Application of the Central Composite Design and Response Surface Methodology to the Treatment of Wastewater Contaminated with Monoethanolamine using Fenton's Reagent.

by
Niamnah Ayae

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

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Putri Nadzrul Faizura bt. Megat Khamaruddin)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

CERTIFICATION OF ORIGINALITY

This is to certify 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.

NIAMNAH AYAE

ABSTRACT

Monoethanolamine (MEA) is a solvent which frequently used for acidic gases removal in natural gas sweetening process.A substantial amount of MEA contaminated wastewater was generated during maintenance and cleaning of absorption and stripping column.The MEA compound are not readily biodegradable due to a high COD level of MEA containing in wastewater.

Therefore, the treatment of wastewater contaminated with MEA using Fenton's oxidation is studied in the present research. The analysis method used response surface methodology (RSM). The experiments were designed using central composite design (CCD).

In this work, The objectives are to investigate the influences of two important process parameters which are initial concentration of H_2O_2 and Fe^{2+} on the rate of MEA degradation and also to determine the optimum conditions for the degradation of MEA. Approximately, 92% of MEA concentration were degraded at the optimum condition of H_2O_2 and Fe^{2+} concentration were at 1.396 M and 0.0172 M respectively.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, to meet the ever-increasing requirements of human beings have led to the new developments in the variety of fields which have also led to the presence of new compounds in the effluent streams of processing plants, which are not readily degraded by the conventional effluent treatment methods (Bauer and Fallmann, 1997), In order to cope with the vast problems arising through growing industrialization , the focus on waste minimization in recent years has also resulted in the production of concentrated or toxic residues. It is of utmost importance to dispose of these residues in a proper manner as well as to keep the concentration of chemicals in the effluent stream to a certain minimum level in order to comply with the environmental laws, which are becoming more stringent these days. Thus, research into new or more efficient wastewater treatment technologies so as to degrade the complex refractory molecules into simpler molecules is vital to combat the deteriorating water quality (Gogate et. 2004)**.**

1.2 Problem statement

Throughout the Gas Sweetening process in natural gas industries, the alkannolamine is often used as the solvent to remove acid gases containing CO_2 and H_2S from natural gas streams . Substantial quantity of aqueous MEA appear in the wastewater during the cleaning and maintenance of the absorption and stripping towers as well as during the process downtime.

To treat the wastewater contaminated with the MEA aqueous solution, most of the plant has been encountered with the similar problem which wastewater cannot be cleaned in the conventional biological oxidation unit, since MEA is difficult to biodegrade due to the high range of chemical oxygen demand (COD) level. Hence the advance oxidation process by Fenton’s Reagent has been introduced to investigate the degradation of the MEA in wastewater effluent.

1.3 Objectives

- The objective of this project study is to apply Central Composite Design (CCD) based Response Surface Methodology (RSM) to analyze the process parameters on the degradation of MEA by Fenton Reagent .
- To investigate the effects of important process variables like Fe (II) concentration, H2O2 concentration, solution pH on MEA degradation performance
- To search for the optimal values for attaining a suitable operating condition of MEA degradation.

1.4 Scopes of Study

- In this project study, the laboratory set up will conduct to monitor the degradation rate of the MEA and the effect of the different process variables on the rate and extent of the MEA degradation.
- The optimum process conditions will be developed using Central Composite Design (CCD) based Response Surface Methodology (RSM) ; an effective experiment design procedure

1.5 Relevancy and Feasibility of the Project

Environmental issues have become a big concern to every organization all around the world. Arising through the growing industrialization and the new developments in the variety of fields have led to the presence of new compounds in the effluent streams of processing plants which cause environmental pollution. In which chemical engineers have also focused and play a significant role in developing advanced technologies and operating strategies to reduce the pollution produced from the processing plant in order to comply with environmental law as well as to sustain a healthy environment. As a chemical engineering student, this project study is very relevant to the author's field of study and it will provide a good challenge to pave the way for the author to become a good engineer in the future.

The project is feasible since it is within the scope and time frame. The chemical compounds are provided in UTP laboratory's stock. Besides that, the HPLC and other equipments are readily available at the university Lab (Block 3 and 4) and thus there is no wastage of time in ordering and waiting for their arrival.

CHAPTER 2

LITERATURE REVIEW

2.1 Monoethanolamine (MEA)

Monoethanolamine (MEA) is an organic chemical compound which has both primary amine(due to an amino group in its molecule) and a primary alcohol (due to a hydroxyl group).Like other amines, MEA acts as a weak base, toxic, flammable, corrosive, colorless and viscous liquid with an odor similar to ammonia. MEA is produced by reacting ethylene oxide with ammonia (Harold *et al*., 2004)

MEA is one of the most widely used alkanolamines for removing sour gases (e.g..,H_2S and CO_2) from natural gas during refining in the so-called 'sweetening process' (J.R. Gallagher *et al.*,1995). It is also used in the formulation of surface-active agent, emulsifier, polishes, pharmaceuticals, corrosion inhibitors, and as a chemical intermediate (Sabtanti et al., 2009).

MEA is often used for alkalinization of water in steam cycles of power plants with pressurized water reactors to control corrosion of metals. The water /steam circulation system of nuclear power plants and thermal power stations uses an ion-exchange resin column to capture MEA, and it is released into the wastewater through a resin regeneration process. The waste water from the purged solution and the regeneration plant contains high concentration MEA that must be appropriately treated to meet the environmental discharge standard (Dong-Jin Kim et al., 2010). Wastewater from TFT-LCD (thin film transistor liquid crystal display) and PDP (plasma display panel) manufacturing plants also contain as much as 1000 mg/L of MEA (T.K. Chen et al.,2003) .

In the petrochemical industry, especially in natural gas processing plant, raw natural gas which contains carbon dioxide needs to be treated to remove the CO_2 prioritizing further processing activities. This CO_2 is considerably as interference in the processing activities and would thwart the production quality (M.N. Razali et al., 2010).

Technologies to separate CO_2 from flue gases are based on absorption, adsorption, membranes or other physical and biological separation methods .The most commercially used technology is amine based CO_2 absorption systems. The reason being used widely are the system can be used to dilute systems and low CO_2 concentration, easy to use and can be retrofitted to any plants. Absorption processes are based on thermally regenerable solvents, which have a strong affinity for CO_2.The solvent is regenerated at elevated temperature, thus required thermal energy for regeneration (Abu-Zahra et al., 2007).

Currently, aqueous mono-ethanolamine (MEA) is widely used for removing carbon dioxide and hydrogen sulfide from flue gas streams (Harold et al., 2004).

2.2 Alkanolamine as Solvent

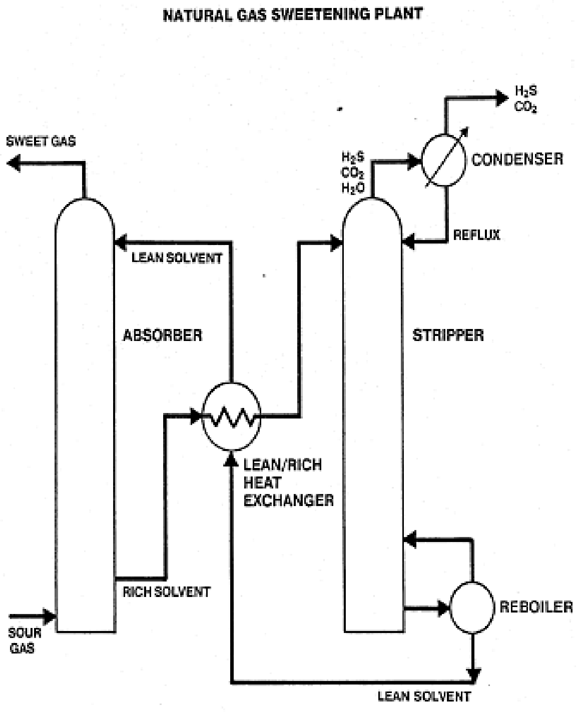
Acid gases like CO2, H2S and other sulphuric components are usually to some extent present in natural gas and industrial gases. They may have to be removed (selectively) from these gas streams for operational, economic or environmental reasons. One of the most commonly used processes for the removal of acid components is absorption in alkanolamine based solvents. In this process the acidic components react with an alkanolamine absorption liquid via an exothermic, reversible reaction in a gas/liquid contactor. In a following process step the acidic components are removed from the solvent in a regenerator, usually at low pressure and/or high temperature (P.J.G. Huttenhuis et al., 2007).Industrially important alkanol amines for this operation are monoethanol amine (MEA), diethanol amine (DEA), di-isopropanol amine(DIPA) and N-methyl diethanol amine (MDEA) (B.P Mandal et al.,2005).

2.3 Amine Sweetening Process

Natural gas has a wide range of acid gas concentrations, from parts per million to 50 volume Percent and higher, depending on the nature of the rock formation from which it comes. Because of the corrosiveness of H_2S and $C0_2$ in the presence of water and because of the toxicity of H_2S and the lack of heating value of $C0_2$, sales gas is required to be sweetened to contain no more than a quarter grain H_2S per 100 standard cubic feet (4 parts per million) and to have a heating value of no less than 920 to 980 Btu/SCF, depending on the contract.

The most widely used processes to sweeten natural gas are those using the alkanolamines, and of the alkanolamines the two most common are monoethanolamine (MEA) and diethanolamine (DEA). The monoethanolamine and diethanolamine sweetening processes are similar in their flow schemes and operations. They are used as aqueous solvents to selectively absorb H_2S and $C0_2$ from sour natural gas streams. The sour gas is introduced at the bottom of an absorber and flows up the tower countercurrent to an aqueous amine stream. Within the tower the acid gases are absorbed by the amine. The amine is described as being lean in acid gas as it enters the top of the absorber, and rich as it exits the bottom, loaded with acid gas. From the absorber the rich amine is directed to the top of a stripping tower where a drop in pressure and application of heat enables the solvent to be stripped of the acid gases. The amine, again lean, is circulated back to the absorber for sweetening (Figure 1) (M.N. Razali et al., 2010)..

Figure2. 1 Gas Sweetening Process



NATURAL GAS SWEETENING PLANT

Figure 1. Simplified amine gas sweetening process flow diagram

One of the operational difficulties experienced in the CO2 absorption process is when the heavy hydrocarbon component carried over with the feed gas entering to the absorber that the foaming may be developed. Besides, the reaction of CO_2 and MEA will produce some salt therefore increasing in the amount of suspended solids in absorber which also contributed to the foaming problem.

The decreasing in absorption efficiency and quality of product gas as well as the increasing in amine losses are the problem caused by foaming phenomenon. The properties of the stripper are deteriorated and thus result in the difficulties in optimizing the absorption processes. MEA is not appropriate to feed back to the stripper and it has been removed as wastewater (M.N. Razali et al., 2010)..

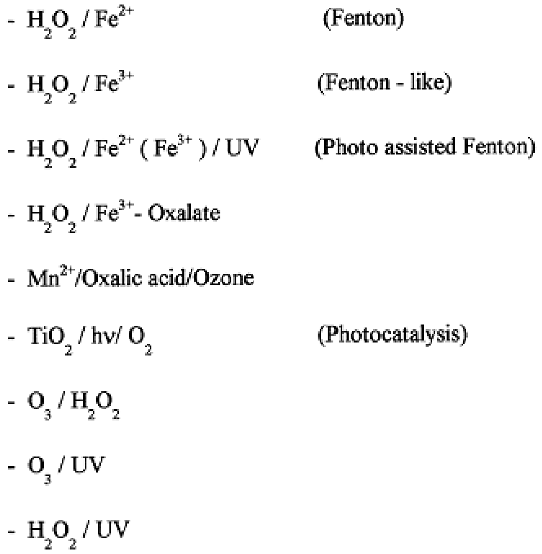
The MEA wastewater will upset the Wastewater Treatment Plant (WTP) once enters into the WTP unit by increasing the load and significantly increase the COD, suspended solids and oil concentration which complicate the effective treatment of such wastewater. In many occations, the concentration of amine in the wastewater trigger the COD to exceed the 200,000 ppm level and not possible to be treated in the WTP(M.N. Razali et al., 2010).

2.4 Advance Oxidation Process

Nowadays, due to the increasing presence of refractory pollutants in the effluent streams of wastewater which the conventional biological methods cannot be used for complete treatment of the effluent (Bauer and Fallmann, 1997). In this context, conventional biological processes do not always provide satisfactory results, especially for industrial wastewater treatment, since many of the organic substances produced by the chemical industry are toxic or resistant to biological treatment (Muñoz & Guieysee, 2006). There is a continuously increasing worldwide concern for the development of alternative water reuse technologies, and hence, the introduction of newer technologies to degrade these refractory molecules into smaller molecules, which can be further oxidized by biological methods, has become imperative. A lot of researches have been addressed with this aim in the last decade pointing out the prominent role of a special class of oxidation techniques defined as advanced oxidation processes (AOP) which usually operate at or near ambient temperature and pressure (W.H. Glaze et al.,1987).

Advanced Oxidation Processes (AOPs) are considered a highly competitive water treatment technology for the removal of those organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability. These processes are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in the effluent water (Gogate, P. R., & Pandit, A. B., 2004). These processes include cavitation , photocatalytic oxidation using ultraviolet radiation/near UV light/Sun light in the presence of semiconductor catalyst and Fenton chemistry (using the reaction between Fe ions and hydrogen peroxide, i.e. Fenton's reagent (Venkatadri and Peters, 1993). Hydroxyl radicals are powerful oxidizing reagents with an oxidation potential of 2.33 V and exhibits faster rates of oxidation reactions as compared to that using conventional oxidants like hydrogen peroxide or $KMnO_4$ .Hydroxyl radicals react with most organic and many inorganic solutes with high rate constants (Glaze et al., 1992) usually in the order of 10^6–10^9 M−1 s−1(Farhataziz, 1997).

Figure2.2 :Advance oxidation process



- H_2O_2 / Fe^{2+}	(Fenton)
- H_2O_2 / Fe^{3+}	(Fenton - like)
- H_2O_2 / Fe^{2+} (Fe^{3+}) / UV	(Photo assisted Fenton)
- H_2O_2 / Fe^{3+}- Oxalate	
- Mn^{2+}/Oxalic acid/Ozone	
- TiO_2 / hv/ O_2	(Photocatalysis)
- O_3 / H_2O_2	
- O_3 / UV	
- H_2O_2 / UV	

Fig. 1. Advanced oxidation processes.

2.5 Fenton’s Reagent

Fenton’s reagent is known as one of the most highly effective mixture in an oxidizing process for destroying toxic and many of hazardous organic pollutants from water by the destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts. Fenton’s reagent is a mixture of hydrogen peroxide in the presence of ferrous salts (walling 1975). The oxidation system based on the Fenton's reagent has been used for the treatment of both organic and inorganic substances under laboratory conditions as well as real effluents from different resources like chemical manufacturers, refinery and fuel terminals etc. (Bigda, 1996). Production of OH radicals by Fenton reagent occurs by means of addition of H_2O_2 to Fe^{2+} salts

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{*} \quad (1)$$

This is a very simple way of producing OH radical s neither special reactants nor special apparatus being required. This reactant is an attractive oxidative system for wastewater treatment due to the fact that iron is very abundant and non toxic element and hydrogen peroxide is easy to handle and environmentally safe. It must be stressed that the behavior of the system cannot be completely explained on the basis of the sole reaction (1). In fact, as it has been pointed out in many recent studies (J.J. Pignatello et al., 1992) the adoption of a proper value of pH (2.7–2.8) can result in the reduction of Fe^{3+} to Fe^{2+} (Fenton-like)

$$Fe3^{+} + H_2O_2 \leftrightarrow H^{+} + FeOOH^{2+} \quad (2)$$

$$FeOOH^{2+} \rightarrow HO_2^{*} + Fe^{2+} \quad (3)$$

Proceeding at an appreciable rate. In these conditions, iron can be considered as a real catalyst (Andreozzi, R et al., 1999). Hydroxyl radicals can oxidize organics (RH) by abstraction of protons producing organic radicals (R•), which are highly reactive and can be further oxidized (Walling and Kato, 1971)

$$RH + OH\cdot \rightarrow H_2O + R\cdot \rightarrow \text{further oxidation}$$

Walling simplified the overall Fenton chemistry [reaction (1)] by accounting for the dissociation water

$$2Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + 2H_2O$$

This equation suggests that the presence of H^{+} is required in the decomposition of H_2O_2, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. Previous Fenton studies have shown that acidic pH levels near 3 are usually optimum for Fenton oxidations (Hickey et al., 1995).

2.6 Previous research studies on the degradation of amine using Fenton's reagent

The Fenton oxidation of natural gas plant wastewater with initial COD concentration of 17,000 mg/L has been studied by Abdul Aziz Omar *et al*. 2010. In this research study , Diisopropanolamine (DIPA) was used as a model compound in simulated wastewater. The experiment was carried out to investigate the effect of different molar ratio, solution's initial pH and hydrogen peroxide concentration on the rate of COD removal.

To study effect of molar ratios of H_2O_2/Fe^{2+}, a set of experiments was conducted at different molar ratio of 5,10,20 and 30 by using a constant amount of hydrogen peroxide at 216 ml/L and the highest COD percentage removal was obtained at a molar ratio of 10 with 64% COD removal. This research study also conducts a series of experiment at different PH values of 2, 3, 4,and 5 and the optimum degradation of amine was achieved at pH 3 with 73% COD removal.

Beside molar ratio and pH value, the hydrogen peroxide concentration is another main factor that affects the degradation of recalcitrant compounds by Fenton's oxidation. So that effect of hydrogen peroxide to the degradation efficiency was studied by varying its amount used in a set of experiment in the range of 86 to 260 ml/L. The finding of the experiment shows that the highest COD removal was obtained at the concentration of 216 ml/L.

Therefore, the application of Fenton's oxidation to degrade natural gas wastewaters has been proved to be efficient with the highest 73% of COD removal achieved.

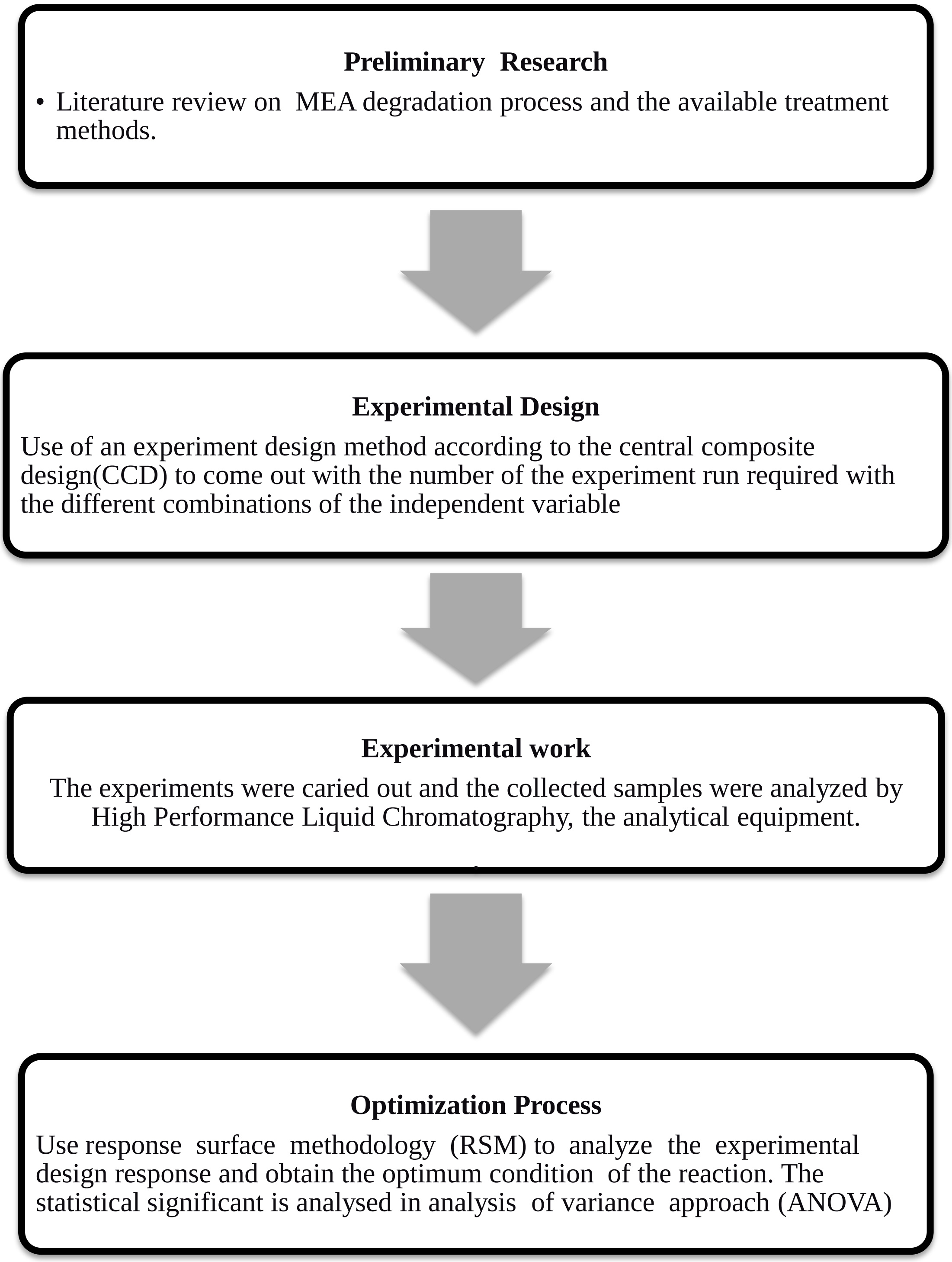
A similar study was reported by subtanti et al 2009 on the degradation of monoethanolamine (MEA) in aqueous solution by Fenton's reagent with biological post-treatment. Several factors have been investigated in this study are the effect of initial concentration of MEA, H2O2, Fe^{2+} and pH values. The result of the study of the effect of initial concentration of MEA was found that the COD values degraded vary rapidly at a high initial amine concentration.

The finding for optimum pH value was found to be 3 which is same finding reported in previous research mentioned earlier. The effect of H_2O_2 dosing Fenton's treatment was investigated at a range of 1.415 to 2.831M and the highest COD removal occurs at concentration 2.123 M. The effect of dosing of Fe^{2+} on degradation rate also studied in the range of 0.014M to 0.043 M .The COD removal reaches the optimum value 0.0288M.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology



Preliminary Research

- Literature review on MEA degradation process and the available treatment methods.

Experimental Design

Use of an experiment design method according to the central composite design(CCD) to come out with the number of the experiment run required with the different combinations of the independent variable

Experimental work

The experiments were caried out and the collected samples were analyzed by High Performance Liquid Chromatography, the analytical equipment.

Optimization Process

Use response surface methodology (RSM) to analyze the experimental design response and obtain the optimum condition of the reaction. The statistical significant is analysed in analysis of variance approach (ANOVA)

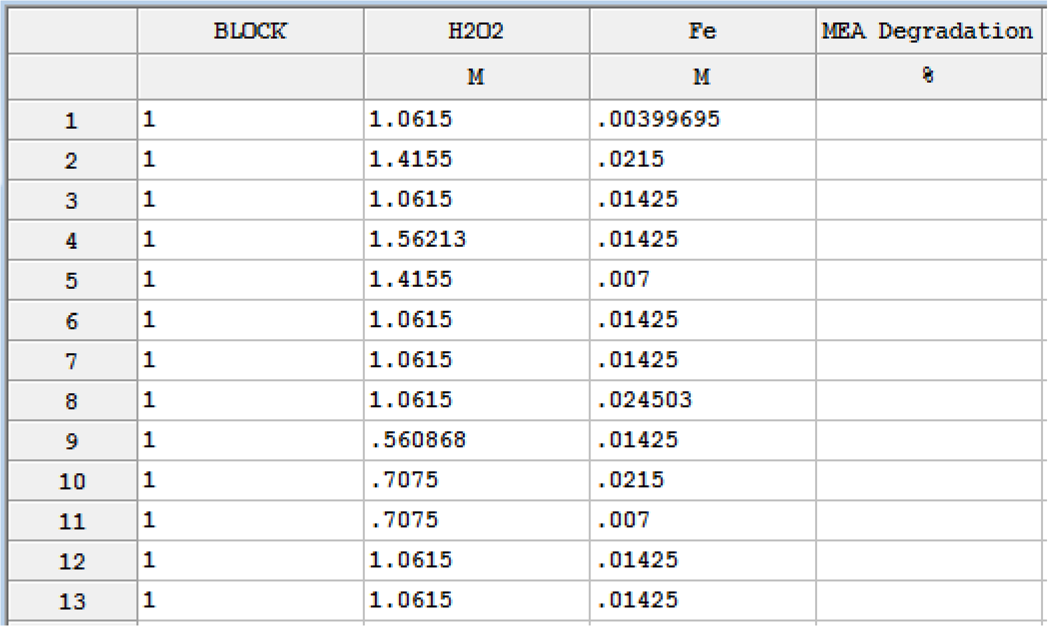
3.1.1 Experimental Design

The experimental design was conducted by using Portable Statgraphics Centurion Statistical software. The factor's range using in designing experiments in this experimental design software refers to the range of factor has been studied in previous research on the degradation of MEA in aqueous solution by Fenton's reagent conducted by sabtanti et al 2009. The parameter range used as the reference are tabulated below:

Table 3.1 :Process parameter range

System Variable	Range (Literature)	Range (used in this study)
H2O2 Concentration	1.415 -2.831	0.7075-1.4155
Ferrous ion concentration	0.014-0.043	0.007-0.0215

Table 3. 2 : Experimental Design Table From Statgraphics Centurion Statistical software



	BLOCK	H2O2	Fe	MEA Degradation
		M	M	%
1	1	1.0615	.00399695	
2	1	1.4155	.0215	
3	1	1.0615	.01425	
4	1	1.56213	.01425	
5	1	1.4155	.007	
6	1	1.0615	.01425	
7	1	1.0615	.01425	
8	1	1.0615	.024503	
9	1	.560868	.01425	
10	1	.7075	.0215	
11	1	.7075	.007	
12	1	1.0615	.01425	
13	1	1.0615	.01425	

The experiment of MEA degradation using Fenton's reagent will be conducted with a total number of 13 experiments. The percentage of MEA degradation is the expected result obtained from the experiment which required for later input to the software in order to analyze the design based on the response surface methodology for further analysis and identify the optimum values of these two factors for the MEA degradation.

Design Summary

Response Surface Design Attributes

Design class: Response Surface

Design name: Central composite design: 2^2 + star

Design characteristic: Rotatable

File name: <Untitled>

Base Design

Number of experimental factors: 2

Number of blocks: 1

Number of responses: 1

Number of runs: 13, including 5 centerpoints per block

Error degrees of freedom: 7

Randomized: Yes

Factors	***Low***	***High***	***Units***	***Continuous***
H2O2	0.7075	1.4155	M	Yes
Fe	0.007	0.0215	M	Yes

Responses	***Units***
MEA Degradation	%

The StatAdvisor

You have created a Central composite design: 2^2 + star design which will study the effects of 2 factors in 13 runs. The design is to be run in a single block. The order of the experiments has been fully randomized. This will provide protection against the effects of lurking variables.

3.1.2 Experiment Methodology.

1. Specific concentration of the MEA was prepared as the reaction solution.

2. Measured volume of reaction solution was placed in the reactor. This volume depended on the volume of hydrogen peroxide that was dosed for each particular experimental run. Both magnetic stirrer and recirculation water bath were switched on at this point.

3. PH of the reaction solution was correct according to the parameter setup for each experimental run.

4. Weighed ferrous sulfate crystals were added to the solution. This weight depends on the calculated dosage for each particular experimental run. These crystals were solubilised in the reaction solution due to the mixing.

5 Upon reaching the specified temperature, hydrogen peroxide was added and the reaction time begins. Reaction time was set at 30 minutes and 60 minutes, depending on the experimental run.

6. Five ml of samples was collected using a 5-mL pipette.

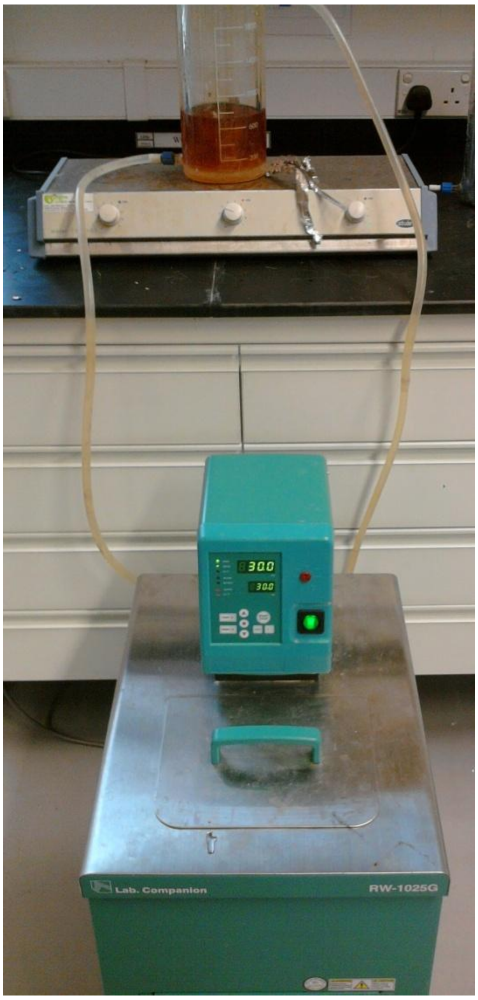
7. These samples were treated with two drops of 10 M sodium hydroxide to stop the reaction right after sampling. Highly concentrated sodium hydroxide was used to increase the pH of the samples above the effective limit of the reaction. The method used for this study was based on the method used by Pontes et al. (2010).

8 These samples were then placed in a water bath. The temperature set was 60°C to remove any residual hydrogen peroxide. This is the temperature where hydrogen peroxide is expected to undergo self-degradation of water and oxygen according to its Material Safety and Data Sheet.

9. Samples were cooled and filtered using syringe filter, Whatman Puradisc Aqua 30 with 0.45 mm with cellulose acetate membrane to remove suspended solids.

10. Samples to be analyzed using HPLC were transferred to 2 ml screw cap sample vials without dilution.

Figure3. 1 : experimentent Setup of the expeiment



3.1.2.1 List of Chemical uses :

- Monoethanolamine (MEA)
- Ferrous sulfate ($FeSO4·7H2O$)
- Hydrogen Peroxide ($H2O2$)
- Sodium Hydroxide (NaOH)
- Sulfuric Acid (H_2SO_4)

3.1.2.2 Equipment /Apparatus uses :

- Reactor
- Magnetic Stirrers and Recirculation water bath
- Cellulose acetate membrane
- Syringe filter
- Pipette

3.1.2.3 Analytical Equipments

- High-Performance Liquid Chromatography -HPLC

3.1.3 Statistical Analysis Methodology

The optimization of Fenton reagent conditions was an important problem in the development of economically feasible bioprocesses. Response Surface Methodology (RSM) is used to develop an effective experimental design procedure which is a collection of statistical techniques for design of experiments, building models, evaluating the effects of factors and searching for the optimum conditions for process's optimization.

A prior knowledge and understanding of the process and the process variables under investigation are necessary for achieving a more realistic model. A 2^{6-2} Fractional Factorial Designs (FFD) was used to pick factors that influence the effectiveness of the degradation of MEA significantly and insignificant ones were eliminated in order to obtain a smaller, more manageable set of factors. In developing the regression equation, the test variables were coded-according to the equation:

$$X_j = (Z_j - Z_{0j}) / \Delta_j \qquad (1)$$

Where X_j is the coded value of the independent variable, Z_j is the real value of the independent variable, Z_{0j} is the value of the independent variable on the center point and Δ_j is the step change value. The linear model observed is expressed as
follows:

$$Y = \beta_0 + \sum_{j=1}^{3} \beta_j x_j \qquad (2)$$

Where Y is the predicted response, X_j are input variables which influence the response variable Y; β_0 is the intercept β_j is the jth linear coefficient.

If the mean of the center points exceeds the mean of factorial points, the optimum would be near or with the experimental design space. If the mean of the centre points was less than the mean of the factorial points, the optimum would be outside the experimental design space and the method of the steepest ascent should be applied. The direction

On the steepest ascent is parallel to the normal contour line of the response curve of the model (Eq. 1) and passes through the center point of FFD. The increment is a direct ratio to regression coefficients β_j . Experiments were performed along the steepest ascent path until the response did not increase any more. This point would be near the optimal point and can be used as a center point to optimize the medium parameters.

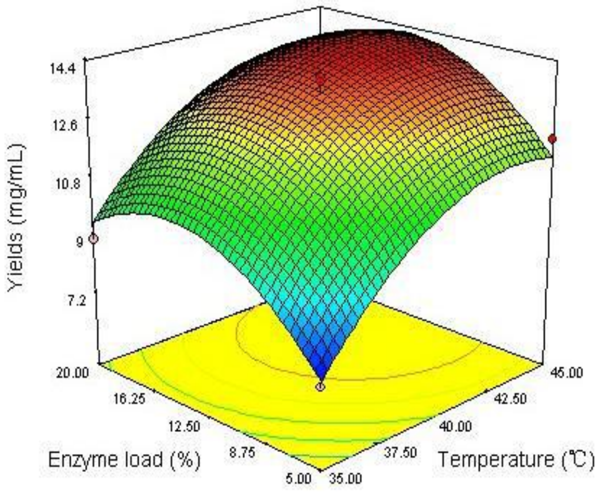
Once critical factors were identified via screening and significant gross curvature was detected in the design space, the central composite design was proceeded obtain a quadratic model, consisting of trials plus a star configuration to estimate quadratic effects and central points to estimate the pure process variability and reassess gross curvature, with COD level as response. For two factors, the model obtained was expressed as follows:

$$Y= \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_{11}^2 + \beta_{22} X_{22}^2 + \beta_{12} X_{12} \quad (3)$$

Where Y is the measured response, β_0 is the intercept term, β_1 and β2 are linear coefficients, β_{12} is the logarithmic coefficient, β_{11} and β_{22} are quadratic coefficients, and X_1 and X_2 were coded independent variables. Low and high factor settings are coded as -1 and 1, the midpoint coded as 0. The factor settings of trails that ran along axes drawn from the middle of the cube through the centers of each face of the tube are coded as -1.414 or 1.414. The Statgraphics Centurion software, version 15.2.11.0 was used for regression and graphical analysis of the data obtained by ridge analysis.

The statistical analysis of the model was performed in the form of Analysis of Variance (ANOVA).

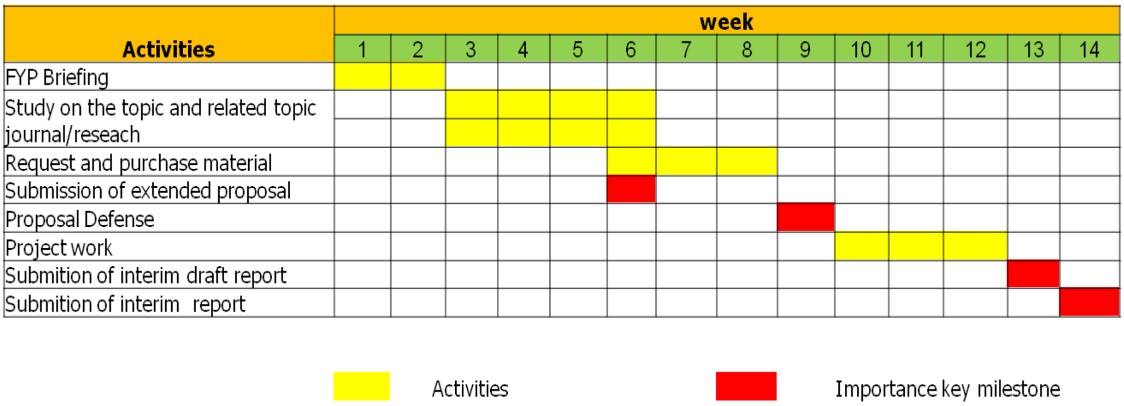
Figure3. 2:Example of RSM Optimization analysis by 3D model



3.2 Project Gantt Chart

FYP I

Figure3. 3 : FYP I Project Gantt Chart

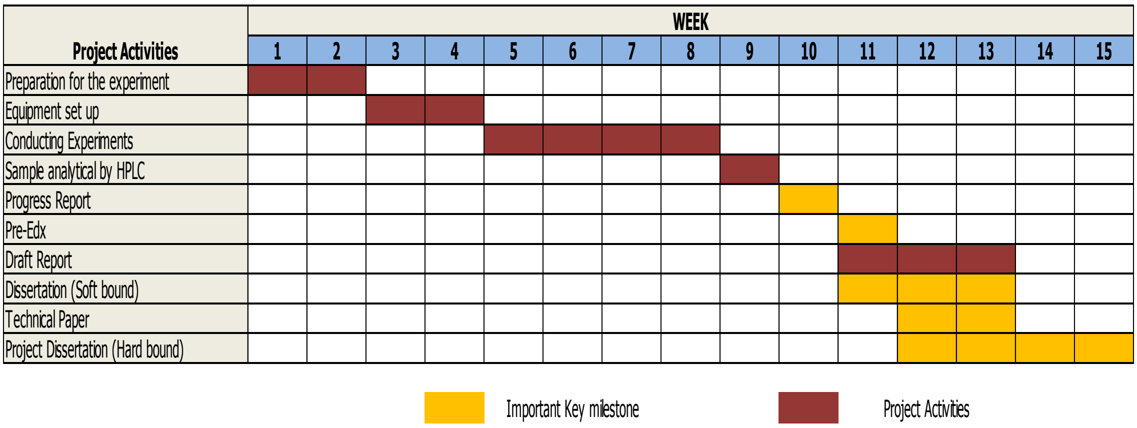


Activities	week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
FYP Briefing	🟨	🟨												
Study on the topic and related topic journal/reseach			🟨	🟨	🟨	🟨								
Request and purchase material						🟨	🟨	🟨						
Submission of extended proposal						🟥								
Proposal Defense									🟥					
Project work										🟨	🟨	🟨		
Submition of interim draft report													🟥	
Submition of interim report														🟥

🟨 Activities 🟥 Importance key milestone

FYP II

Figure3. 4: FYP II Project Gantt Chart



Project Activities	WEEK														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Preparation for the experiment	🟫	🟫													
Equipment set up			🟫	🟫											
Conducting Experiments					🟫	🟫	🟫	🟫							
Sample analytical by HPLC									🟫						
Progress Report										🟧					
Pre-Edx											🟧				
Draft Report											🟫	🟫	🟫		
Dissertation (Soft bound)											🟧	🟧	🟧		
Technical Paper												🟧	🟧		
Project Dissertation (Hard bound)												🟧	🟧	🟧	🟧

🟧 Important Key milestone 🟫 Project Activities

CHAPTER 4

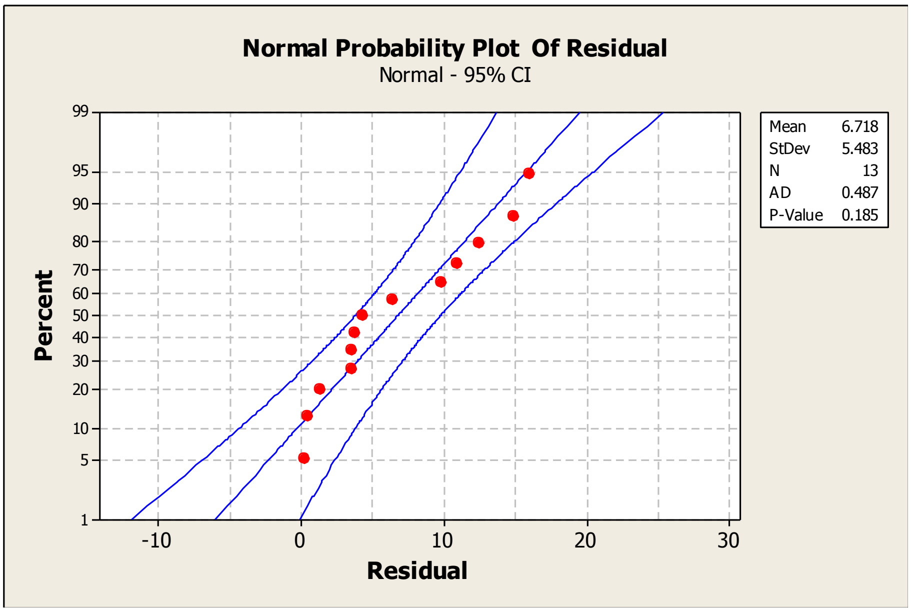
RESULT AND DISCUSSION

The 13 runs of experiments on the treatment of the 16,000 ppm monoethanolamine (MEA) contaminated in wastewater were carried out in accordance with Table 4.1 which was generated from Statgraphic Centurion software. The experiments were conducted at a constant temperature of 30 degC and at an initial pH of 3 with a 30 min reaction time. The result in the table shows the percentage MEA degradation at each of the experiment runs that varies in the independent factor, Fe^{2+} and H_2O_2 .

Table 4. 1 The input factor of [H2O2] , [Fe^{2+}] and % of MEA Degradation

H2O2 (M)	Fe2+ (M)	% MEA Degradation
1.061500	0.024503	78.428
1.415500	0.007000	83.757
0.560868	0.014250	15.803
0.707500	0.021500	82.625
1.061500	0.003997	43.172
1.061500	0.014250	90.588
1.415500	0.021500	93.783
0.707500	0.007000	33.078
1.061500	0.014250	80.119
1.061500	0.014250	76.147
1.061500	0.014250	76.158
1.061500	0.014250	75.360

Figure 4. 1 : Normal Probability Plot of Residual



The normal probability plot of residual with a 95% confidence limit is also depicted in Figure 4.1 All the value point are presented within the range of the upper and lower limit. The normal probability plot of the residuals is approximately linear supporting the condition that the error terms are indeed normally distributed.

The optimum response and relationship between the factors and response were obtained by using response surface methodology. The quadratic regression model for the percentage of MEA degradation is given in Table 4.2.

Table 4. 2 : Regression coeffs. For MEA degradation

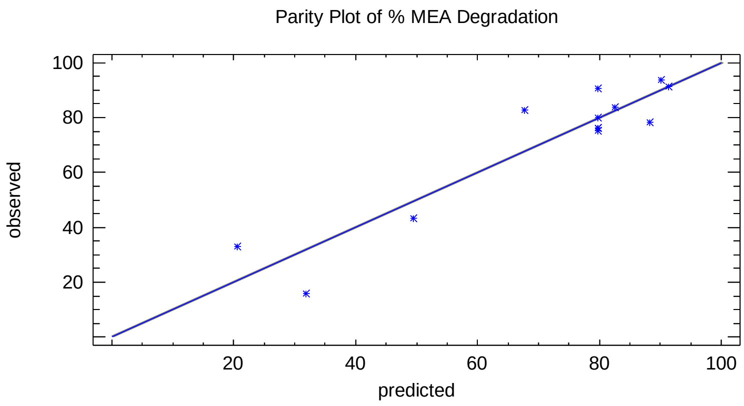
Coefficient	***Estimate***
Constant	-170.764
A:H2O2	267.55
B: Fe	8900.38
AA	-72.1598
AB	-3849.78
BB	-102704.
R^2 (%)	86.6137
Adjusted R^2 (%)	77.0521

From table 4.2 , the regression coefficients generated by RSM are represented and the equation of the fitted model is given below

Y = -170.764+267.55*A+8900.38*B-72.1598*A^ 2- 3849.78*A*B -102704. *B^2

Where, Y= % MEA degradation, A= $[H_2O_{2]}$ and B= $[Fe^{2+}]$

Figure 4. 2 : Parity Plot of % MEA Degradation



The parity plot showed a satisfactory correlation between experimental values and predicted values (Fig. 4.2) obtained from the fitted model equation, wherein the points cluster around the diagonal, which indicates the good fit of the model, since the deviation between the experimental and predicted values was small. This result indicates that the second-order polynomial model was highly significant and adequate to represent the actual relationship between the response and the independent variable .

The effect of factors towards the response is examined by the represented contour plot of model regression from Table 4.2 .The 2D and 3D curvature plots are depicted in figure 4.3 and 4.4 respectively .

Figure 4. 3 : 2D contour plot of MEA Degradation

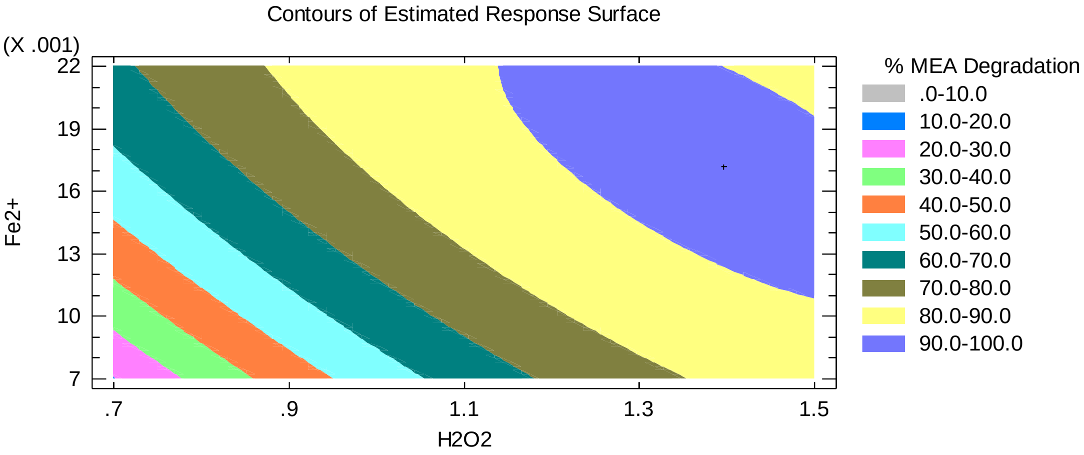
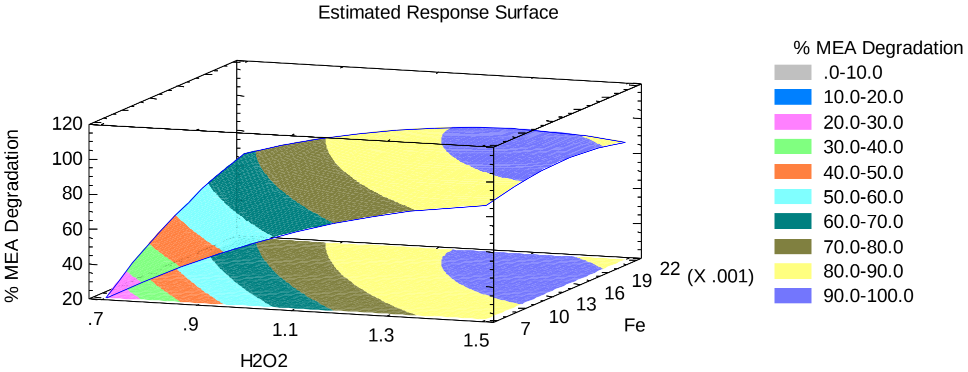


Figure 4. 4 :3D contour plot of MEA Degradation



For wastewater treatment using Fenton reagent , the major reactions for generation of the oxidizing radicals may be represented as

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + \cdot O_2H \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$H_2N - CH_2 - CH_3 - OH + \cdot OH \rightarrow H_2N - CH_2 - COOH + H_2O \ldots\ldots (3)$$

$$H_2N - CH_2 - COOH + \cdot OH \rightarrow Degradation\, product \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

As illustrated in Figure 4.3 and 4.4 , Increasing in degradation rate of MEA results from an increasing of H_2O_2 concentrations to a certain level due to the increasing sources of *OH radicals. Hence , the oxidation processes also increase accordingly. However, higher concentration of H_2O_2 lead to a lower degradation rate of MEA because a high concentration of H_2O_2 prevents efficient utilization of the hydroxyl radicals. It acts as a scavenger of *OH radicals and will produce O_2 that does not help in the degradation process. As can seen in the reaction mechanism shown below:

$$H_2O_2 + \cdot OH \rightarrow HO_2^{\cdot} + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

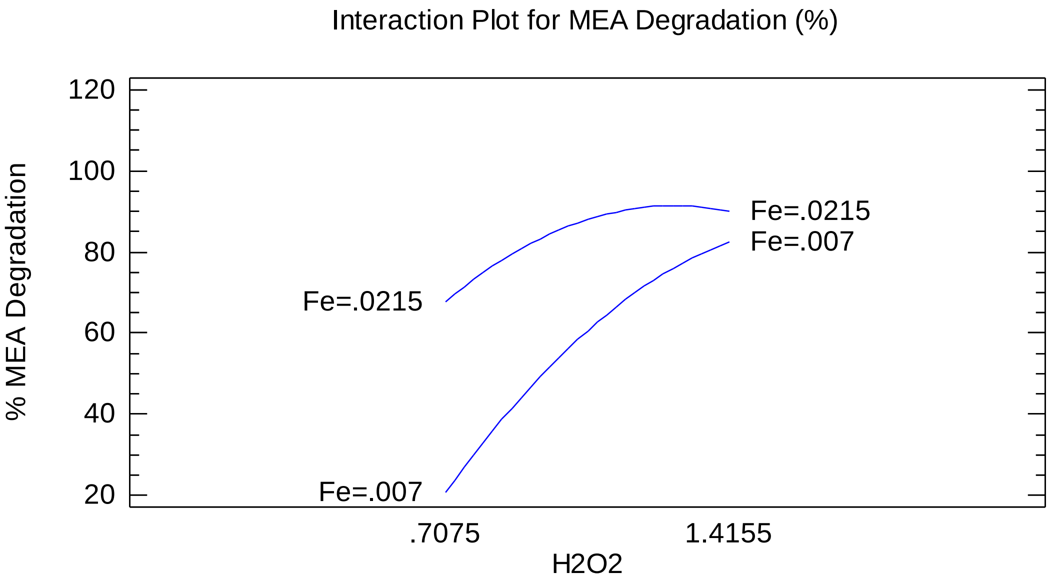
$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Moreover, the figures also illustrated the effect of Fe $^{2+}$ concentration towards the MEA degradation. Increasing of the Fe $^{2+}$ concentration result to an increasing of MEA degradation rate, since the required amount of *OH radicals for substrate oxidation are generated by $Fe^{2+.}$ In contrast , decreasing of the MEA degradation also occurs due to a further increase of Fe^{2+} concentrations beyond a certain level that produce the excess Fe^{2+} which led to the scavenging reaction . The *OH tend to react with the excess Fe^{2+} instead of attacking the MEA substrate.

The non parallel lines of the interaction plot represented in figure 4.4 , shown that there is a significant interaction of these 2 factors which the effect of Fe^{2+}

concentration on the MEA degradation changes depending on the level of the H_2O_2 concentration. Therefore, In order to maximize the rate of MEA degradation. The doses of the H_2O_2 and Fe^{2+} concentration must be retained at an optimum level.

Figure 4.5 :Interaction Plot for MEA Degradation



The optimum conditions that obtained in the Fenton oxidation process are given in Table 4.3 .

Table 4. 3 : Optimum Condition of MEA Degradation

Factor	***Low***	***High***	***Optimum***
H_2O_2	0.560868	1.56213	1.39581
Fe^{2+}	0.00399695	0.024503	0.0171697

The optimum conditions predicted by the RSM for degradation of wastewater contaminated with MEA at the initial concentration of 16,000 ppm, temperature at 30 C and 30 min of reaction time are at 1.396 M of H_2O_2 concentration and 0.0172 M of Fe^{2+} concentration. The optimum MEA degradation achieved was 92.375% .

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In this study, Central Composite Design (CCD) based Response Surface Methodology (RSM) has been applied to optimize the degradation of Mono-Ethanolamine (MEA) by using Fenton reagent. The effects of 2 important process variables which are Fe (II) concentration and H_2O_2 concentration toward the MEA degradation performance have been investigated. The result shows that the extend of the MEA degradation attain a peak with an increase in Fe (II) and H_2O_2 concentration. For further doses will result in a decrease in degradation rate.

With initial concentration of 16,000 ppm MEA simulated wastewater, the optimum condition for degradation of MEA are found to be at 1.396 M of H_2O_2 concentration and 0.0172 M of Fe^{2+} concentration. The optimum MEA degradation achieved was 92.375%. A significant fitted model equation obtained by response surface methodology (RSM) fitted reasonably well and adequate to represent the actual relationship between the response and the independent variable.

In view of the time constraint, several recommendations are proposed for further expansion or continuation of this research. Firstly, The repetition of the experiment with the duplicate set of the experimental parameters should be carried out in order to ensure the experimental results. Secondly, it is recommended to repeat the experiment by shifting the factor ‘s range to the right of the center point or doubling the current factor’s range in order to obtain the contour plot which clearly represent the peak of the response .This will confirm that the fitted surface has a maximum point in the experimental range studied.

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Kim, D. J., Lim, Y., Cho, D., & Rhee, I. H. (2010). Biodegradation of monoethanolamine in aerobic and anoxic conditions. *Korean Journal of Chemical Engineering, 27*(5), 1521-1526.

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Neyens, E., & Baeyens, J. (2003). A review of classic Fenton’s peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials, 98*(1), 33-50.

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Oller, I., Malato, S., & Sánchez-Pérez, J. (2011). Combination of advanced oxidation processes and biological treatments for wastewater decontamination—A review. *Science of the Total Environment, 409*(20), 4141-4166.

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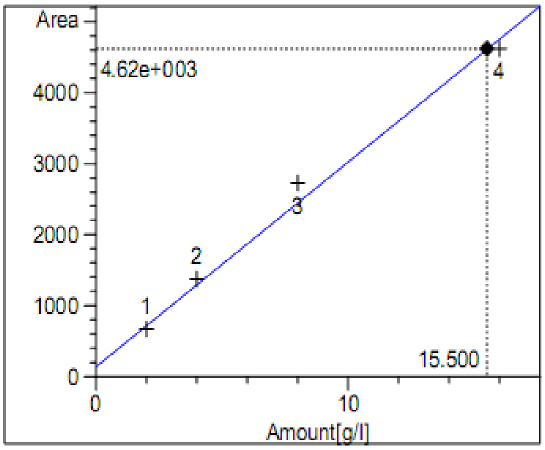
APPENDICES

Apendix 1 : Calibration curves of Monoethanolamine (MEA)

```
=====================================================================
         Retention Time Adjustments for Peak Identification
=====================================================================

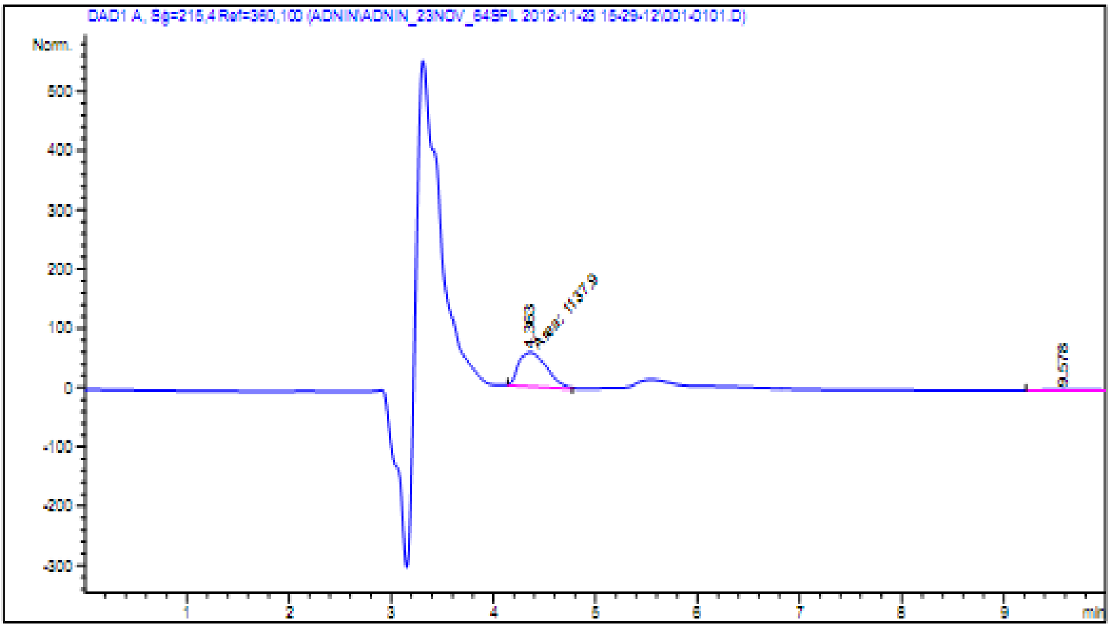
Reference Peak: MEA
Expected Time :  4.282 min
Measured Time :  4.282 min
Deviation     :  0.000 % (used to adjust time windows of other peaks)
=====================================================================
=====================================================================
                         Calibration Curves
=====================================================================
```



```
MEA at exp. RT: 4.282
DAD1 A, Sig=215,4 Ref=360,100
Correlation:             0.99555
Residual Std. Dev.:    199.98676
Formula: y = mx + b
      m:     289.24728
      b:     139.57177
      x: Amount
      y: Area
```

Appendix 2 : Chromatograms of MEA

- **Experiment run#1** (1.061M H_2O_2 ,0.024 M Fe^{2+})



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                     External Standard Report
====================================================================

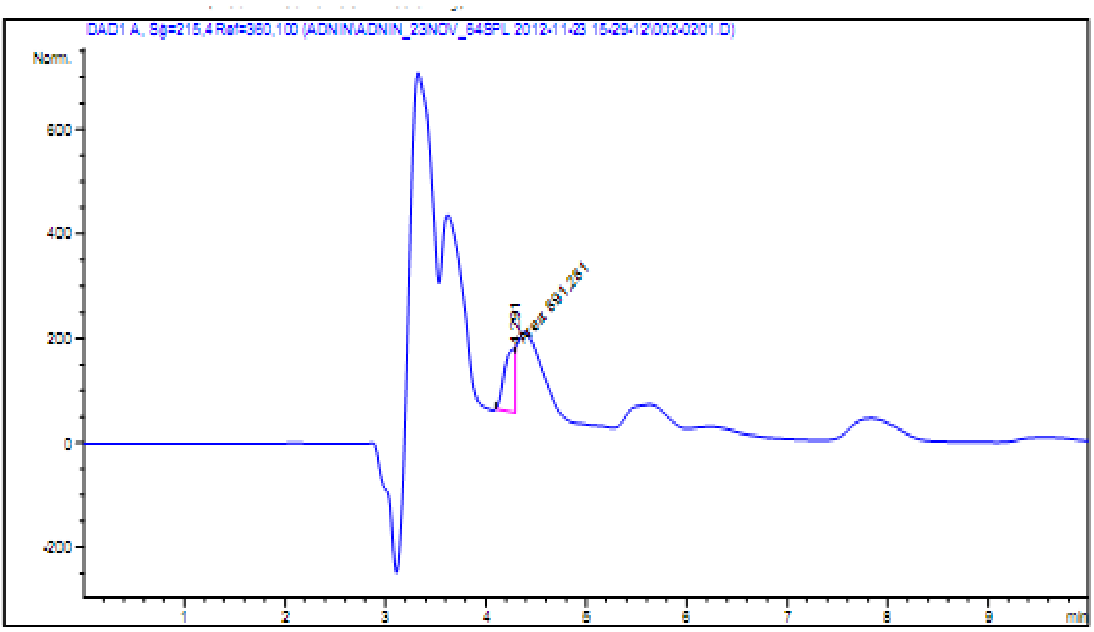
Sorted By             :      Signal
Calib. Data Modified  :      Tuesday, November 27, 2012 5:19:28 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area      Amt/Area     Amount   Grp   Name
 [min]          [mAU*s]                  [g/l]
-------|------|----------|----------|----------|--|------------------
  4.363 MM   +  1137.90344 3.03319e-3    3.45148    MEA

Totals :                                 3.45148
```

- **Experiment run#2** (1.415 M H_2O_2 ,0.007 M Fe^{2+})



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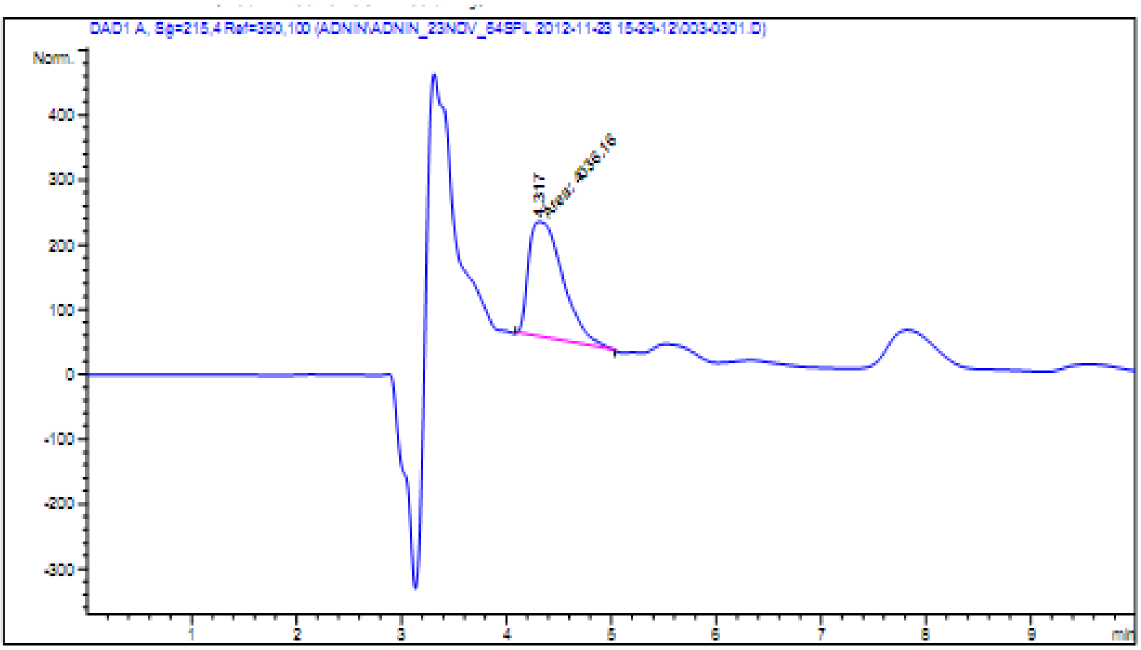
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type    Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [g/l]
-------|------|----------|----------|----------|--|------------------
  4.291 MF  +   891.28149 2.91586e-3    2.59885    MEA

Totals :                               2.59885
```

- **Experiment run#3** (0.5608 M H_2O_2 ,0.01425 M Fe^{2+})



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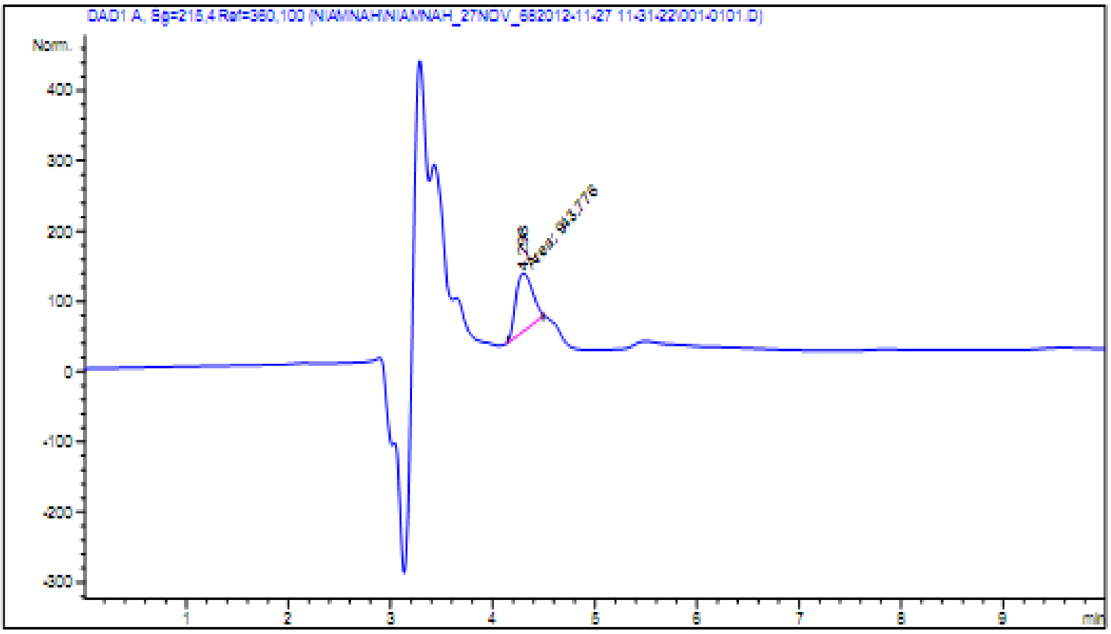
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]               [g/l]
-------|------|----------|----------|----------|--|------------------
  4.317 MM  +  4036.16187 3.33770e-3   13.47148    MEA

Totals :                               13.47148
```

- **Experiment run#4** (0.7075 M H_2O_2 ,0.0215 M Fe^{2+})



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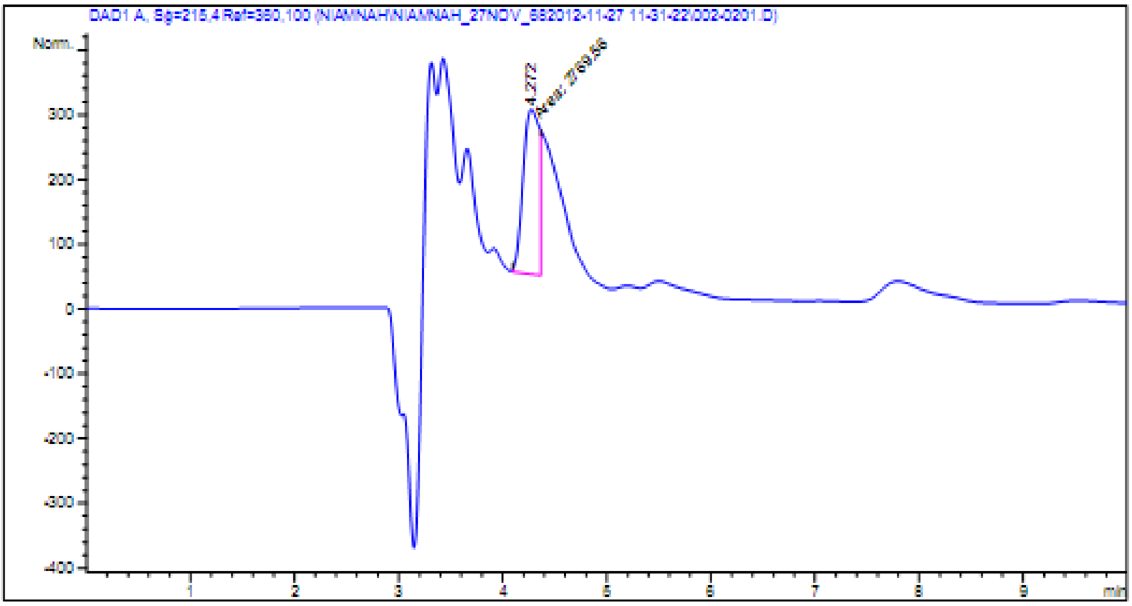
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [g/l]
-------|------|----------|----------|----------|--|------------------
  4.298 MM  +   943.77570 2.94597e-3    2.78033    MEA

Totals :                                2.78033
```

- **Experiment run#5** (1.061M H_2O_2 ,0.0039 M Fe^{2+})



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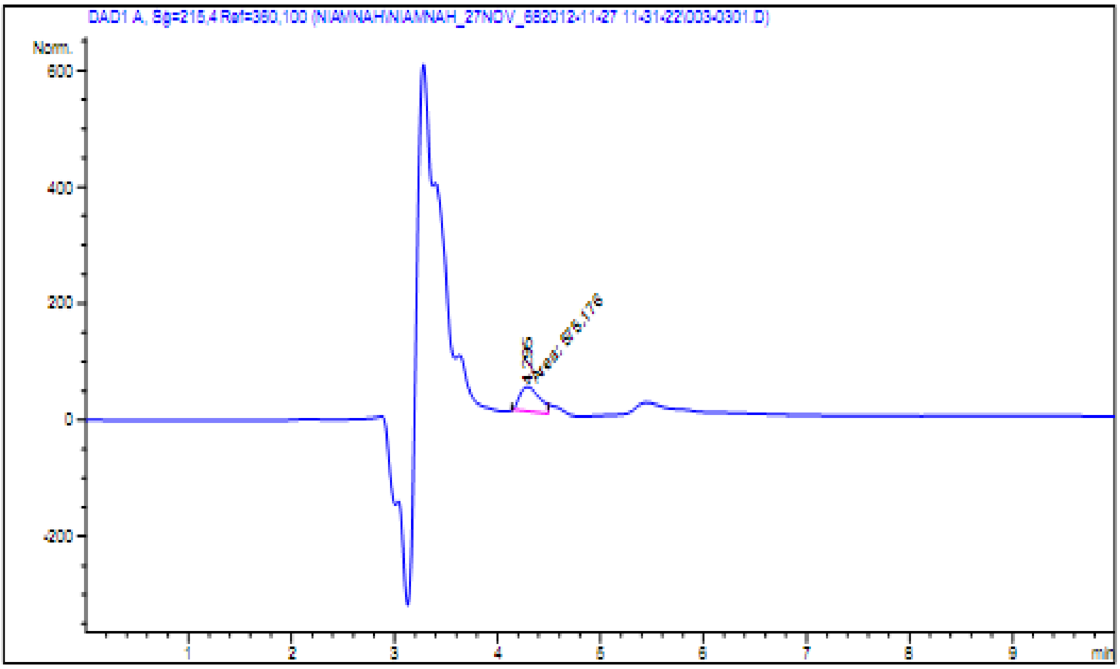
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

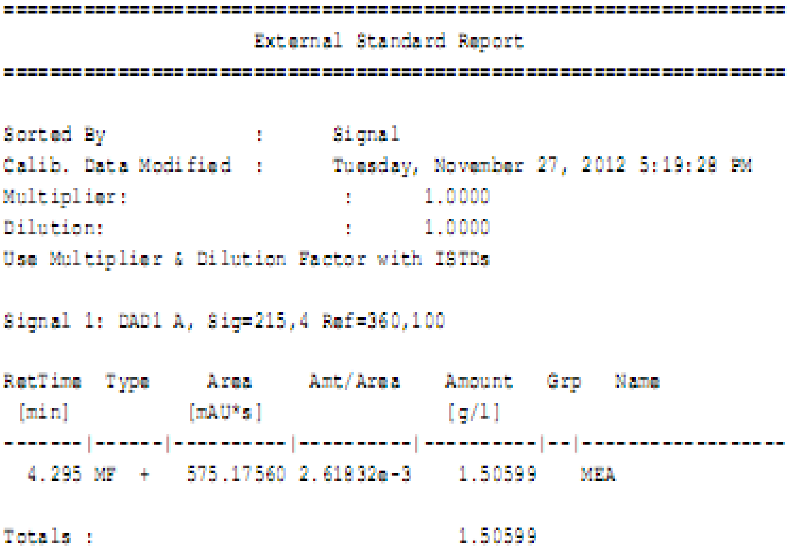
Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area     Amount   Grp   Name
 [min]           [mAU*s]                [g/l]
-------|------|----------|----------|----------|--|------------------
  4.272 MF  +  2769.56274 3.28302e-3    9.09253    MEA

Totals :                                9.09253
```

- **Experiment run#6** (1.0615M H_2O_2 ,0.01425 M Fe^{2+})





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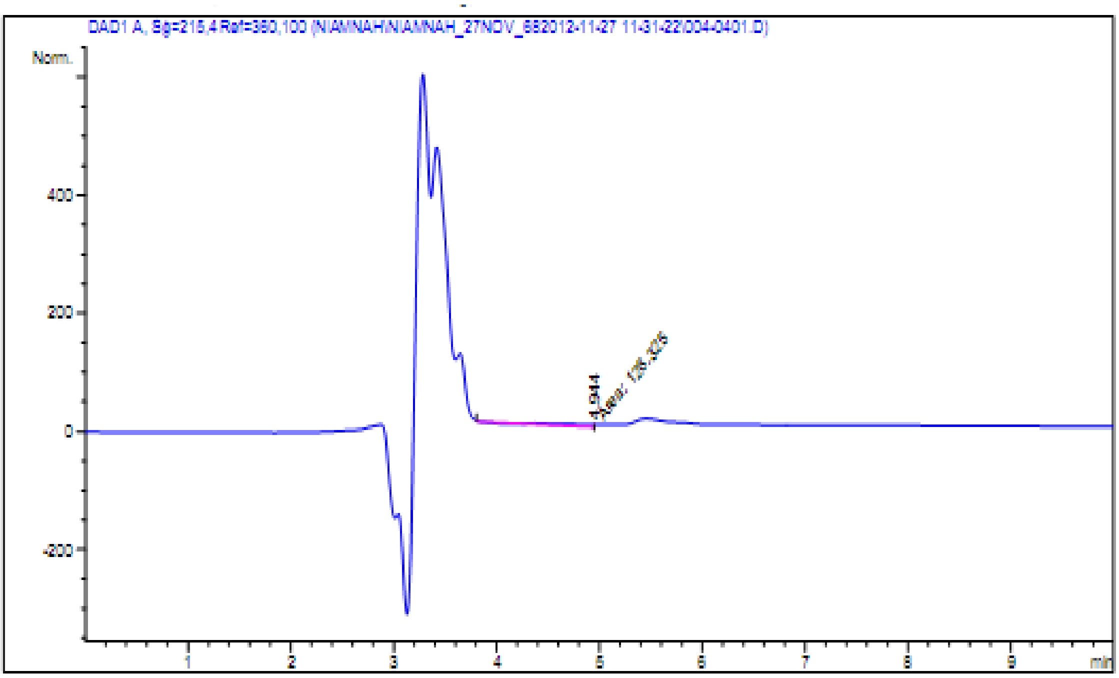
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area     Amount   Grp   Name
 [min]          [mAU*s]                 [g/l]
-------|------|----------|----------|----------|--|------------------
  4.295 MF  +   575.17560 2.61832e-3    1.50599     MEA

Totals :                                1.50599
```

- **Experiment run#7** (1.4155M H_2O_2 ,0.0215 M Fe^{2+})



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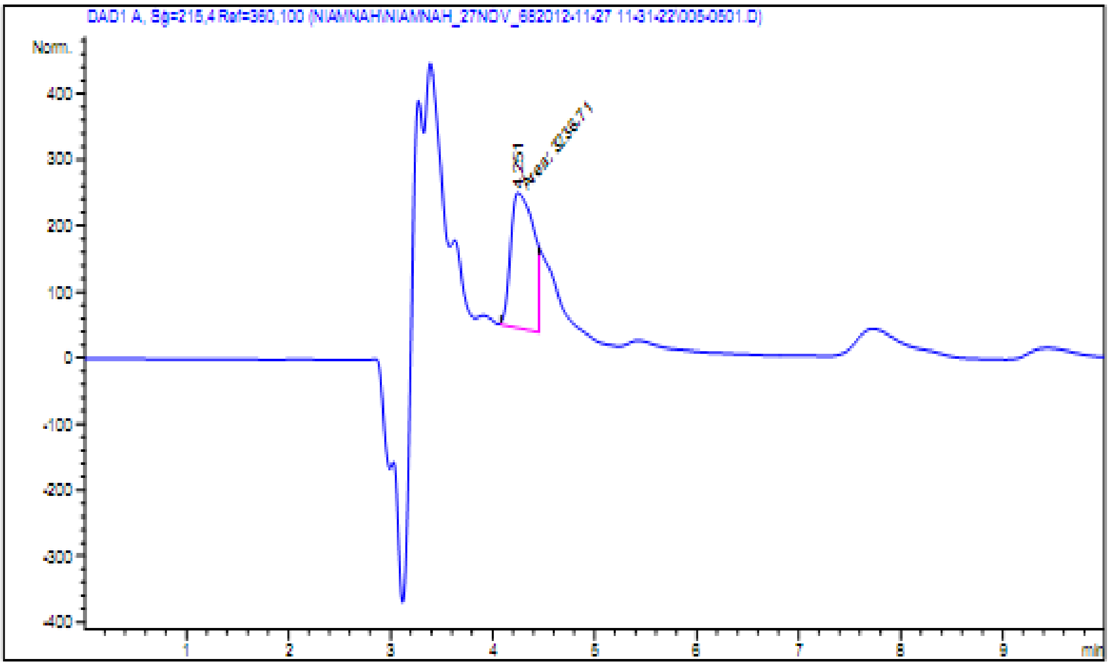
Calib. Data Modified  :      Tuesday, November 27, 2012 5:19:28 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]               [g/l]
-------|------|----------|----------|----------|--|------------------
  4.282              -          -          -          MEA

Totals :                                0.00000
```

- **Experiment run#8** (0.7075M H_2O_2 ,0.007 M Fe^{2+})



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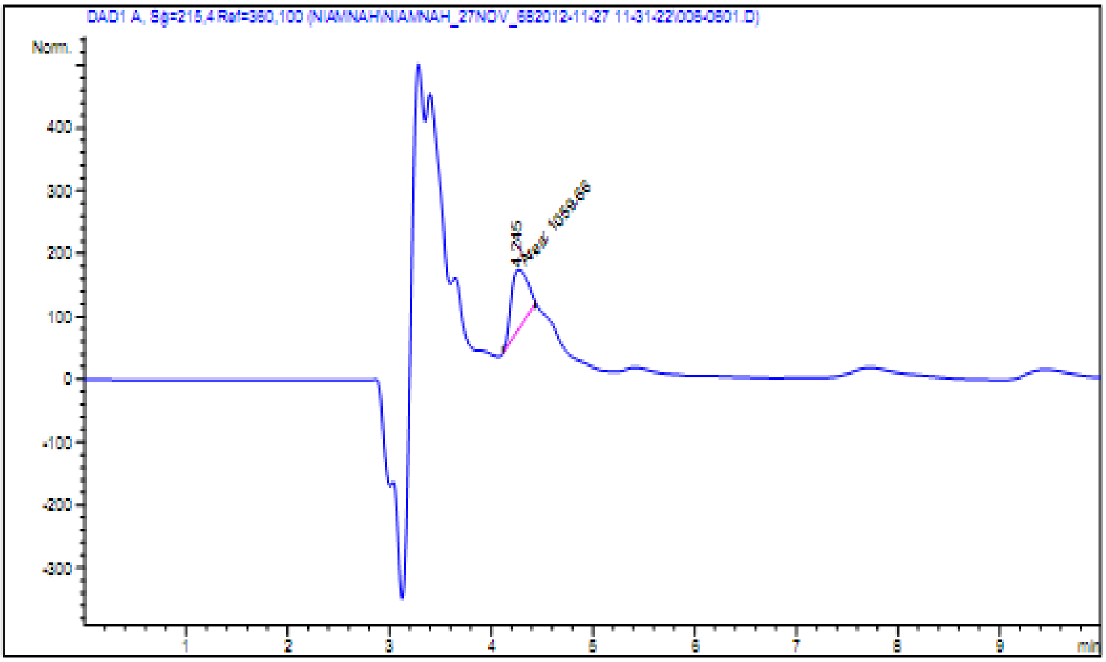
Calib. Data Modified  :      Tuesday, November 27, 2012 5:19:28 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area      Amt/Area     Amount   Grp   Name
 [min]          [mAU*s]                  [g/l]
-------|------|----------|----------|----------|--|------------------
  4.251 MF  +  3236.70605 3.30817e-3   10.70757    MEA

Totals :                                10.70757
```

- **Experiment run#9** (1.061M H_2O_2 ,0.01425 M Fe^{2+})



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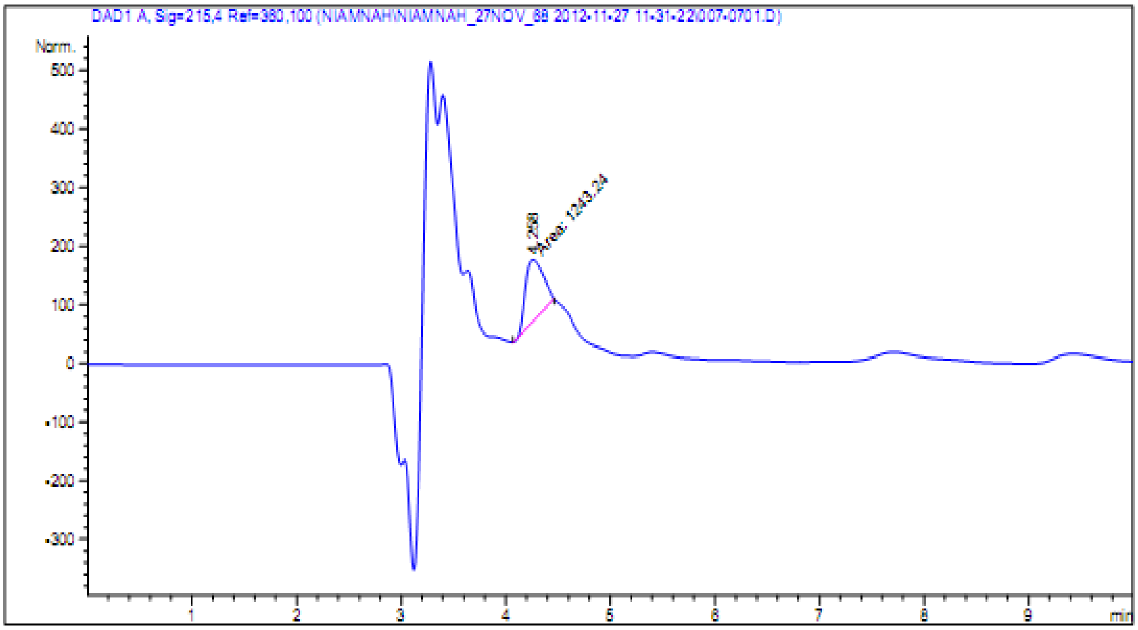
Calib. Data Modified  :      Tuesday, November 27, 2012 5:19:28 PM
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]           [mAU*s]               [g/l]
-------|------|----------|----------|----------|--|------------------
  4.245 MM T+  1059.66406 3.00188e-3    3.18099    MEA

Totals :                                3.18099
```

- **Experiment run#10** (1.0615M H_2O_2 ,0.01425 M Fe^{2+})



```
=====================================================================
                     External Standard Report
=====================================================================

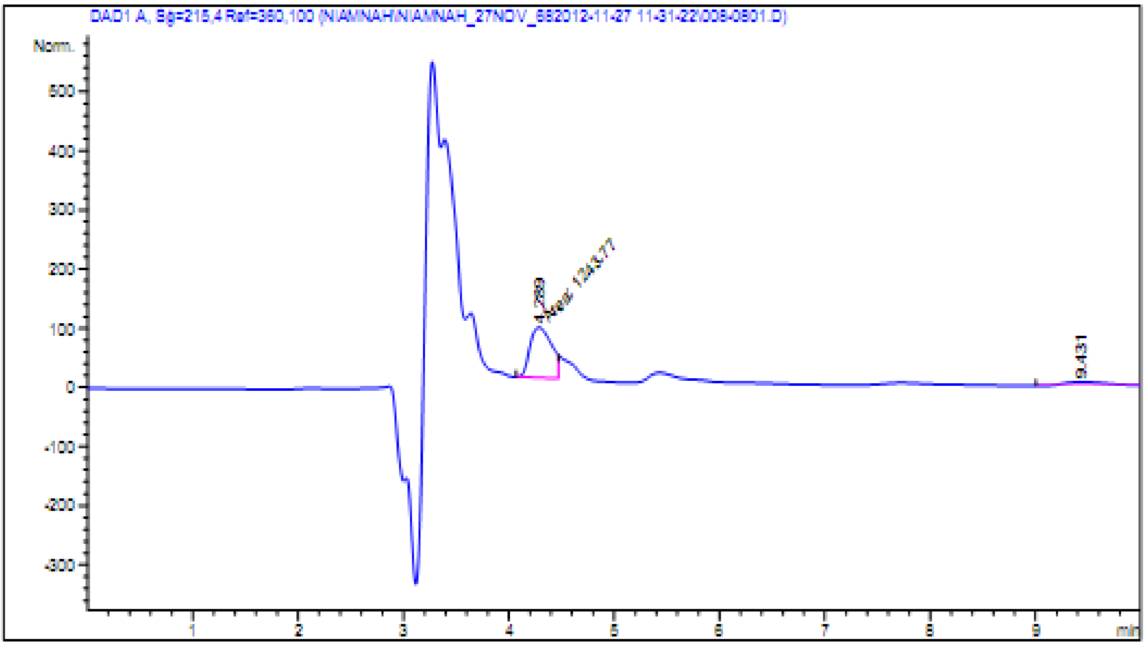
Sorted By              :      Signal
Calib. Data Modified   :      Tuesday, November 27, 2012 5:19:28 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [mAU*s]                  [g/l]
-------|-------|----------|----------|----------|--|------------------
  4.258 MM   +  1243.23718 3.06912e-3    3.81565     MEA

Totals :                                 3.81565
```

- **Experiment run#11** (1.0615M H_2O_2 ,0.01425 M Fe^{2+})



```
=====================================================================
                      External Standard Report
=====================================================================

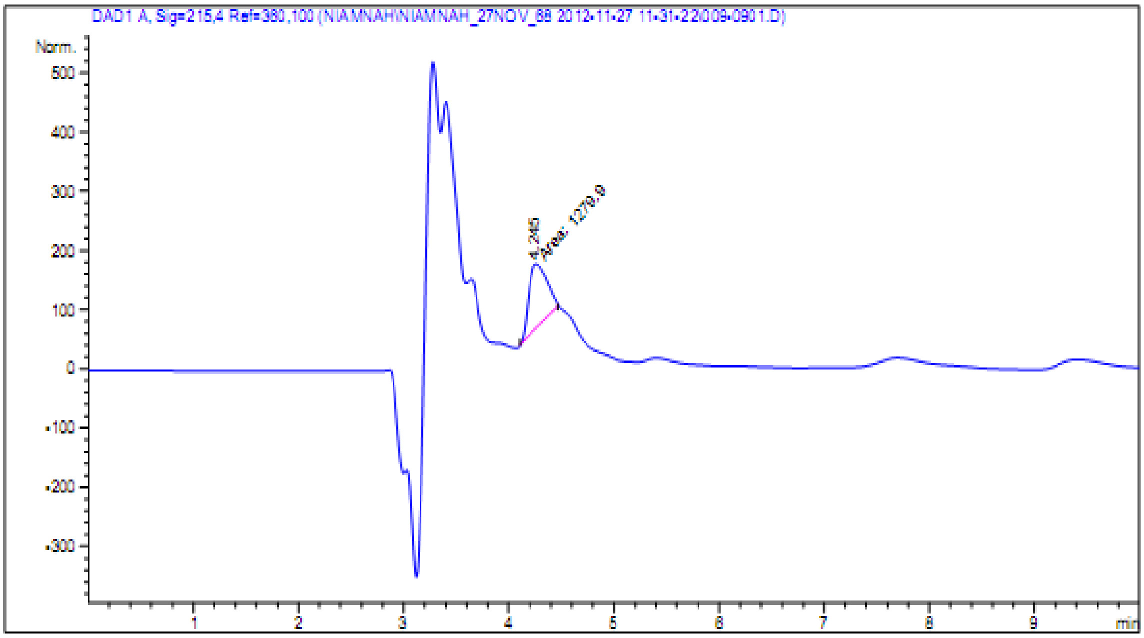
Sorted By             :      Signal
Calib. Data Modified  :      Tuesday, November 27, 2012 5:19:28 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area     Amount   Grp   Name
 [min]          [mAU*s]                 [g/l]
-------|------|----------|----------|----------|--|------------------
  4.289 MF  +  1243.76562 3.06929e-3    3.81747    MEA

Totals :                                3.81747
```

- **Experiment run#12** (1.0615M H_2O_2 ,0.01425 M Fe^{2+})



```
=====================================================================
                     External Standard Report
=====================================================================

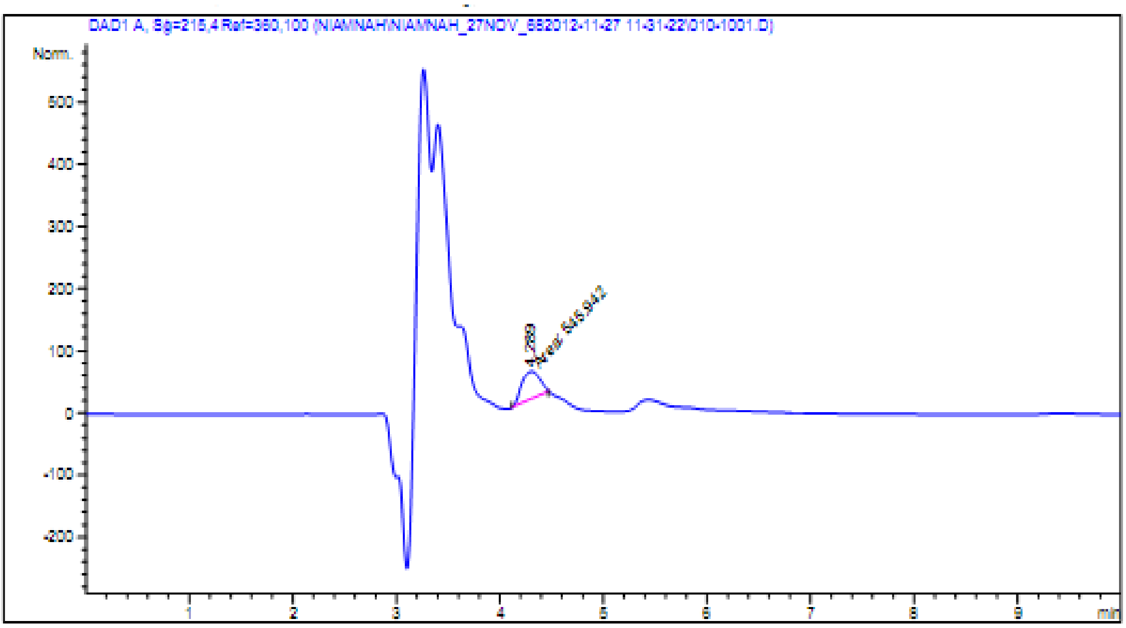
Sorted By              :      Signal
Calib. Data Modified   :      Tuesday, November 27, 2012 5:19:28 PM
Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]               [g/l]
-------|------|----------|----------|----------|--|------------------
  4.245 MM T+  1279.89917 3.08024e-3    3.94240    MEA

Totals :                                3.94240
```

- **Experiment run#13** (1.0615M H_2O_2 ,0.01425 M Fe^{2+})



```
=====================================================================
                      External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      Tuesday, November 27, 2012 5:19:28 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,4 Ref=360,100

RetTime  Type     Area     Amt/Area     Amount   Grp   Name
 [min]          [mAU*s]                 [g/l]
-------|------|----------|----------|----------|--|------------------
  4.289 MM T+    545.94226 2.57339e-3    1.40492    MEA

Totals :                                 1.40492
```

Appendix 3 : Calculations of the percentage MEA Degradation

An example calculation of the percentage MEA degradation will be shown.This example is taken from experiment run# 1 where MEA concentration of sample equal to 3.45148 g/l . Notes that the initial concentration was set at 16 g/l.

$$\%\ \boldsymbol{MEA\ Degradation} = (\boldsymbol{M_i} - \boldsymbol{M_s})\boldsymbol{x}\frac{\mathbf{100}}{\boldsymbol{M_i}}$$

Where , M_i = Initial Concentration of MEA = 16 g/l

M_s = Concentration of MEA in sample

Therefore , $\%\ \boldsymbol{MEA\ Degradation} = (\mathbf{16} - \mathbf{3.45148})\boldsymbol{x}\frac{\mathbf{100}}{\mathbf{16}} = \mathbf{78.428}\ \%$

The same method of calculation is used to calculate for percentage MEA Degradation of other samples. The results are shown in the table below.

H_2O_2 (M)	Fe^{2+} (M)	[MEA]sample (g/l)	% MEA Degradation
1.061500	0.024503	3.45148	**78.428**
1.415500	0.007000	2.59885	**83.757**
0.560868	0.014250	13.47148	**15.803**
0.707500	0.021500	2.78003	**82.625**
1.061500	0.003997	9.09253	**43.172**
1.061500	0.014250	1.50599	**90.588**
1.415500	0.021500	0.9948	**93.783**
0.707500	0.007000	10.70757	**33.078**
1.061500	0.014250	3.18099	**80.119**
1.061500	0.014250	3.8165	**76.147**
1.061500	0.014250	3.8147	**76.158**
1.061500	0.014250	3.9424	**75.360**
1.562130	0.014250	1.40492	**91.219**