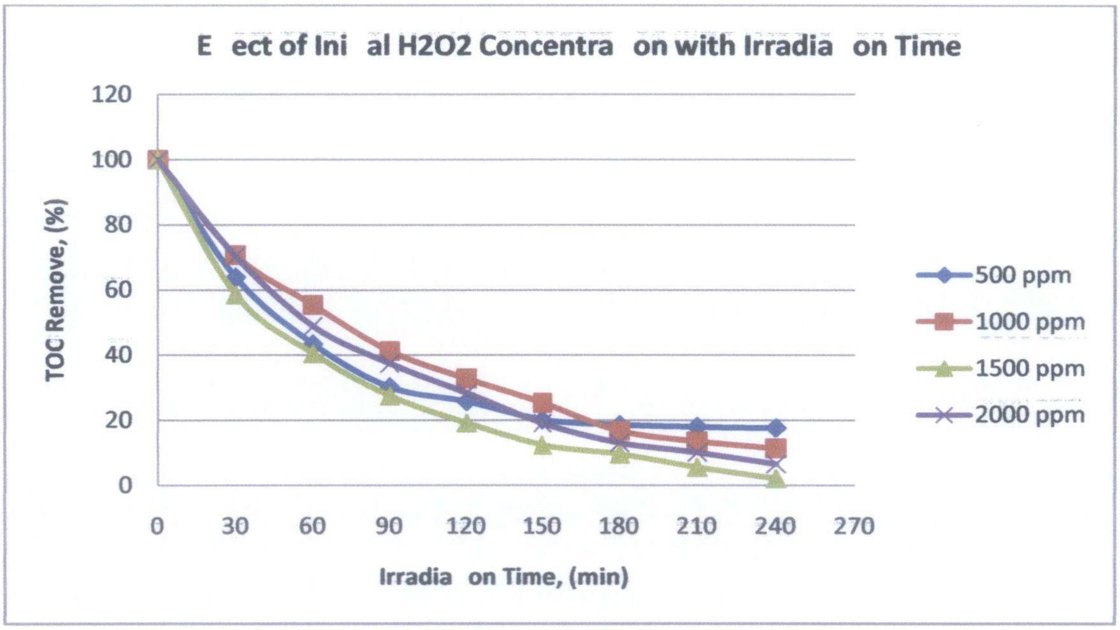


Figure 14: Effect of Different Initial H_2O_2 Concentration with Irradiation Time (DEA=1000ppm, pH=5, Temperature=30°C)

As shown in figure 14, the TOC remove is decreasing along with the irradiation time in the presence of UV radiation and H_2O_2. The degradation efficiency is increasing from 500ppm up to 1500ppm of initial H_2O_2 concentration. However, as the initial H_2O_2 concentration to 2000ppm, the degradation efficiency is decreasing. The reason of this situation is because of the insufficient production of hydroxyl radicals at low initial H_2O_2 concentration. As the initial H_2O_2 concentration increases, the production of hydroxyl radical also increases as well which lead to a faster rate of degradation of Dietanolamine(DEA). However, when initial H_2O_2 concentration increases to 2000ppm, the hydroxyl radicals produced were preferred to react with the excess of H_2O_2 rather than reacting with DEA molecule. Hence, the degradation efficiency is decreased as shown by the purple line in the figure 13. Equations below shows the reaction in the presence both UV radiation and H_2O_2 produced hydroxyl radicals. As the H_2O_2 concentration increases, hydroperoxyl radicals which are less reactive compare to hydroxyl radicals also are being produced (Zang & Farnood, 2005). Therefore, there is no significant in the degradation of DEA as the initial H_2O_2 concentration further increases.

$$H_2O_2 + UV \longrightarrow 2HO\bullet \qquad (8)$$

$$H_2O_2 + HO\bullet \longrightarrow H_2O + HO_2\bullet \qquad (9)$$

$$HO_2\bullet + HO\bullet \longrightarrow H_2O + O_2 \qquad (10)$$

Figure 15 shows the degradation efficiency of Dietanolamine (DEA) for various initial H_2O_2 concentration from 500ppm to 2000ppm. From the chart, the H_2O_2 concentration at 1500ppm appears to be the optimal concentration for degrading Diethanolamine (DEA).

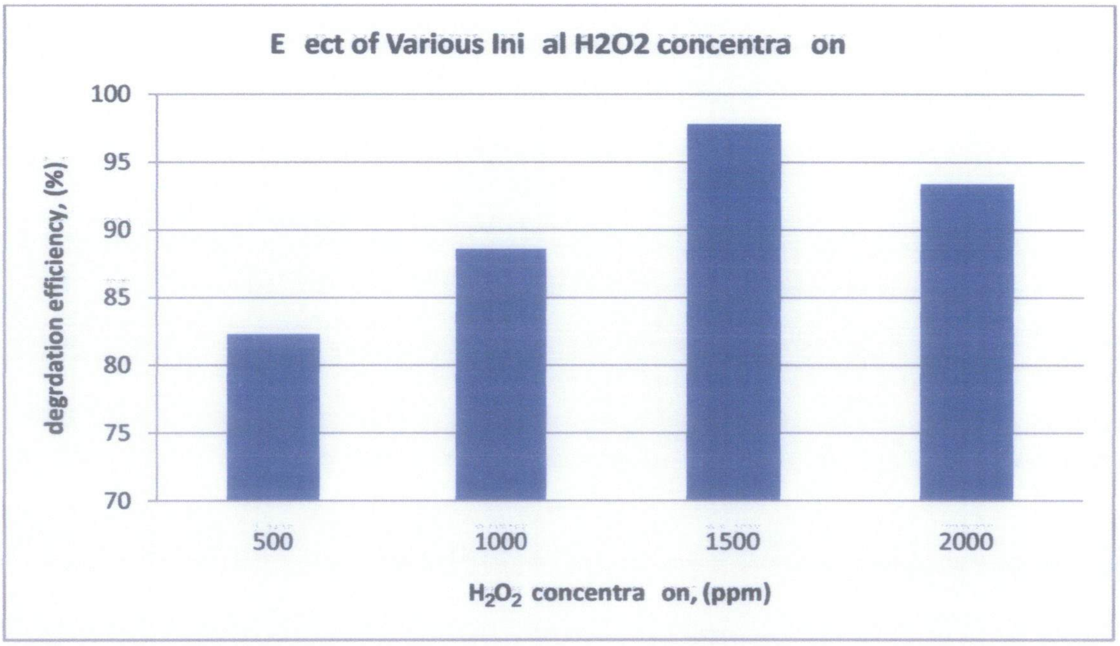


Figure 15: Effect of Various H_2O_2 Concentrations on the Percentage Degradation

4.3 Effect of Initial Diethanolamine (DEA) Concentration

The effect of initial DEA concentration on the degradation efficiency have been observed by adding different concentration of DEA which is range from 500ppm to 2000ppm to the sample. Figure 16 shows the relationship between TOC removes with irradiation time.

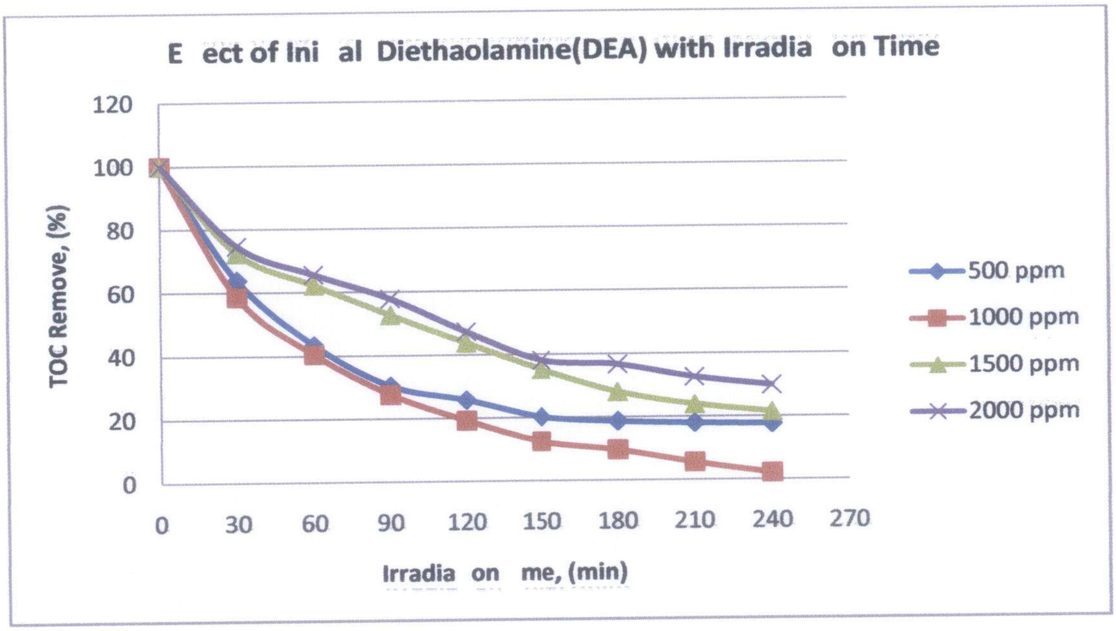


Figure 16: Effect of Different Initial Diethanolamine (DEA) Concentrations with Irradiation Time H_2O_2 =1500ppm, pH=5, Temperature=30°C)

Based on the figure 16, as the irradiation time increases, the TOC removes decreases, hence resulting increases in the degradation efficiency for initial DEA concentration from 500ppm to 1000ppm. However, after 1000ppm of DEA concentration (1000-2000ppm), it shows that the degradation efficiency of DEA is decreasing which is from 97.8% to 70.2%. This can be explained as the concentration of DEA increases, there is no enough hydroxyl radicals to degrade DEA molecule because throughout the experiment, constant H_2O_2 concentration has been used.

Figure 17 shows the degradation efficiency of Diethanolamine (DEA) for various initial DEA concentrations from 500ppm to 2000ppm. It can be seen that, the optimal concentration for degrading Diethanolamine (DEA) is at 1000ppm of DEA.

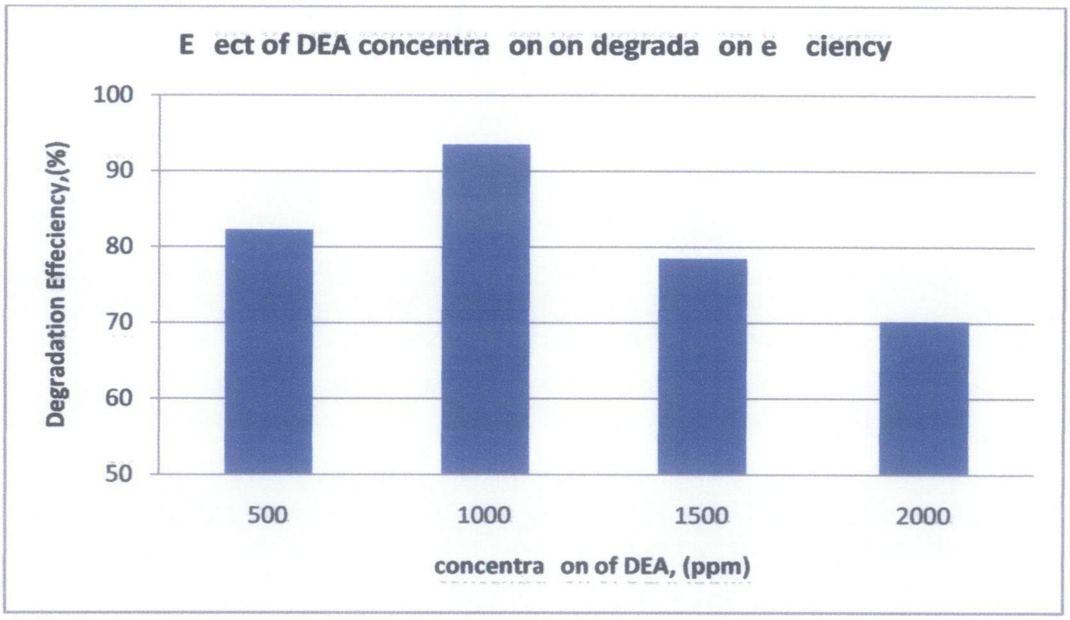


Figure 17: Effect of Various DEA Concentrations on the Degradation Percentage

4.4 Effect of Initial pH

For the effect of initial pH (3,5,7,9) on the degradation of Dietanolamine (DEA), four different experiments have been conducted. The value of pH has been adjusted by adding concentrated hydrochloric acid or sodium hydroxide to the sample solution. Then, the sample pH of the sample is measured by the pH meter. It is known that the pH of the sample is one of the factors that may affect the degradation of sample (Arslan & Balcioğlu, 1999).

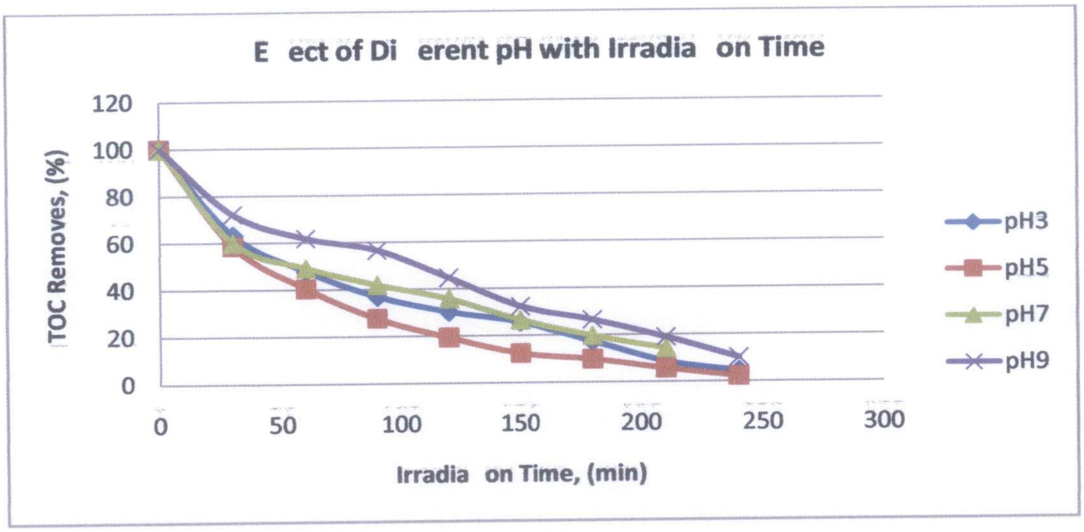


Figure 18: Effect of Different pH with Irradiation Time (DEA=1000ppm, H2O2=1500ppm, Temperature=30 °C)

As the pH increases, we can see that TOC remove has the largest removal at pH equal to 5 within 4 hours of irradiation time. This means the degradation of Diethanolamine (DEA) is more efficient at acidic condition than at alkaline condition. This can be shown in the figure 18 labelled by the green and purple line. The reason why the degradation is more efficient at acidic condition is because more hydroxyl radicals are being produced compared in alkaline condition (Sohrabi, 2008). Hence, resulting high concentration of HO• in acidic condition.

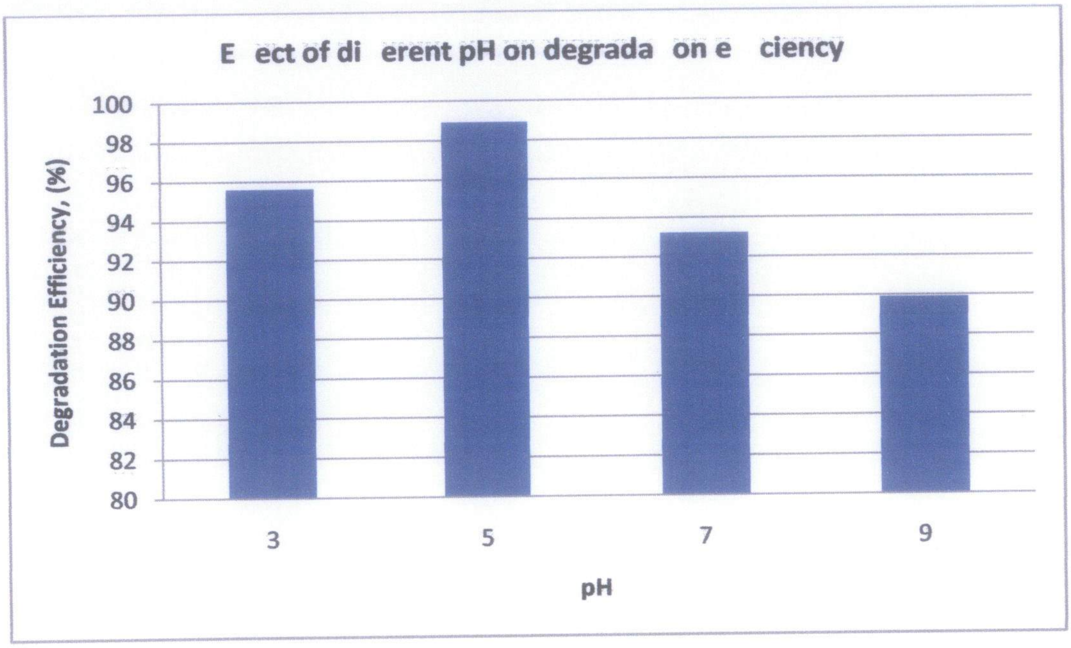


Figure 19: Effect of Various pH on Degradation Percentage

The summary of percentage degradation of diethanolamine (DEA) at different pH is described in figure 19. As the pH increases from 3 to 5, the degradation efficiency is increased. However, further increases of pH (from 5 to 9), causes the percentage of degradation to decrease. Other than that, it can be seen the optimum degradation of Diethanolamine (DEA) is at pH 5.

4.5 Effect of Temperature

The last parameter being investigated is the effect of temperature on degradation of Diethanolamine (DEA). Several experiments being conducted at 30 °C to 50 °C, 1000ppm concentration of DEA and 1500ppm concentration of H_2O_2 and at pH 5. Figure 20 shows the relationship between TOC remove between different temperatures within 240 minutes.

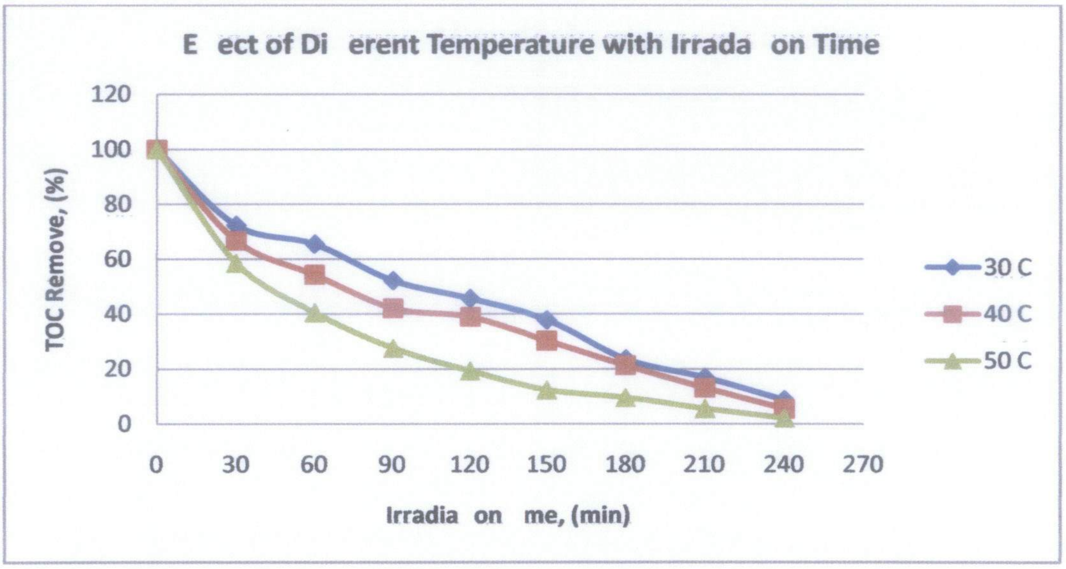


Figure 20: Effect of Temperature with Irradiation time (DEA=1000ppm, H_2O_2 =1500ppm, pH=5)

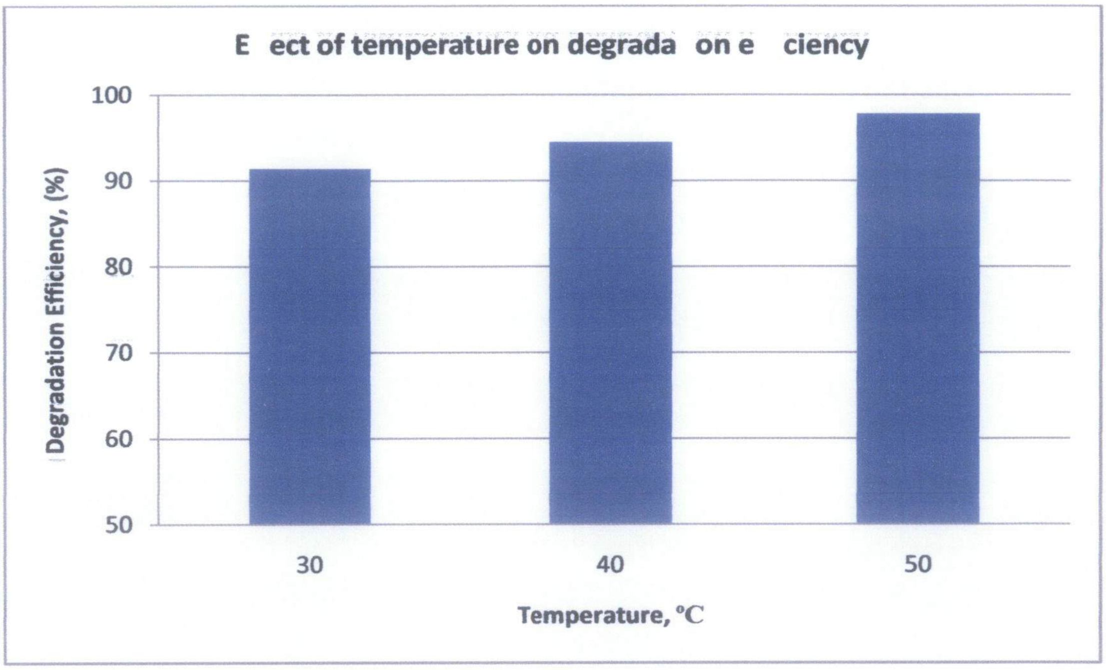


Figure 211: Effect of Variuos Temperature on Degradation Percentage

As the temperature increases (from 30 °C to 50 °C), the degradation percentage of Diethanolamine (DEA) is increasing further shown in the figure 21. Therefore, it can be concluded that as the temperature of the sample increases, the activation energy of H_2O_2 to hydroxyl radicals decreases which then lead to higher percentage degradation of DEA.

4.6 Optimization

Screening of independent factors that affect the degradation percentage was carried out according to table 3 by using Portable Statgraphics Centurion software. The range and level of the factors (initial concentration of H_2O_2, initial pH and temperature) were determined based on the initial screening results while the other factors (DEA concentration, UV intensity and irradiation time) were kept constant. Based on the figure 22, it indicates the Pareto chart of standardized effect at p=0.05 which shows that all the three factors, initial concentration of H2O2, initial pH and temperature have a significant contribution to the degradation percentage of Diethanolamine (DEA).

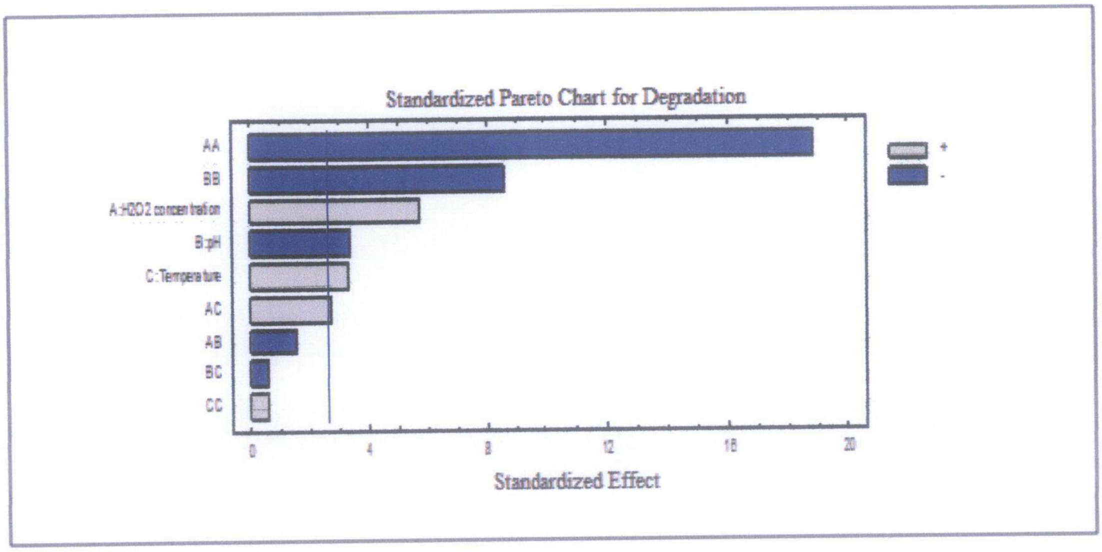


Figure 222: Pareto chart of standardized effect for percentage of degradation

The optimum response and relationship between the factors and response were obtained by using Response Surface Methodology (RSM). The quadratic regression model for the percentage of degradation is shown in the equation below:

$$Y = 44.9531 + 0.05475\,x_1 + 5.90417\,x_2 - 0.219167\,x_3 - 0.0000187167\,x_1^2 - 0.000375\,x_1x_2 + 0.00013\,x_1x_3 - 0.532292\,x_2^2 - 0.0075x_2x_3 + 0.00145833\,x_3^2$$

$R^2 = 0.989$

X_1 = H_2O_2 concentration

X_2 = pH

X_3 = temperature

Therefore, based on the model, the predicted value percentage degradation was calculated and has been compared with the observed value through experiments. The results are summarized in the table 3 and graph below in figure 23:

Table 3: Comparison of degradation efficiency between predicted and observed values

Exp Num	H2O2 Concentration (ppm)	pH	Temperature (°C)	Degradation (%) observed	Degradation (%) predicted
1	1500.0	5.0	40.0	98.20	98.23
2	2000.0	5.0	50.0	95.50	95.86
3	1000.0	7.0	40.0	89.80	90.27
4	2000.0	5.0	30.0	93.20	93.46
5	1000.0	5.0	50.0	92.90	92.64
6	1500.0	7.0	30.0	95.40	95.29
7	1000.0	3.0	40.0	90.50	90.65
8	1500.0	3.0	50.0	97.40	97.51
9	2000.0	7.0	40.0	91.60	91.45
10	1000.0	5.0	30.0	93.20	92.84
11	1500.0	5.0	40.0	98.00	98.23
12	1500.0	7.0	50.0	96.30	96.09
13	1500.0	5.0	40.0	98.50	98.23
14	1500.0	3.0	30.0	95.90	96.11
15	2000.0	3.0	40.0	93.80	93.32

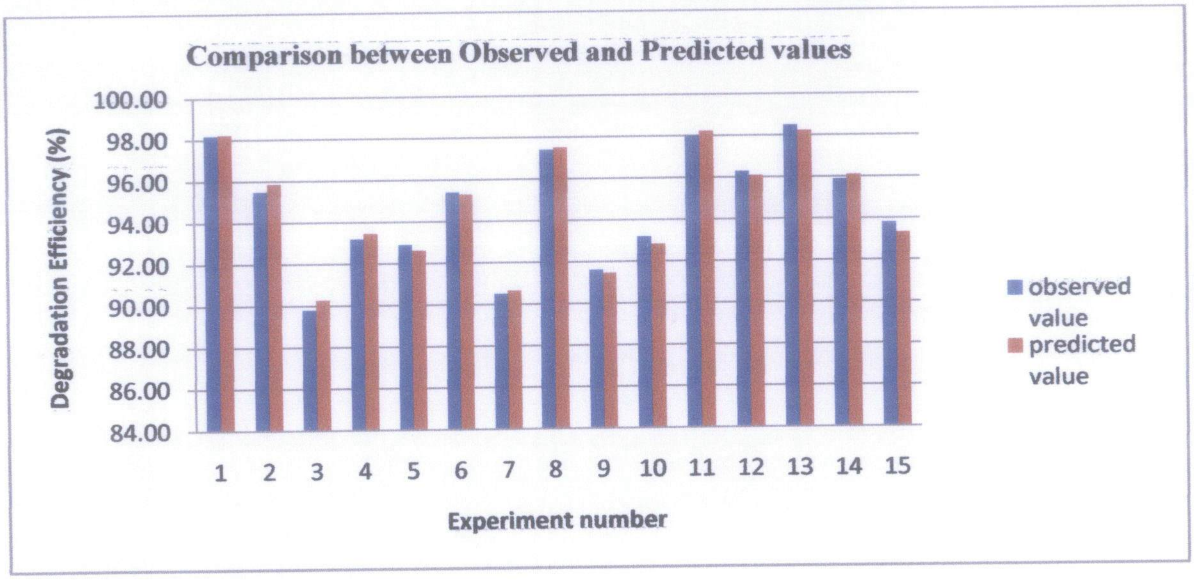


Figure 233: Comparison between observed and predicted values (chart)

Other than that, the relationship between the observed and predicted values for degradation of DEA is shown in the figure 24. Based on the graph, there is not much different between the degradation efficiency between observed and predicted values. With R^2=0.989, a straight line has obtained and as shown in the graph, the observed value is directly proportional to the predicted values.

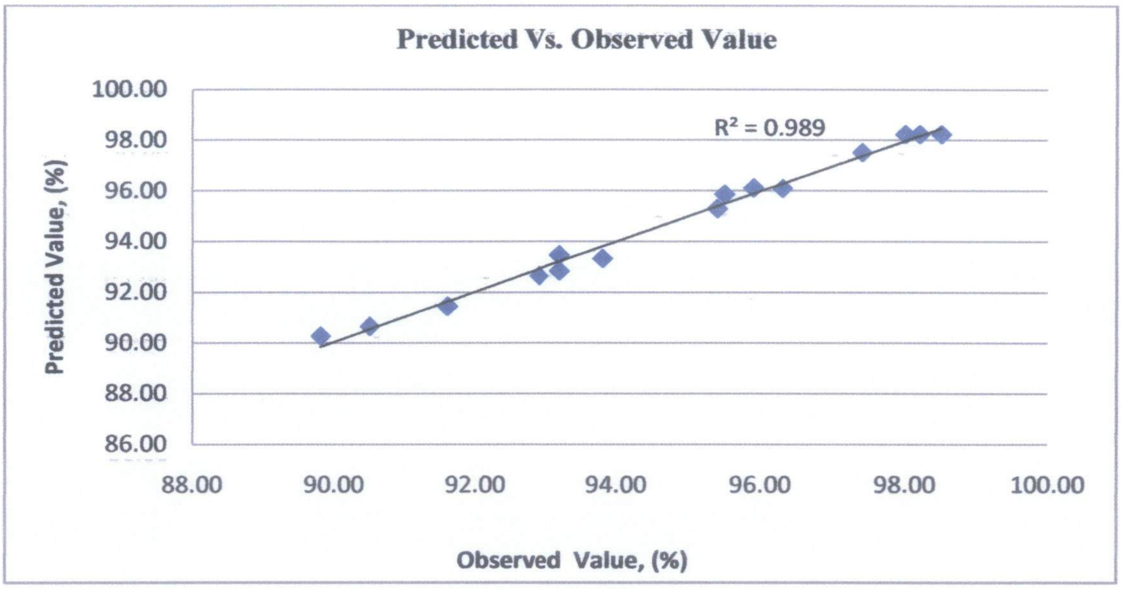


Figure 244: Relationship between predicted and observed values (graph)

Other than that, in order to visualize the effect of factors towards the response which is degradation percentage, a graphical representation known as contour plot and 3D curvature of the regression model are shown in the figure25.

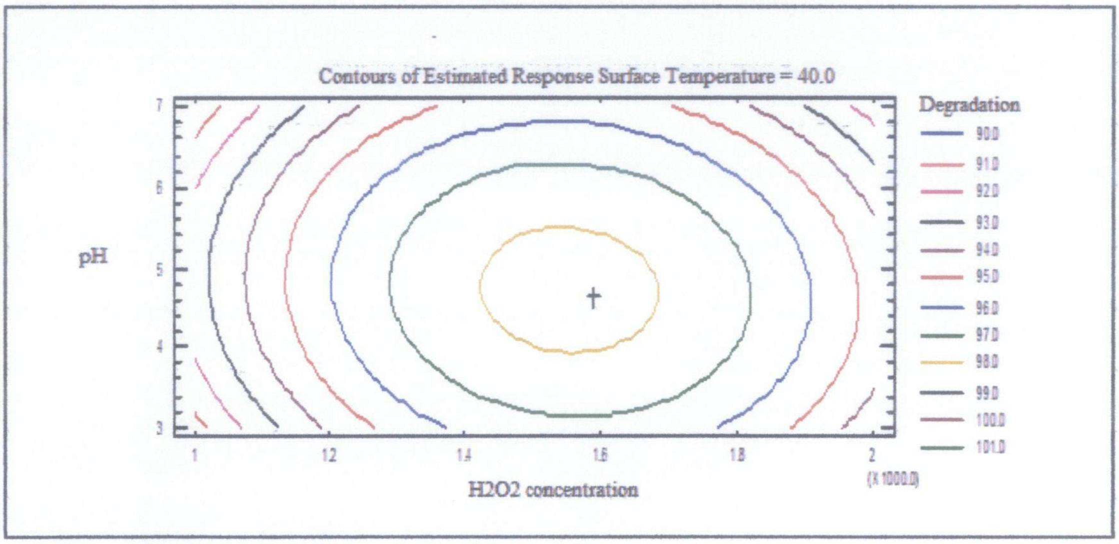


Figure 255: Contour plot for degradation of DEA at constant temperature

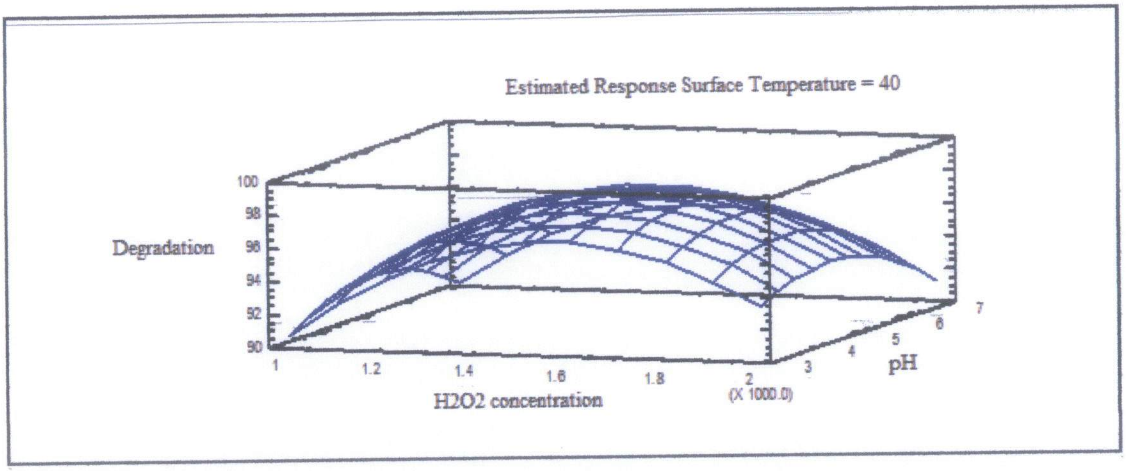


Figure 266: The effect of initial H2O2 concentration and pH and DEA degradation for 1500ppm initial concentration (temperature=40C)

As shown in the 3D semi spherical response plot in figure 26, the DEA degradation percentage increased as the pH increase until its optimum value which is about pH 4.6. However, after its optimum pH, the degradation of DEA seems decreased throughout the irradiation time. This is because the decomposition of H_2O_2 into hydroxyl radicals works best in the acidic condition as mention earlier. Besides that, it also can be seen that as the initial concentration of H_2O_2 increase, the DEA degradation also keep increase due to the generation of hydroxyl radical. However, after reached at its optimum value which is at 1590.13 ppm of H_2O_2 concentration, the degradation percentage is decreasing. The reason is because there are excess of hydroxyl radicals produced as throughout the experiment, constant initial concentration of dietanolamine (DEA) has been used.

The optimum condition obtained by using box-Behnken Response Surface Methodology is tabulated in table 4, the optimum condition for H_2O_2 concentration is 1590.13 ppm, pH 4.63 and at temperature 50°C and its degradation efficiency predicted is 99.14%. However, in order to validate the validity of regression equation, another two experiments were conducted at optimum condition. Based on the result obtained, the average degradation is 98.99. The error of the model predicted and experimental value of degradation efficiency is 0.15% which is in satisfactory agreement with the predicted value.

Table 4: The optimum condition for degradtion of Diethanolamine (DEA)

Factor	Low	High	Optimum
H2O2 concentration	1000.0	2000.0	1590.13
pH	3.0	7.0	4.63369
Temperature	30.0	50.0	50.0

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, the degradation of Diethanolamine (DEA) by using UltraViolet and Hydrogen Peroxide UV/ H_2O_2 is efficiently to be applied. Experiments on various parameters have been conducted to evaluate the degradation percentage of Diethanolamine within 4 hours of irradiation time. The parameters that have been done are the effect of initial H_2O_2 concentration, initial Diethanolamine concentration, initial pH and temperature. As the initial concentration hydrogen peroxide increases, the degradation percentage increases as well up until 1500ppm. However, further increase causes decreases in the degradation percentage. The optimum initial concentration oh hydrogen peroxide observed is at 1500ppm. For the second parameter, the degradation percentage also increases as the initial concentration of Diethanolamine increases. However, after 1000ppm, the degradation percentage decreases. Hence, the optimum initial condition for initial concentration of Diethanolamine is at 1000ppm. Thirdly, for the effect of pH to the degradation of Diethanolamine, the degradation increases up until pH 5, then decrease when the pH increases. This shows that, the degradation of Diethanolamine works best at in acidic condition which is 5. Last but not least is the effect of temperature on the degradation percentage. As the temperature increases from 30 °C to 50 °C, the degradation keep increasing further. Based on Response Surface Methodology (RSM), the optimum condition for the oxidation of 400mL of total volume of 1000ppm initial concentration of diethanolamine (DEA) by using the UV/ H_2O_2 method was at temperature 50°C, pH 4.63 and 1590.13 ppm of initial concentration of H_2O_2 which results in degradation efficiency of 99.14%. The error of the model predicted and experimental value was found to be 0.15%. Therefore this proves that the Box-Behnken Response Surface Methodology (RSM) was reliable to study the optimization of the degradation study of Diethaolamine (DEA) using UV/ H_2O_2 method.

5.2 Recommendation

In general, the results obtained shows that the use of UV/ H_2O_2 technology has very good potential for degrading Diethanolamine (DEA) in solution.

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