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

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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A project dissertation submitted to the
Chemical Engineering Programme
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# CERTIFICATION OF ORIGINALITY

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

___________________________

**MALAYARASAN SILO RATNAM**

# ABSTRACT

This report discusses about the final year project entitled "Application of the Central Composite Design and Response Surface Methodology to the Treatment of Wastewater Contaminated with Diethanolamine using Fenton's Reagent". The purpose of this project is to study on the degradation of Diethanolamine using Fenton's oxidation and to determine the optimum dosage of the reagents that gives the maximum rate of degradation. The reagents are hydrogen peroxide and ferrous ion. In this project, the degradation of diethanolamine using Fenton's reagent and the influence of reagents dosage is tested through experimental work .The optimum conditions for its degradation is determined using statistical approach by using central composite design and response surface methodology. Based on the experimental and statistical approach, the optimum value of $H_2O_2$ concentration, and $FeSO_4$, $7H_2O$ concentration are 2.119M and 0.0396M respectively.

# INTRODUCTION

## 1.1 Background Study

The preservation of our environment is a very important and pressing topic, particularly when we deal with energy issues. There are a few types of fossil fuels that are widely used for energy production, including petroleum, coal and natural gas. Natural gas, the most flexible of all primary fossil fuels, is the fastest growing energy source in the world. Natural gas is considered as an environmental friendly clean fuel, offering important environmental benefits when compared to other fossil fuels, as the combustion of natural gas does not releases any ash or particulate matter. However, natural gas must be purified in order to remove impurities, particularly $CO_2$ and $H_2S$ down to pipeline quality before it can be used for domestic and industrial purposes.

There are many acid-gas sweetening processes available for removal of $CO_2$ and $H_2S$ from natural gas. Among the available technologies, amine-based sweetening processes are the most prominent and have been the process of choice for removal of $CO_2$ and $H_2S$ from sour gas as it provides flexibility, low cost and high reliability. Some well-known alkanolamines for scrubbing acidic gases are monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA) and di-isopropanolamine (DIPA)

However, during amine adsorption-desorption process, a small amount of amine is carried over and discharged in to the effluent stream. This carryover usually caused by foaming or excessive gas velocities in the absorption tower, leakage due to spills or corrosion and during process turnaround.

Amines containing wastewater is generally characterized by high chemical demand (COD), typically about 17,000 mg/L( A.A Omar et.al,). Thus, the wastewater from amine sweetening plants cannot be directly discharged to the surrounding water. Sometimes, during shutdown and maintenance processes of these facilities, high amount of residual alkanolamine may be carried over into the wastewater, as a result of which they can disturb the biological treatment system of the plant.

Diethanolamine (DEA) in aqueous solutions is commonly used for scrubbing of carbon dioxide from natural gas. The DEA are not readily biodegradable and such wastewater cannot be treated in the conventional treatment facility. Advanced Oxidation Processes (AOP's), such as oxidation by Fenton's reagent, UV/$H_2O_2$ and UV/Ozone offer a class of techniques of treatment or partial degradation of refractory organics which are not readily agreeable to conventional biological oxidation.

Application of the central composite design will be very much effective in analysing the optimum factors in oxidation process by Fenton's reagent. Central composite design is an experimental design, useful in response surface methodology, for building a second order (quadratic) model for the response variable without needing to use a complete three-level factorial experiment.

## 1.2 Problem Statement

The problem statement is to identify the optimum value of the two important factors that affect the partial degradation of the DEA from wastewater using statistical methodology. The two factors are ferrous ion concentration and hydrogen peroxide.

Secondly, to identify the suitable statistical approach to find the optimum value of the affecting factors for DEA degradation. These limitations of statistical methods can be solved by optimizing the important parameters using response surface methodology (RSM). RSM is a collection of mathematical and statistical techniques for developing, improving and optimizing processes. RSM is used to determine the optimum condition for specified parameters and to predict the future response using the response surface model.

## 1.3 Objective

1) To study the application of the central composite design and response surface methodology to the treatment of wastewater contaminated with di-ethanolamine using Fenton's reagent by design an experimental methodology using RSM and CCD.

2) To conduct the experiment based on the design of experiments from the RSM and CCD.

3) To optimize the degradation of di-ethanolamine using experimental design application.

## 1.4 Scope of study

The scope of work can be divided into three stages based on the objectives. For the first stage of the project, the author will focus on research and literature review on previous studies related to this topic. This includes deciding on the DEA and the parameters that is going to be studied. The second stage is conducting the experiments. The lab experiment would be conducted by varying few parameters such as H2O2 concentration and effect of $FeSO_4$, 7H2O concentration. The final stage would be in finding the optimum condition that gives the maximum rate of degradation of the DEA

# LITERATURE REVIEW

## 2.1 Statistical Analysis

The optimization of the important parameters is an important problem in the development of economically feasible wastewater treatments. Combined interactions of medium parameters for the production of the desired product are large and the optimum process conditions may be developed using an effective experimental design procedure. Response Surface Methodology (RSM), which is a collection of statistical techniques for design of experiments, building models, evaluating the effects of factors and searching for the optimum conditions, has successfully been used in many processes. Response Surface

The objective of this work was to apply Central Composite Design (CCD) based Response Surface Methodology (RSM) to analyse the effects of the process parameters on wastewater treatment containing diethnolamine, which to identify the optimum value to increase the efficiency.

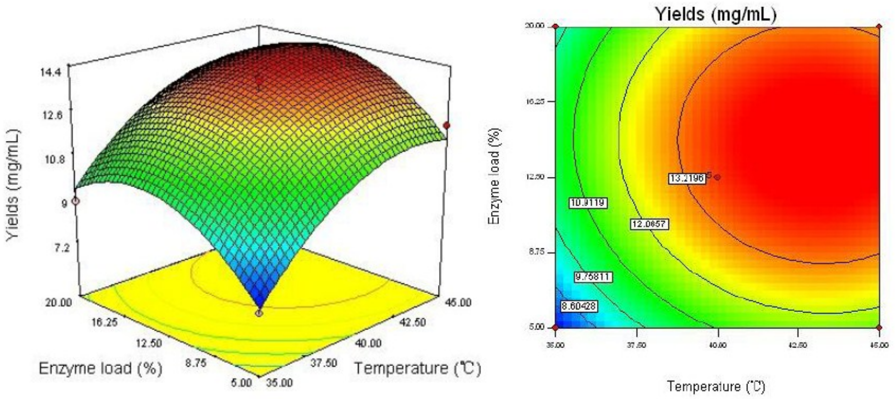

**Figure 2.1 Example of RSM Optimization analysis by 3D model and 2D model**

A $2^{6-2}$ Fractional Factorial Designs (FFD) was used to pick factors that influence degradation of diethanolamine from wastewater treatment 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:

$$Xj = (Z_j - Z_{0j}) / \Delta j \qquad (1)$$

Where Xj 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 centre 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; $\beta_0$ is the intercept; $\beta_j$ is the $j^{th}$ 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 of the steepest ascent is parallel to the normal contour line of response curve of the model (Eq. 1) and passes through the center point of FFD. Increment is direct ratio to regression coefficients$\beta_j$.

Experiments will be performed along then steepest ascent path until the response did not increase anymore. This point would be near the optimal point and can be used as 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 of the degradation of diethanolamine.

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, $\beta_0$ is the intercept term, $\beta_1$ and $\beta_2$ are linear coefficients, $\beta_{12}$ is the logarithmic coefficient, $\beta_{11}$and $\beta_{22}$ 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 SPSS software, version10.25 was used for regression and graphical analysis of the data obtained by ridge analysis. The MINITAB software, version 14.1 was used to draw contour plots. The statistical analysis of the model was performed in the form of Analysis of Variance (ANOVA)

## 2.2 Advanced Oxidation Processes

Advance Oxidation Processes (AOP) is the alternative methods for decolourizing and reducing waste water effluents generated by industries (Alhamedi et al., 2009). Behnajady *et al.*, (2006) stated that AOPs are also a non-destructive physical water treatment processes, because they are able to eliminate compound rather than changing them into another medium such as solid waste. The use of AOPs, like UV/$H_2O_2$ (Korbahti and Rauf, 2008), photocatalytic (Attia *et al.*, 2008), Fenton and photo-Fenton processes (Çatalkaya and Sengul, 2006), has shown promising results as these processes appear to have the ability to completely decolorize and partially mineralize the textile industry dyes in short reaction time (Rauf *et al.*, 2008), (Körbahti and Rauf, 2008b) and (Bali *et al.*, 2004).

In view of its efficiency and relative ease of operation, one of the best known AOP's is the $2O_2$/UV. Process involving the use of UV radiation and $H_2O_2$ are characterized by the generation of hydroxyl radicals (Behnajady *et al.*, 2006). UV wavelengths of 200 – 280 nm lead to dissociation of $H_2O_2$, with mercury lamps emitting at 254 nm being the most used. UV/$H_2O_2$ systems generate hydroxyl radicals (●OH) which are highly powerful oxidizing agents. Hydroxyl radicals can oxidized organic compounds (RH) producing organic radicals (●R), which also highly reactive and can be further oxidized (Bali *et al.*, 2004). These radicals can then attack the dye molecules to undergo a series of reactions in which the organic molecules will be eliminated or converted into a simple molecules or harmless compound (Alhamedi *et al.*, 2009). The main reaction that occurs during UV/$H_2O_2$ oxidation process is as follows:

$$H_2O_2 + UV \rightarrow 2OH\bullet \qquad (2.1)$$

$$H_2O_2 \leftrightarrow HO2^- + H^+ \qquad (2.2)$$

$$RH + OH\bullet \rightarrow H_2O + R\bullet \rightarrow \text{further oxidation} \qquad (2.3)$$

where R is the carbon chain.

The hydroxyl radicals will oxidize organic compounds producing organic radicals, which also a highly reactive and can undergo further oxidation. When generated, these radicals will react quickly and usually randomly with most organic compounds. The resulting organic radicals then reacts with oxygen to initiate series of degradative oxidation reaction that lead to mineralization of products such as $CO_2$ and $H_2O$ (Çatalkaya and Sengul, 2006). The other possible reactions that may occur during the UV/$H_2O_2$ process are hydrogen abstraction, electrophilic addition and electron transfer reactions (Behnajady *et al.*, 2006). Although AOPs have much kind of advantages in wastewater treatment, one major problem in AOPs is the high energy demand for UV lamps which lead to high operational cost. In order to minimize the irradiation time, energy consumption, and operational cost, there is necessary to optimize the pH condition, temperature, chemical concentration, and pollutant/oxidant ratio, therefore are very important (Çatalkaya and Sengul, 2006). For this aim, the application of experimental design is the best solution where it will be used to optimize the important parameters that affected the efficiency of wastewater treatment.

## 2.3 Fenton’s reagent

Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or waste waters. Fenton's reagent can be used to destroy organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE).

It was developed in the 1890s by Henry John Horstman Fenton as an analytical reagent.Ferrous Iron(II) is oxidized by hydrogen peroxide to ferric iron(III), a hydroxyl radical and a hydroxyl anion. Iron(III) is then reduced back to iron(II), a peroxide radical and a proton by the same hydrogen peroxide (disproportionation).The hydroxyl free radical generated by Fenton’s reagent is a powerful, non-selective oxidant. Oxidation of an organic compound by Fenton’s reagent is rapid and exothermic (heat-producing) and results in the reduction of contaminants to primarily carbon dioxide and oxygen

$$Fe2+ + H2O2 \rightarrow Fe3+ + OH\cdot + OH- \qquad (1)$$

$$Fe3+ + H2O2 \rightarrow Fe2+ + OOH\cdot + H+ \qquad (2)$$

Reaction (1) was suggested by Haber and Weiss in the 1930s. In the net reaction the presence of iron is truly catalytic and two molecules of hydrogen peroxide are converted into two hydroxyl radicals and water. The generated radicals then engage in secondary reactions.

Iron(II) sulfate is a typical iron compound in Fenton's reagent. The exact mechanisms are debated (also non-OH· oxidizing mechanisms of organic compounds have been suggested) and, therefore, it may be appropriate to broadly discuss 'Fenton chemistry' rather than a 'Fenton reaction'.

In the Electro-Fenton process, hydrogen peroxide is produced in the required amount from the electrochemical reduction of oxygen.

Fenton's reagent is also used in organic synthesis for the hydroxylation of arenes in a radical substitution reaction such as the classical conversion of benzene into phenol.

$$C6H6 + FeSO4 + H2O2 \rightarrow C6H5OH \tag{3}$$

A recent hydroxylation example involves the oxidation of barbituric acid to alloxane.Another application of the reagent in organic synthesis is in coupling reactions of alkanes. As an example tert-butanol is dimerized with Fenton's reagent and sulfuric acid to 2,5-dimethyl-2,5-hexanediol.

## 2.3 Diethanolamine (DEA)

Diethanolamine, often abbreviated as DEA, is an organic compound with the formula $HN(CH2CH2OH)2$. This colourless liquid is polyfunctional, being a secondary amine and a diol. Like other organic amines, diethanolamine acts as a weak base. Reflecting the hydrophilic character of the alcohol groups, DEA is soluble in water, and is even hygroscopic. Amides prepared from DEA are often also hydrophilic.

The reaction of ethylene oxide with aqueous ammonia first produces ethanolamine:

$$C_2H_4O + NH_3 \rightarrow H_2NCH_2CH_2OH \tag{1}$$

which reacts with a second and third equivalent of ethylene oxide to give DEA and triethanolamine.

$$C_2H_4O + H_2NCH_2CH_2OH \rightarrow HN(CH_2CH_2OH)_2 \tag{2}$$

$$C_2H_4O + HN(CH_2CH_2OH)_2 \rightarrow N(CH_2CH_2OH)_3 \tag{3}$$

About 300mil kg are produced annually in this way. The ratio of the products can be controlled by changing the stoichiometry of the reactants.

DEA is used as a surfactant and a corrosion inhibitor. It is used to remove hydrogen sulfide and carbon dioxide from natural gas.

In oil refineries, a DEA in water solution is commonly used to remove hydrogen sulfide from various process gases. It has an advantage over a similar amine ethanolamine in that a higher concentration may be used for the same corrosion potential. This allows refiners to scrub hydrogen sulfide at a lower circulating amine rate with less overall energy usage.
DEA is versatile chemical intermediate, principal derivatives include ethyleneimine and ethylenediamine. Dehydration of DEA with sulfuric acid gives morpholine:
Amides derived from DEA and fatty acids, known as diethanolamides, are amphiphilic.

Amines containing wastewater is generally characterized by high chemical oxygen demand (COD) typically about 17,000 mg/L. Thus the wastewater from amine sweetening plants cannot be directly discharged to the surrounding water; otherwise, it can deplete dissolved oxygen in receiving waters, stimulate aquatic plant growth, exhibit toxicity towards aquatic life, present a public health hazard, and affect the suitability of wastewater for reuse purposes. Treatment of amine wastewater using existing wastewater treatment plant without any dilution is very challenging since it can affect the performance of the activated sludge.

# METHODOLOGY AND PROJECT WORK

## 3.1 Statistical Analysis Methodology

The statistical analysis begins with the experimental design approach in the STATGRAPHICS Centurion software. The range values of the two parameters which are the X1: $H_2O_2$ Concentration and X2: $FeSO_4$, $7H_2O$ Concentration was obtained from the literature review. Below are the range values:

**X1: $H_2O_2$ Concentration: 0.61-2.44 M**

**X2: $FeSO_4$, $7H_2O$ Concentration: 1.8- 40 mM**

**Response Surface Design Attributes**

Design class: Response Surface
Design name: Central composite design: 2^2 + star
Design characteristic: Rotatable
File name: DEA Optimization

**Base Design**
Number of experimental factors: 2
Number of blocks: 1
Number of responses: 1
Number of runs: 13, including 5 counterpoints per block
Error degrees of freedom: 7
Randomized: Yes

| *Factors* | *Low* | *High* | *Units* | *Continuous* |
|---|---|---|---|---|
| H2O2 Concentration | 0.61 | 2.44 | M | Yes |
| FeSO4 7H2O Concentration | 1.8 | 40 | mM | Yes |

**Table 3.1 : Hydrogen peroxide concentration and ferrous ion concentration**

Based on the software, table 3.1 is created with 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.

| BLOCKS | Hydrogen peroxide (M) | Ferrous ion (M) | DEA degradation (%) |
|---|---|---|---|
| **1** | **2.81901** | **0.0209** | |
| **2** | **0.61** | **0.0018** | |
| **3** | **2.44** | **0.0018** | |
| **4** | **1.525** | **0.0209** | |
| **5** | **1.525** | **0.0209** | |
| **6** | **1.525** | **0.0209** | |
| **7** | **1.525** | **0.0209** | |
| **8** | **1.525** | **0.00611148** | |
| **9** | **0.61** | **0.04** | |
| **10** | **0.230995** | **0.0209** | |
| **11** | **1.525** | **0.0479115** | |
| **12** | **1.525** | **0.0209** | |
| **13** | **2.44** | **0.04** | |

**Table 3.2 The number of experiments and the factor values for the experiment**

Based on table 3.2, a total number of 13 experiments will be conducted. The centre points selected for the experiments were 5, to make sure the distribution of the experimental factors value, and to increase the efficiency of the experiments.

Experiments with X1 and X2 value are to measure the DEA degradation value. Once the degradation value is identified for all the 13 experiments, the values will be submitted in the software to generate the response surface curve for further analysis and studies to identify the optimum values of these two factors (X1 & X2) for the DEA degradation.

## 3.2 Experimental Methodology

Specific concentration of DIPA was prepared as the reaction solution.

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 recirculating water bath were switched on at this point.

pH of the reaction solution was corrected according to the parameter setup for each experimental run.

Weighed ferrous sulphate 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.

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.

Five mL of samples were collected using a 5-mL pipette.

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).[P1]

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 were hydrogen peroxide is expected to undergo self-degradation to water and oxygen according to its Material Safety and Data Sheet.

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

Samples to be analysed using HPLC were transferred to 2 mL screw cap sample vials without dilution.

Samples to be analysed for COD were diluted accordingly. Then, 2 mL of the diluted samples were transferred to the HACH® high range COD vials.

## 3.4 Experimental Approach

The experiments were conducted in double walled glass reactor (1 L volume), with a ground glass cover that can be fixed by clips. The solution of DEA was adjusted to pH 3 by drop-wise addition of 2M sulphuric acid and 1M & 10M sodium hydroxide. Temperature was maintained by circulating water at a controlled value (30$^{O}$C) through the glass jacket of the reactor. Mixing of the internal solution was carried out with a stirring bar and a magnetic stirrer placed under the reactor. The requested amount of ferrous sulphate (FeSO4, 7H2O) was added and the content was mixed well. This was followed by addition of a measured quantity of 30% H2O2. The effective reaction volume was about 800 ml. The reaction started immediately and the temperature was maintained by the cooling water circulating through the jacket as stated before. Samples of the liquid were withdrawn after 30 minutes using a syringe and analysed for the COD, unreacted amine, and residual H2O2.

Figure 3.1 shows the reactor setup for the mixing of DEA with hydrogen peroxide and the ferrous sulphate. The temperature is set to 30$^{o}$C.  Water in and water out is connected to the

**Figure 3.1**: **The setup of reactor for the experimental runs.**

The samples prepared according to the experimental procedure. Figure below shows the samples examples. The samples are done for all the 13 experiments based on the RSM analysis.

# RESULTS AND DISCUSSION

## 4.1 Experimental Result

Table 4.1 below is the result of HPLC test based on the samples (From sample 1 to sample 13).

| BLOCKS | Hydrogen peroxide (M) | Ferrous ion (M) | DEA degradation (%) |
|---|---|---|---|
| **1** | 2.81901 | 0.0209 | 57.14 |
| **2** | 0.61 | 0.0018 | 34.61 |
| **3** | 2.44 | 0.0018 | 74.47 |
| **4** | 1.525 | 0.0209 | 81.57 |
| **5** | 1.525 | 0.0209 | 75.64 |
| **6** | 1.525 | 0.0209 | 73.26 |
| **7** | 1.525 | 0.0209 | 74.91 |
| **8** | 1.525 | 0.00611148 | 43.22 |
| **9** | 0.61 | 0.04 | 49.36 |
| **10** | 0.230995 | 0.0209 | 46.7 |
| **11** | 1.525 | 0.0479115 | 78.91 |
| **12** | 1.525 | 0.0209 | 75.98 |
| **13** | 2.44 | 0.04 | 93.46 |

**Table 4.1**: **Amount of DEA degradation in percentage**

The DEA degradation is calculated based on the result obtained from the HPLC curve.

$$DEA\ degradation = \frac{Total\ concentration\ used - concentration\ after\ degradation}{Total\ concentration\ used}\ x\ 100\%$$

Example for sample 4:

DEA degradation = [(16 -2.94726)/16] *100

= 0.8157 *100

= 81.57%

The degradation amount of DEA is calculated based on the HPLC reading on degradation performance of DEA. Example of the HPLC reading is available in appendix 1.

## 4.2 Optimization

**Estimated effects for DEA Degradation (Percentage %)**

| *Effect* | *Estimate* | *Stnd. Error* | *V.I.F.* |
|---|---|---|---|
| average | 75.736 | 4.58063 | |
| A:Hydrogen Peroxide | 24.6811 | 7.24261 | 1.0 |
| B:Ferrous ion | 21.0533 | 7.24261 | 1.0 |
| AA | -20.5748 | 7.76682 | 1.01731 |
| AB | 2.12 | 10.2426 | 1.0 |
| BB | -11.4298 | 7.76683 | 1.01731 |

**Table 4.2 Standard errors are based on total error with 7 d.f.**

Table 4.2 shows each of the estimated effects and interactions. Also shown is the standard error of each of the effects, which measures their sampling error. Note also that the largest variance inflation factor (V.I.F.) equals 1.01731. For a perfectly orthogonal design, all of the factors would equal 1. Factors of 10 or larger are usually interpreted as indicating serious confounding amongst the effects.

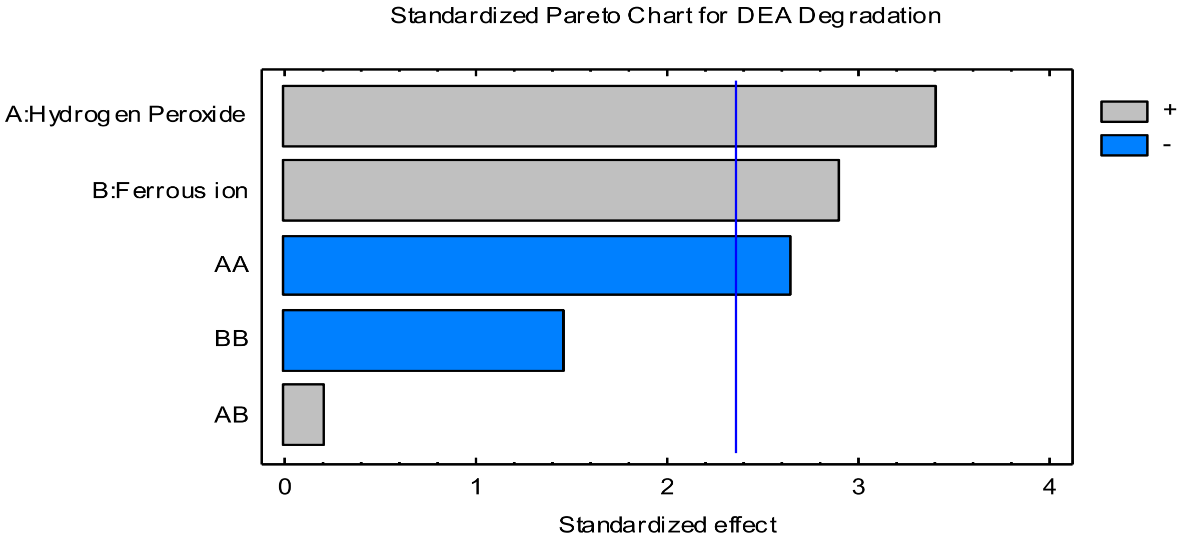

**Figure 4.1 Standardized Pareto Chart for DEA Degradation**

**Analysis of Variance for DEA Degradation**

| *Source* | *Sum of Squares* | *Df* | *Mean Square* | *F-Ratio* | *P-Value* |
|---|---|---|---|---|---|
| A:Hydrogen Peroxide | 1218.32 | 1 | 1218.32 | 11.61 | 0.0113 |
| B:Ferrous ion | 886.485 | 1 | 886.485 | 8.45 | 0.0228 |
| AA | 736.216 | 1 | 736.216 | 7.02 | 0.0330 |
| AB | 4.4944 | 1 | 4.4944 | 0.04 | 0.8419 |
| BB | 227.199 | 1 | 227.199 | 2.17 | 0.1846 |
| Total error | 734.376 | 7 | 104.911 | | |
| Total (corr.) | 3715.22 | 12 | | | |

**Table 4.3 Analysis of Variance for DEA Degradation**

R-squared = 80.2333 percent
R-squared (adjusted for d.f.) = 66.1142 percent
Standard Error of Est. = 10.2426
Mean absolute error = 5.56466
Durbin-Watson statistic = 1.44795 (P=0.0891)
Lag 1 residual autocorrelation = 0.0476383

Table 4.3 (ANOVA table) partitions the variability in DEA Degradation into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 3 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 80.2333% of the variability in DEA Degradation. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 66.1142%. The standard error of the estimate shows the standard deviation of the residuals to be 10.2426. The mean absolute error (MAE) of 5.56466 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

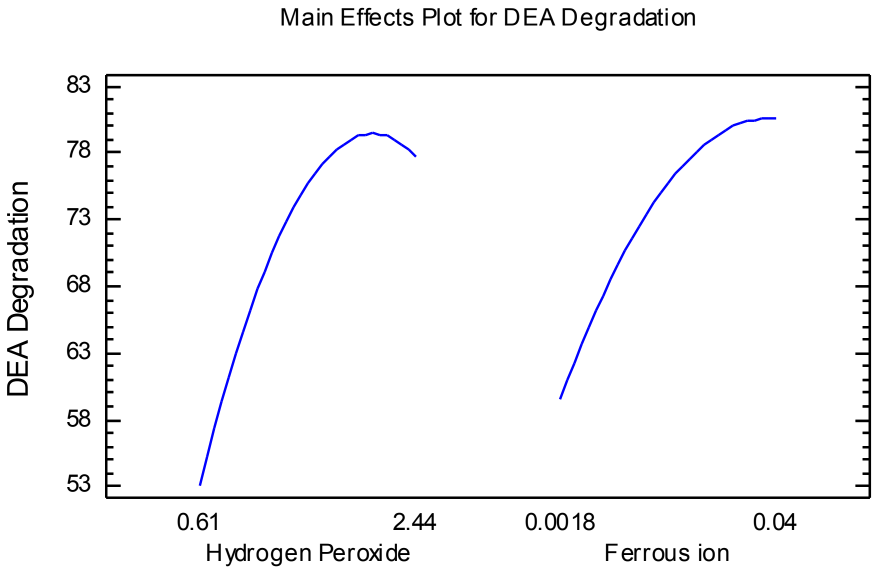

**Figure 4.2: Main Effects plot for DEA Degradation**

Based on the figure 4.2, it can conclude that the DEA degradation level is low when the hydrogen peroxide level is low. As you can see, the degradation rate is increasing as the Hydrogen peroxide amount is increasing. It reached optimum reaction at 2.44M. After that the degradation rate started to reduce. Approximately 80% degradation is achieved at the optimum value which is at 2.44M $H_2O_2$ concentration.

Same situation goes to ferrous ion. The degradation rate is low when the amount of ferrous ion is low. The degradation rate is increasing continuously until it reaches 0.04M. Starting from 0.04M, the degradation rate is significantly stable or showing its reaches the optimum value.

Regression coeffs. for DEA Degradation

| Coefficient | Estimate |
|---|---|
| **constant** | 10.164 |
| **A:Hydrogen Peroxide** | 49.6962 |
| **B:Ferrous ion** | 1113.45 |
| **AA** | -12.2875 |
| **AB** | 60.6529 |
| **BB** | -15665.4 |

**Table 4.4: Regression coeffs. for DEA Degradation**

From this value, we can come with the general equation for the DEA degradation process.

$$\begin{aligned} DEA\ Degradation &= \mathbf{10.164} + \mathbf{49.6962} * \boldsymbol{Hydrogen\ Peroxide} + \mathbf{1113.45} \\ &* \boldsymbol{Ferrous\ ion} - \mathbf{12.2875} * \boldsymbol{Hydrogen\ Peroxide^2} \\ &+ \mathbf{60.6529} * \boldsymbol{Hydrogen\ Peroxide} * \boldsymbol{Ferrous\ ion} \\ &- \mathbf{15665.4} * \boldsymbol{Ferrous\ ion^2} \end{aligned}$$

where the values of the variables are specified in their original units.

Based on the formula, we can conclude that ferrous ion is more significant towards the degradation of DEA as compared to hydrogen peroxide. From the equation, the coefficient of hydrogen peroxide is 49.6962 while for ferrous is 1113.45. From this, we can conclude that ferrous ion will play better role for the degradation process as compared to hydrogen peroxide.

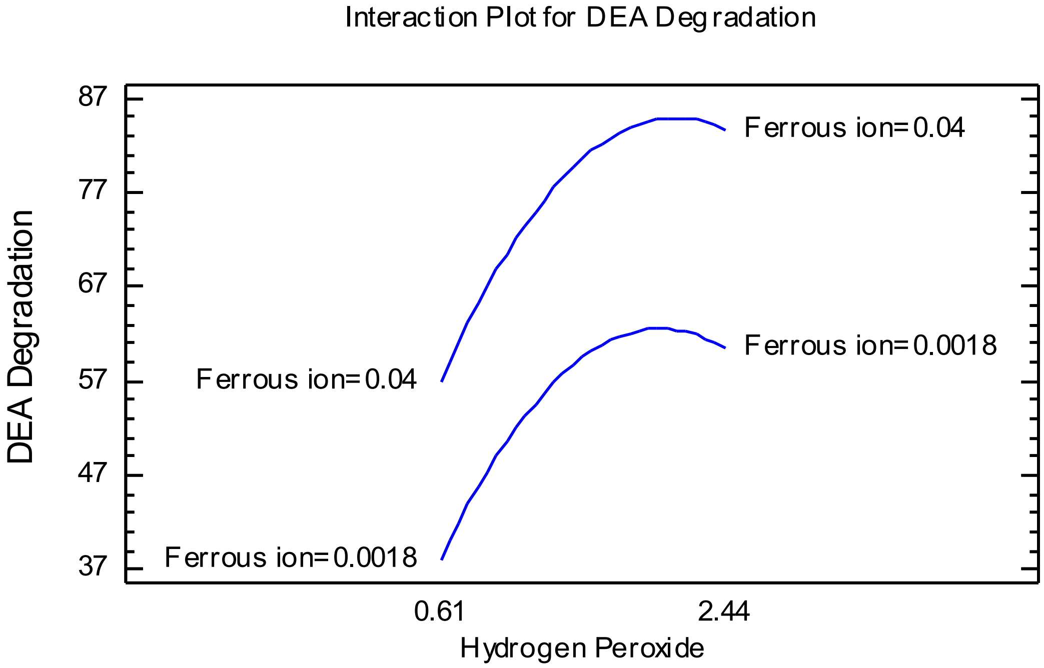

**Figure 4.3**: **Interaction Plot for DEA Degradation**

The interaction plot in figure 4.3 showing the relationship between the two variables-ferrous ion and hydrogen peroxide. It shows how the ferrous ion reacts at the minimum value

(0.0018M) and the maximum value (0.04M) towards the $H_2O_2$. From the plot, we can conclude that at low ferrous ion value (0.0018M), the reaction rate increase from 0.61M of $H_2O_2$ till 2.11M $H_2O_2$. Same scenario happens at the 0.04M of ferrous ion. Both concentration values of ferrous ion indicate that, optimum value of DEA degradation is at 2.1M-2.2 M of $H_2O_2$.

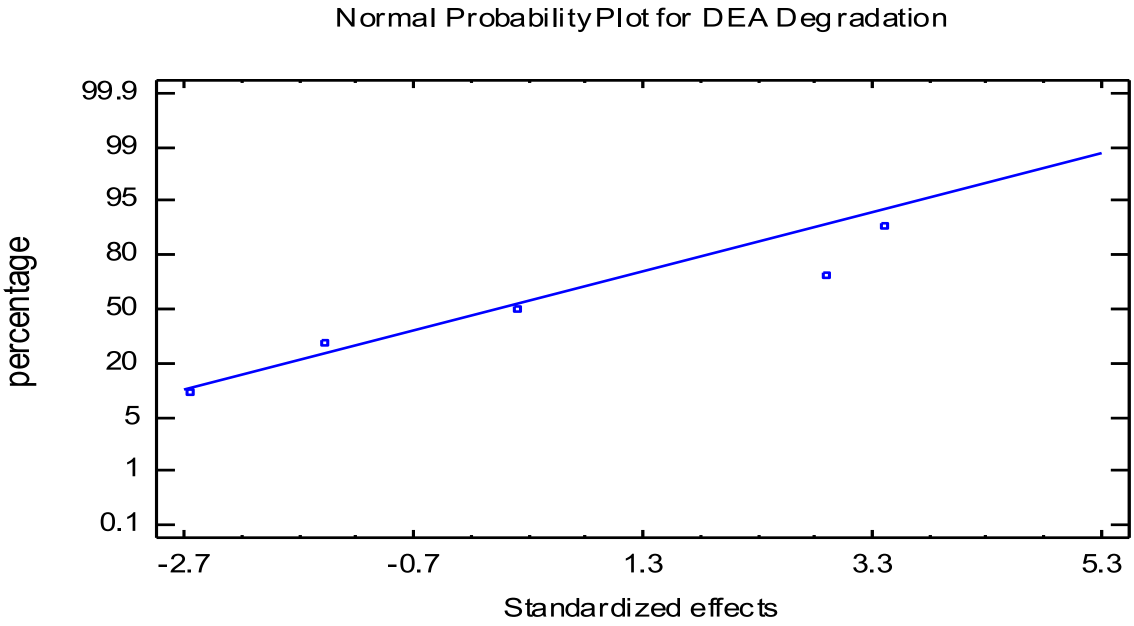

**Figure 4.4**: **Normal Probability plot for DEA degradation**

Figure 4.4 shows the relationship between the standardized effects and the DEA degradation percentage. We can find the Experimental value and the theoretical value from the table below. If the points are in between the range of the theoretical values, then, we can say that the degradation performance is good. From, the figure, all the points are in between the range. Hence, it has a good degradation performance.

Estimation Results for DEA Degradation

| Row | Observed Value | Fitted Value | Lower 95.0% CL for Mean | Upper 95.0% CL for Mean |
|---|---|---|---|---|
| **1** | 57.14 | 72.6133 | 53.4657 | 91.7609 |
| **2** | 34.61 | 37.9265 | 18.779 | 57.0741 |
| **3** | 74.47 | 60.4876 | 41.3401 | 79.6352 |
| **4** | 78.89 | 75.736 | 64.9045 | 86.5675 |
| **5** | 75.64 | 75.736 | 64.9045 | 86.5675 |
| **6** | 73.26 | 75.736 | 64.9045 | 86.5675 |
| **7** | 74.91 | 75.736 | 64.9045 | 86.5675 |
| **8** | 43.22 | 49.4193 | 30.2717 | 68.5669 |
| **9** | 49.36 | 56.8598 | 37.7123 | 76.0074 |
| **10** | 46.7 | 37.7091 | 18.5615 | 56.8566 |
| **11** | 78.91 | 79.1932 | 60.0456 | 98.3408 |
| **12** | 75.98 | 75.736 | 64.9045 | 86.5675 |
| **13** | 93.46 | 83.661 | 64.5134 | 102.809 |

**Table 4.5**: **Estimation result for DEA degradation**

Table 4.5 contains information about values of DEA Degradation generated using the fitted model. The table includes:

(1) The observed value of DEA Degradation (if any)

(2) The predicted value of DEA Degradation using the fitted model

(3) 95.0% confidence limits for the mean response

The table below shows the percentage error in experimental value as compared to the theoretical/fitted value.

| Row | Observed Value | Fitted Value | Error in Percentage difference (%) |
|---|---|---|---|
| **1** | 57.14 | 72.6133 | 21.30918 |
| **2** | 34.61 | 37.9265 | 8.744545 |
| **3** | 74.47 | 60.4876 | 23.11614 |
| **4** | 78.89 | 75.736 | 4.164466 |
| **5** | 75.64 | 75.736 | 0.126756 |
| **6** | 73.26 | 75.736 | 3.269251 |
| **7** | 74.91 | 75.736 | 1.090631 |
| **8** | 43.22 | 49.4193 | 12.54429 |
| **9** | 49.36 | 56.8598 | 13.18999 |
| **10** | 46.7 | 37.7091 | 23.84279 |
| **11** | 78.91 | 79.1932 | 0.357606 |
| **12** | 75.98 | 75.736 | 0.322172 |
| **13** | 93.46 | 83.661 | 11.71275 |

**Table 4.6 Error in Experimental values.**

From table 4.6, we can analyse that most of the value errors are less than 15%. The mean error value is around 9.522351%, which is less than 10 %. This error could be because of the experimental errors or other random errors cause by the student during the experiment. Errors such as inaccurate chemical amount used in experiment could be an example of error. Other than that, instrument calibration error also would affect the experimental result. We also can consider environmental factors such as light intensity; humidity and surrounding temperature in lab which will cause error to the samples.

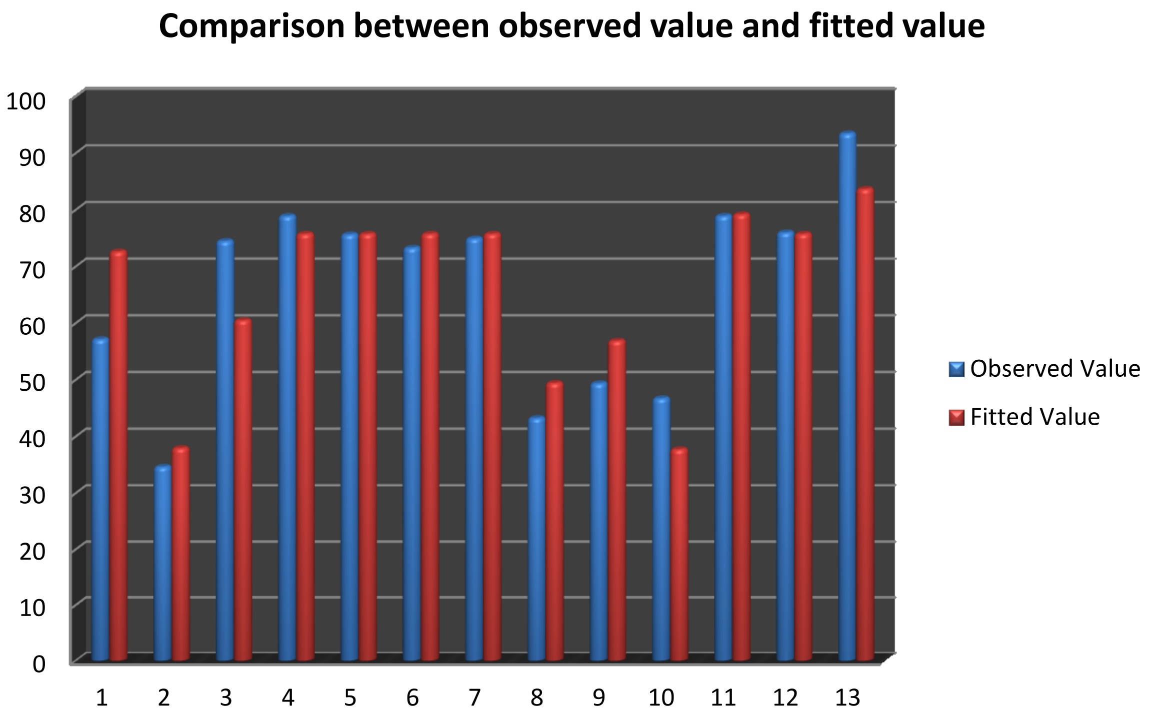

**Figure 4.5 Comparison between observed value and fitted value**

Figure 4.5 the comparison between the experimental value and the estimation value from the software. From the chart, we can conclude that most of the experimental values are similar to the fitted values except for run 1, 3 and 13, where the difference is more than 10 %.

## 4.3 Response Surface Curve

The regression equation was graphically represented by 3D response surface and 2D contour plots. From three dimensional response surface curves and contour plots shown in Figures 8, the effect of the independent variables and their mutual interaction on the degradation of DEA can be seen**.**

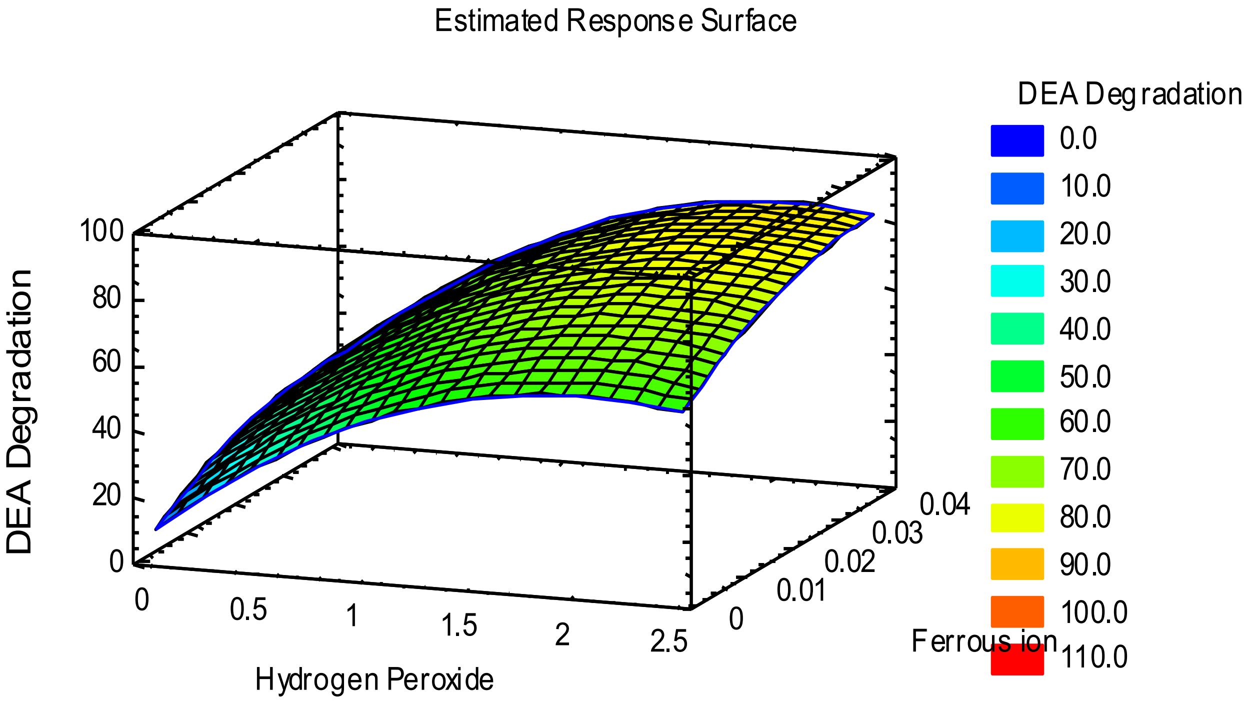

**Figure 4.6**: **Estimated Response Surface for DEA degradation**

Based on the figure 4.6:

Optimum value for the degradation of DEA = 84.9137

| **Factor** | **Low** | **High** | **Optimum** |
|---|---|---|---|
| **Hydrogen Peroxide** | 0.230995 | 2.81901 | **2.11995** |
| **Ferrous ion** | 0.00611148 | 0.0479115 | **0.0396437** |

**Table 4.7**: **Optimum value for DEA degradation**

The maximum or the optimum degradation can happen when the hydrogen peroxide value is around 2.11995M and ferrous ion at 0.0396437.

## 4.4 Effect of Hydrogen Peroxide.

Based on the result obtained, its find that the optimum value for the hydrogen peroxide for the DEA degradation is 2.12. The degradation of DEA is low at low hydrogen peroxide concentration (0.23M- 0.61M). The degradation is also decreasing after 2.44 Generally, the DEA concentration decreased along with time in the presence of H2O2. The degradation percentage increased with increasing of H2O2 from 1.525M until 2.44.M. However, further increase in H2O2 concentration from 2.44M to 2.819M decreases the degradation percentage. This can be explained by two opposing effects. The degradation rate was limited at low H2O2 concentration, as the formation of hydroxyl radicals was insufficient. At higher H2O2 concentration, more hydroxyl radicals were available to attack the aromatic rings leading to a faster oxidation rate (Equation 1 and 2). However, above 2.44M, these free radicals preferred to react with the excess of H2O2 rather than with the DEA (Legrini et al., 1993, Galindo & Kalt, 1999). Hydroperoxyl radicals (HO2•) as the competitive reaction product are much less reactive than OH• and increase in H2O2 do not seem to contribute to the degradation of the DEA.

$$H_2O_2 + UV \rightarrow 2HO\bullet \qquad (1)$$

$$H_2O_2 + HO\bullet \rightarrow H_2O + HO_2\bullet \qquad (2)$$

$$HO_2\bullet + HO\bullet \rightarrow H_2O + O_2 \qquad (3)$$

## 4.5 Effect of $FeSO_4$, $7H_2O$ concentration

The optimum value of the ferrous ion for the degradation of DEA is 0.0396437M. The degradation value is lower when the concentration of ferrous sulphate is in between 0.0018M-0.006M. Then, the degradation of DEA value increases from concentration 0.02M-0.04M. Finally, the degradation rate reduces from concentration 0.04M-0.0479M.

At lower concentration, the amount of $Fe^{2+}$ in the system was not sufficient to generate required amount of hydroxyl radicals for substrate oxidation (reaction 4). In contrast, at higher concentration excess $Fe^{2+}$ led to the scavenging reaction (5). The hydroxyl radicals react with ferrous ion instead of attacking the organic substrate.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH \qquad (4)$$

$$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} \qquad (5)$$

# CONCLUSION

The aim of this project is to study the degradation of DEA using the Fenton's oxidation system and find the optimum operating condition for the degradation process. The study covers two important parameters which are $H_2O_2$ concentration and $FeSO_4$, $7H_2O$ concentration.

The experiment was design successfully using response surface methodology and central composite design. The Experiments were conducted based on the design of experiment from the stat graphics centurion software and the optimization of $H_2O_2$ concentration and FeSO4, $7H_2O$ concentration for DEA degradation is achieved

The optimum $H_2O_2$ concentration and FeSO4, $7H_2O$ concentration for DEA degradation is 2.119M and 0.0396M respectively, which is almost similar with literature data concerning the Fenton degradation of most organic substrates.

Response Surface Methodology (RSM) was performed to optimize the process parameters for DEA degradation. A highly significant quadratic polynomial obtained by Central Composite Design (CCD) was very useful for determining the optimal process parameter values of degradation process that have significant effects on DEA removal.

Finally, the objective of this paper is achieved.

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# APPENDIX

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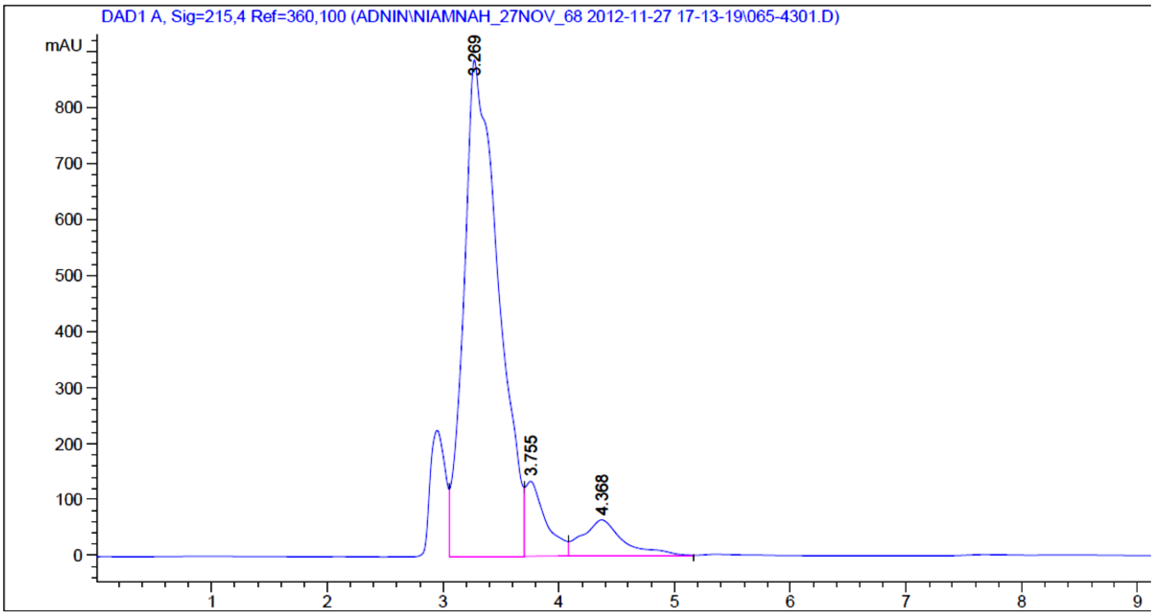

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Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

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RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [mAU*s]                  [g/l]
-------|------|----------|----------|----------|--|------------------
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Totals :                                2.94726
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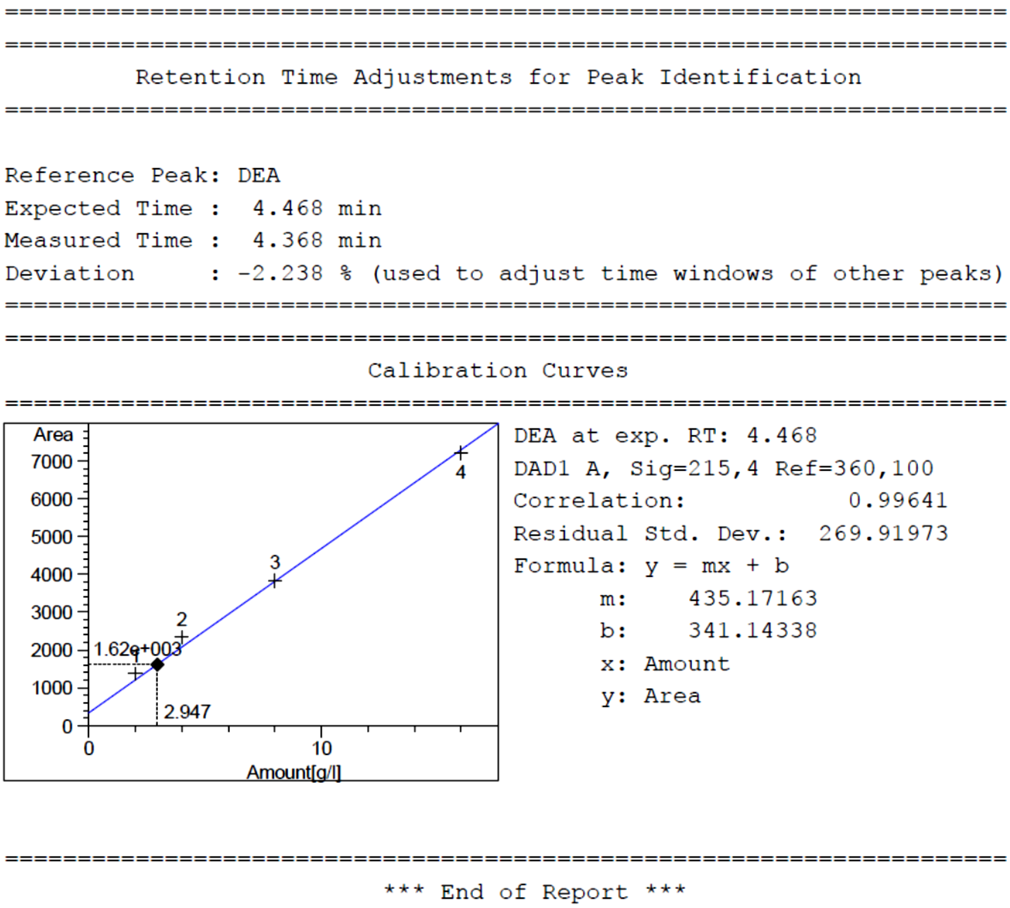

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=====================================================================

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Measured Time :  4.368 min
Deviation     : -2.238 % (used to adjust time windows of other peaks)
=====================================================================
=====================================================================
                         Calibration Curves
=====================================================================
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                                  Correlation:            0.99641
                                  Residual Std. Dev.:   269.91973
                                  Formula: y = mx + b
                                        m:     435.17163
                                        b:     341.14338
                                        x: Amount
                                        y: Area

=====================================================================
                        *** End of Report ***
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Appendix 1. HPLC Reading