Monoethanolamine (MEA) Wastewater Treatment using Photo-Fenton Oxidation

by

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CERTIFICATION OF APPROVAL

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Approved by,

(Azizul B Buang)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own 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.

(CHE NURJULAIKHA BT HAJI CHE MASZELAN)

ABSTRACT

The aim of this project is to study the removal efficiency of monoethanolamine (MEA) in wastewater using a type of advanced oxidation process (AOP) which is photo-Fenton oxidation process. MEA is an organic compound that possesses the properties of weak base in its aqueous form. This makes MEA useful for scrubbing acidic gases such as carbon dioxide, CO_2 in flue gas from oil and gas industries. However, small portion of MEA is carried out during the process and being discharged into the wastewater and. The organic properties of MEA make it resilience to the conventional wastewater treatment such as activated sludge treatment. Hence, possible ways of treating MEA have been studied such as using adsorption method and membrane technology. In this project, another potential method is being observed, which is using photo-Fenton oxidation. Photo-Fenton oxidation is a method of producing hydroxyl radical from reaction of ferrous ion, Fe^{2+} and hydrogen peroxide, H_2O_2 with UV light enhancing the process through photoreduction. From experiments conducted, the results show that higher removal of Total Organic Carbon (TOC) in the MEA wastewater after being treated using photo-Fenton oxidation which is 94.47%, compared to the conventional Fenton oxidation at 93.15%. It is also found that the optimum concentration of ferrous ion is at 0.014 M whereby for hydrogen peroxide, the optimum concentration is at 1.6 M with both giving highest TOC removal at 99.93%. The results prove that the percentage of TOC removal is higher with presence of UV light compared to without UV light. This is because more hydroxyl radicals are produced through photoreduction and increase the rate of MEA mineralization to form the degradation product. The optimum concentration of ferrous ion and hydrogen peroxide can be explained by the scavenging effect due to excess amount of both reactants for the oxidation process. This is why the optimum concentration is not found to be at the highest amount tested in the experiment.

ACKNOWLEDGEMENT

In completion of this final year project, I would like to thank Universiti Teknologi Petronas for providing me with the opportunity to conduct this study. I would also like to express my gratitude to my supervisor, Mr Azizul Buang for his unconditional guide and support throughout the project. I am also grateful to Miss Raihan Mahirah Ramli for the experience she shared with me on conducting experiment related to this project area. Not forgetting, special thanks to lab technicians for their co-operation that helps me to conduct my experiment smoothly. Finally, I would like to thank my parents for their continuous support and encouragement which driven me to complete this project.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

This project is related to wastewater treatment focusing in treating monoethanolamine (MEA) which is a common contaminant in wastewater coming out from gas processing plant. The method that is incorporated in treating the wastewater for this project is Photo-Fenton Oxidation Process. Fenton oxidation is a type of advanced oxidation processes (AOP) which is getting more attention nowadays as it is proved to be effective for the degradation of organics which are resistant to conventional biological treatment (Harimurti et al., 2009).

The purpose of this experiment is to study the removal efficiency of MEA using photo-Fenton oxidation process, thus the experiment is conducted with and without UV light to observe the difference. Optimal condition in term of ferrous ion, Fe^{2+} and hydrogen peroxide, H_2O_2 concentration for this project is also being observed. The UV radiation is introduced in the Fenton oxidation process to increase the degradation rate of MEA. The experiment is conducted using synthetically-produced wastewater sample containing MEA. As mentioned before, the 2 parameters tested as the variables are 1) effect of H_2O_2 concentration and 2) effect of Fe^{2+} concentration. The performance of degradation is measured based on the reduction of total organic carbon (TOC) value of the sample. All experiments are conducted with the radiation of UV from the light source.

1.2 Problem Statement

Alkanolamine is practically used in natural gas processing plant industries for the removal of acid gases from raw natural gas. These acid gases, particularly carbon dioxide (CO_2) and hydrogen sulphide (H_2S), are considered as impurities. The process of removing the impurities from raw natural gas using alkanolamine is known as gas sweetening. Example of alkanolamine solutions used are monoethanolamine (MEA), diisopropanolamine (DEPA) and methyldiethanolamine (MDEA).

However, problem arises during regeneration process in gas purification, whereby a small amount of alkanolamine is carried over and discharged in the wastewater. This alkanolamines present in the wastewater are not readily biodegradable, thus the conventional wastewater treatment facility e.g activated sludge biological oxidation cannot be used in treating them.

The COD of the wastewater discharged containing amine is high, exceeding 20,000 mg/l (MLNG, 2007) and ranging 5,000 to 25,000 ppm (Binyam et al., 2009). This added challenges in treating them conventionally, as plant extension is required and there is a possibility to disturb the process performance.

Thus, in order to encounter this arising problem in the growing industrialization, alternatives of alkanolamine wastewater treatment are explored. From literature study, Advanced Oxidation Processes (AOP) are found to be an effective ways for the treatment and one of the promising options under this process is through photo-Fenton Oxidation.

1.3 Objectives

There are two objectives for this project, which are:

i. To study the removal efficiency of MEA using photo-Fenton oxidation process.
ii. The optimum concentration of ferrous ion, Fe^{2+} and hydrogen peroxide, H_2O_2.

The removal of MEA is measured based on the TOC value in the wastewater sample after going through the photo-Fenton oxidation process.

1.4 Scope of Study

The experiment used monoethanolamine (MEA) as the alkanolamine contaminant in the wastewater and going through Fenton Oxidation for the degradation of the organic compound. UV radiation is incorporated, hence called Photo-Fenton Oxidation, to increase the degradation effectiveness in terms TOC value reduction. The experiment is repeated for two different operating parameters:

i. Effect of H_2O_2 concentration
ii. Effect of Fe^{2+} concentration

1.5 Relevancy of Project

This project is important as it deals with current issue in oil and gas industry which is the wastewater treatment. Advanced oxidation process (AOP) is believed to be one of the effective ways to replace the conventional MEA wastewater treatment. Hence, this project is relevant as Photo-Fenton Oxidation for MEA removal has not been widely addressed yet.

1.6 Feasibility of Project

This project is feasible as it deals with narrowed scope of experiment whereby only 2 parameters are tested. It is within capability to be executed with helps and guidance from the supervisor and the coordinator. With the acquirement of equipment and materials needed, this project is managed to be completed within the time allocated.

CHAPTER 2

LITERATURE REVIEW

2.1 Monoethanolamine (MEA), C_2H_7NO

2.1.1 Characteristics of MEA

Monoethanolamine (MEA) is an organic chemical compound that belongs to primary amine and primary alcohol. Figure 2.1 shows the chemical structure of MEA. Its amine properties make MEA act as a weak base in aqueous form. MEA is a flammable, corrosive, colourless and viscous liquid at room temperature. It also possessed an ammoniac odour. MEA is miscible with water, acetone, ethanol, and chloroform, also slightly soluble in ether. MEA is a toxic and corrosive chemical to human skin. In Malaysia, exposure limit of MEA should not be exceeded from 2-3 ppm.

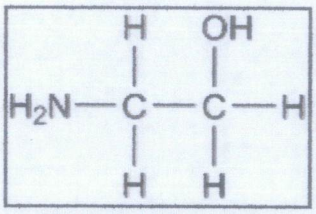

Fig. 2.1: Chemical Structure of MEA

2.1.2 Uses of MEA

MEA is recommended as synthesis intermediate in manufacturing of alkanoamides because it reacts with fatty acid and coconut oil. This makes MEA useful in variety of industrial application as a feedstock. For example, detergents for laundry and dishwashing liquid, degreasers and disinfectants contain MEA in its formulation. MEA also used as neutralizer in car wash shampoos and wax remover. In agrochemical field, MEA act as neutralizer agent for anionic emulsifiers.

2.1.3 Monotethanolamine in CO_2 scrubbing

In aqueous solution, MEA can be used for scrubbing acidic molecules such as carbon dioxide and hydrogen sulfide. This characteristic makes MEA useful in gas stream scrubbing for the removal of CO_2 in flue gas emitted from oil and gas industries. Aqueous solution of MEA which act as a weak base can dissolve CO_2 in the flue gas and neutralized the acidic compounds of CO_2.

Figure 2.2 shows the conventional MEA CO_2 capture flow sheet (Alie et al., 2004). The flue gas containing carbon dioxide enters the absorber countercurrently with the aqueous MEA. MEA as weak base will reacts exothermally with carbon dioxide which is a weak acid to form a water soluble salt. The salt solution rich with MEA will then be preheated and then sent to a stripper. In the stripper, the solution is separated back into CO_2 gas and MEA. CO_2 will leave through the top of the stripper while MEA will be recycled back to the absorber.

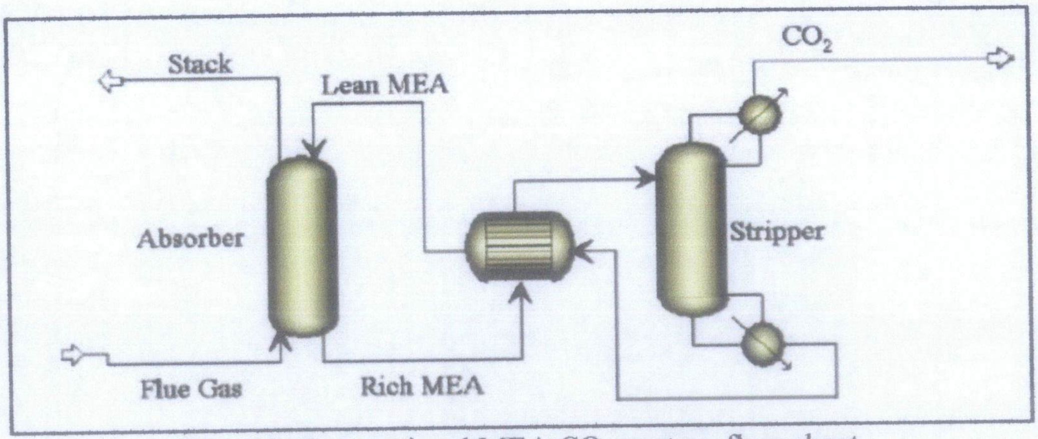

Fig. 2.2: Conventional MEA CO_2 capture flow sheet

Scrubbing of CO_2 from flue gas using alkanolamines solution especially MEA is widely studied and used for it is very reactive and able to effect high volume of acid removal at a fast rate (Supap et al., 2008). Problem arises when small amount of MEA is carried out during the process and being discharged in the wastewater. This causes the increase in the chemical oxygen demand (COD) value of the wastewater. Another issue arises from this technology is the high energy requirement for it to be operated, hence various studies were conducted especially in process simulation to maximize the performance of the process.

2.2 Fenton Oxidation

2.2.1 Advance Oxidation Process (AOP)

Advanced Oxidation Process (AOP) is the oxidative degradation process for organic compounds in aquatic media by catalytic, chemical and photo-chemical methods (Legrini et al., 1993). AOPs are categorized into homogenous and heterogeneous processes depending on the physical state of the catalyst. Homogenous AOP gives low mass-transfer resistance between phases and favours faster degradation of pollutants, thus making it more in advantage compared to heterogeneous AOP (Kavitha et al., 2004).

The key point in AOP is that the process promotes the use of hydroxyl radical (•OH) in degrading wide range of organics in water. Hydroxyl radical has a high oxidation potential and acts rapidly with organic compound. In fact, the hydroxyl radicals are almost twice as reactive as chlorine with an oxidation potential next to fluorine (Bigda, 1995). Hydroxyl radical is also considered as the main oxidant species by having a standard reduction potential of 2.7 V in acid solution and 1.8 V in neutral solution (Buxton et al., 1988).

In general, there are three steps involved in AOP. First, hydroxyl radical is formed from primary oxidants such as ozone (O_3) and hydrogen peroxide (H_2O_2), or catalyst such as titanium dioxide. The radicals then do the initial attack on target molecules until the target reach ultimate mineralization.

2.2.2 Characteristic of Fenton Oxidation

Fenton Oxidation is a type of AOP whereby a mixture of hydrogen peroxide and ferrous sulphate in aqueous solution is used to oxidise organic compound in water. The first description of catalytic decomposition of hydrogen peroxide by ferrous ion was done by Fenton in 1894 and since then, it is one of the most commonly used AOPs for wastewater treatment. This is because Fenton method is more efficient and requires lower capital costs than other AOPs (Hermosilla et al., 2008), as well as the reagent components are safe to handle (Kavitha et al., 2004).

From Equation 1 below, ferrous iron, Fe^{2+} is oxidized by hydrogen peroxide to ferric iron, $Fe^{3+,}$ a hydroxyl radical and a hydroxyl anion. Later in Equation 2, Fe^{3+} is reduced back to Fe^{2+} alongside with the production of a superoxide radical and a hydrogen proton. The ability of hydrogen peroxide to create two different oxygen-radical species makes the reaction useful for oxidation process in wastewater treatment. Equation 3 shows the reaction of radicals oxidizing organic compound R.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad k_1 = 70.0\ M^{-1}.\ s^{-1} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^+ \qquad k_2 <<< k_1 \qquad (2)$$

$$HO\cdot + RH \rightarrow H_2O + R\cdot \qquad k \approx 10^7 - 10^{10}\ M^{-1}.\ s^{-1} \qquad (3)$$

The examples of organic compound that can be oxidised by this reaction are phenols, formaldehyde and pesticides. The effectiveness of this reaction makes it a well-known matter in the study of wastewater treatment in textile, agriculture, pesticides, pharmaceutical and natural gas industries. Fenton reaction knowledge is also important in biomedical field, as the reaction might cause side effect to patients with active infections.

2.2.3 Photo-Fenton Oxidation Process

Apart from the conventional Fenton process from chemical solutions, photo-Fenton process is the upgraded Fenton process technology available. In photo-Fenton process, photoreduction of the complex $Fe(OH)^{2+}$ occur with the presence of ultraviolet (UV) or adequate visible light (wavelength of 290nm – 400nm) whereby the UV light helps to accelerate the mineralization rate of organics (Priambodo et al., 2011).

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + \cdot OH \qquad (4)$$

The photo-Fenton process has two major features. The first one is shown as Equation 4 above which is the reduction of ferric to ferrous iron to produce additional hydroxyl radicals (Kavitha et al., 2004). The second feature of photo-Fenton process is the photo-decarbocylation of ferric carboxylates (Kavitha et al., 2004) as shown in Equation 5 and 6.

$$\mathrm{Fe(III)\,(OH)^{2+}(RCO_2)^{\,2+}} + \xrightarrow{hv} \mathrm{Fe^{2+}} + \mathrm{CO_2} + \mathrm{R}\cdot \qquad (5)$$

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{RO\cdot_2} \rightarrow \text{Products} \qquad (6)$$

The amount of catalytic iron required and volume of sludge produced can be reduced. Besides, additional organic compound which is the carboxylates may also be effectively treated (Hermosilla et al., 2008).

There were several studies that show the treatment of wastewater using photo-Fenton reaction. For example, degradation of phenols using 150 W mercury lamp (Kavitha et al., 2004) shows that the mineralizing efficiency of phenol using photo-Fenton is 97%, compared to 41% obtained from Fenton process alone. Treatment of landfill leachate by using 450 W mercury lamp for photo-Fenton (Hermosilla et al., 2008) resulted in same COD removals as in Fenton reaction, but huge reduction of ferrous iron concentration used by 32 times is observed. In coloured wastewater treatment (Tokumura et al., 2013), the combination of photo-Fenton reaction using three 6-W UV-A fluorescent lamp together with electrochemical corrosion of iron gives 81% mineralization. These promising results make photo-Fenton getting more attention in studies of wastewater treatment.

This photoreduction process has an advantage whereby sunlight can be utilized for the source of light hence cutting the cost of UV lamps and electrical energy. However, this project will only integrate photo-Fenton reaction for the wastewater treatment by using light source. The UV light source for research scale can be obtained from UV-A fluorescent lamp or mercury lamp. The light intensity can be measured as the irradiance, W/m^2.

2.3 Photo-Fenton Oxidation for MEA Removals in Wastewater

In this project, the focus of photo-Fenton reaction will be on treating MEA from wastewater particularly in natural gas industries. As mentioned before, MEA is released in the wastewater of CO2 scrubbing in natural gas processing plant. The conventional method such as activated sludge is not helping much in treating wastewater with MEA, as the amine concentration increase the COD level of the wastewater.

There are several studies on the MEA removals in natural gas wastewater such as using adsorption method (Razali et al., 2010). In their study, the adsorption performance of chitosan, activated carbon, alum and zeolite on MEA removal was tested by measuring the COD reduction. The result shown that chitosan gave the highest COD removal, which is up to 83%. The advantage of this method is the MEA removed can be recycled back to the process. However, the cost of adsorbent might be a hindrance for this technique to be commercialized in the real industry.

MEA treatment in wastewater using membrane technology was studied by Binyam et al., (2009). They measure the effectiveness of MEA removal through the flux and rejection characteristic of the membranes to MEA by manipulating the operating pressure, feed concentration, cross-flow velocity and pH. The membranes tested for this study were reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF). The result was promising, whereby RO gave 99% rejection, which is the highest compared to others. Although from this study RO gave a positive result, this membrane method will require more equipment and caused plant expansion if it is to be integrated to the real process.

There was also a previous study on treating MEA using Fenton oxidation followed with biological post-treatment done by Harimurti et al., (2009). The biological post-treatment is done to obtain higher COD removal, as the rate becomes slow after partial degradation if using Fenton oxidation alone. The effectiveness of the method is measured by the COD removal, and it showed that almost complete COD removal could be achieve within 24 hours. From this study, we can see that Fenton oxidation is a feasible way for MEA wastewater treatment, but photo-Fenton process for the MEA wastewater treatment is not widely done yet.

Based on the main reaction that is shown by Equation 1 previously, the important parameters that control the photo-Fenton reaction are the concentration of ferrous ion and hydrogen peroxide. Other parameters that can be manipulated to determine the effective rate of degradation of MEA in the wastewater using photo-Fenton reaction are the initial concentration of MEA in the wastewater, the pH of the solution and the molar ratio of ferrous iron and hydrogen peroxide (H_2O_2/Fe^{2+}).

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Project Activities

Literature Review

- For FYP II, further understanding on the concept and comparison between Fenton oxidation and photo-Fenton oxidation is done.
- More review on literature is done to understand the photocatalytic effect in speeding up the rate of Fenton oxidation process.

Experiment

- Experiment is designed to test for photo-Fenton oxidation action in treating MEA wastewater.
- Chemicals and equipments required for the experiment is prepared and series of experiments are conducted.

Data Collection

- From the experiment conducted, the samples are withdrawn.
- The samples are analysed using Total Organic Carbon (TOC) and the reduced in TOC values are observed.

Conclusion

- The experiment is concluded based on the results at the end of the project.
- Report for the project is prepared.

3.2 Gantt Chart and Key Milestone

Table 3.1: FYP II Gantt Chart

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continues	🟩	🟩	🟩	🟩	🟩	🟩	🟩							
2	Submission of Progress Report								●						
3	Project Work Continues								🟩	🟩	🟩	🟩	🟩		
4	Pre-EDX											●			
5	Submission of Draft Report												●		
6	Submission of Dissertation (soft bound)												●		
7	Submission of Technical Paper												●		
8	Oral Presentation													●	
9	Submission of Dissertation (hard bound)														●

Process 🟩 Milestone ●

3.3 Experiment Methodology

3.3.1 Synthetic MEA Wastewater Sample Preparation

Synthetic wastewater is prepared by diluting MEA in distilled water. MEA concentration in the synthetic wastewater is fixed at 10000 ppm for every run of experiment. 500 ml of MEA synthetic wastewater is needed, hence equation below is used to calculate the amount of MEA used to get the concentration at 10000 ppm.

$$10000\ ppm = 1\%\ density\ of\ MEA\ solution$$

$$0.01 = \frac{1g\ of\ MEA}{100\ ml\ of\ distilled\ water} \times \frac{cm^3}{1.01\ g}$$

$$= \frac{0.99\ cm^3 of\ MEA}{100\ ml\ of\ distilled\ water}$$

For 500 ml of distilled water,

$$\frac{0.99\ ml}{100\ ml\ of\ distilled\ water} \times 500\ ml = 4.95\ ml\ of\ MEA$$

3.3.2 Experiment Setup

Fig. 3.1: Experiment setup of the reactor and UV lamp covered with aluminium foil

Figure 3.1 shows the setup of the experiment. The reactor is made from a plastic bottle covered with aluminium foil to avoid the loss of energy from the UV light to the surrounding. It is placed on a magnetic stirrer to ensure continuous mixing of the solution inside. A thermometer is placed inside the reactor together with the UV lamp. The exposed surface of the reactor is then covered with aluminium foil to minimize surrounding air from entering the reactor.

A pH meter is used to measure the pH value of the sample prior to the treatment. The samples are withdrawn using a 10 ml syringe and put into vials for further analysis using Total Organic Carbon (TOC) analyser for its TOC value. TOC is an indirect measure of organic molecules present in water and measured as carbon (GE Water & Process Techonology, n.d). This measurement is commonly used to determine the degree of organic contamination in water. Since the only organic compound in the synthetic wastewater is MEA, it can be said that decrease of TOC value can represent the decrease in concentration of MEA in the sample, although the exact concentration might be slightly varied.

3.3.3 Substance and Chemicals

Fig. 3.2: Chemicals used for experiments

Figure 3.2 shows the chemicals used in the experiments conducted. The chemicals are:

i. Monoethanolamine from R&M Chemicals
ii. Sodium hydroxide, NaOH from R&M Chemicals
iii. Hydrogen peroxide, H_2O_2 (30% in aqueous solution) from Systerm
iv. Sulphuric acid, H_2SO_4 (98%) from Systerm
v. Iron(II) sulphate heptahydrate, $FeSO_4.7H_2O$ from Hamburg Chemicals

3.3.4 Range of Variables

Table 3.2: Range of variables and the code

Variables	Range of Values				
Hydrogen peroxide (H_2O_2) concentration, M	A_1	A_2	A_3	A_4	A_5
	0.6	1.6	2.6	3.6	4.6
Ferrous ion ($Fe2^+$) concentration, M	B_1	B_2	B_3	B_4	B_5
	0.006	0.010	0.014	0.018	0.022

Table 3.3: Fixed variables

pH value	3
Time for each sample to be withdrawn	Every 10 minutes
Initial MEA concentration	10000 ppm

From previous research (Harimurti et al., 2010), the optimum values of Fe^{2+} for 1 L of MEA wastewater is at 0.028 M. Since in this experiment the volume used is 500 ml, amount of Fe^{2+} tested is reduced to the range of 0.006 M to 0.022 M. In other hand, the optimum H_2O_2 concentration for the previous research is 2.123 M, thus it is reduced to the range of 0.6 M to 4.6 M. 10000 ppm of initial MEA concentration is used because it is the common concentration of MEA wastewater generated from oil and gas industries.

Due to limitation of time and TOC analyser availability, there are total of 10 runs for this experiment. From the experiment, the reduction in TOC value is observed. The combinations of variables tested are shown in the following table.

Table 3.4: Combination of variables

Run	**Variables Test**
1.	A_1:B_3
2.	A_2:B_3
3.	A_3:B_3
4.	A_4:B_3
5.	A_5:B_3
6.	A_2:B_1
7.	A_2:B_2
8.	A_2:B_3
9.	A_2:B_4
10.	A_2:B_5

3.3.5 Experiment Procedure

The reaction is conducted in batch mode for about 20 minutes. Taken the previous research work as guidance (Omar et al., 2010), the procedure for Photo-Fenton reaction with MEA wastewater experiment are:

1. 500ml solution of wastewater with 10000 ppm of MEA concentration was placed in the reactor.

2. The pH value of the mixture was measured using pH meter. The pH value was fixed at 3. The adjustment of pH value was done with 1M of sodium hydroxide and 1M of sulphuric acid.
3. For the 1st run, 2.0 g of solid iron(II) sulphate heptahydrate was weighed and 18 ml of hydrogen peroxide was measured as shown in Figure 3.3.

Fig. 3.3: Synthetic MEA wastewater in 1 L beaker, and hydrogen peroxide and iron(II) sulphate in 50 ml and 25 ml beaker

4. The reactor was put on the magnetic stirrer. UV lamp and thermometer was then placed inside the reactor.
5. The UV lamp and stirrer was switched on as shown in Figure 3.4.

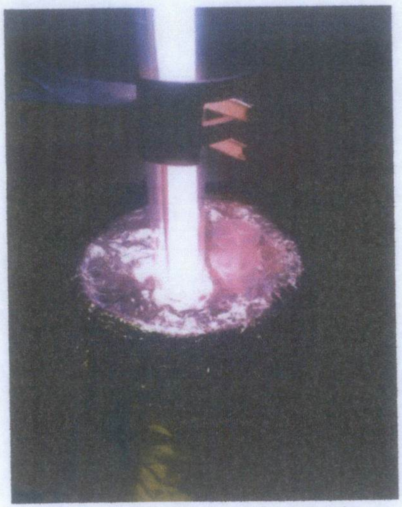

Fig. 3.4: Reactor with UV lamp

6. Iron(II) sulphate heptahydrate was put into the reactor followed by hydrogen peroxide. The reactor's exposed surface was quickly covered with aluminium foil and the stopwatch was started.
7. 5 ml of solution from the reaction was withdrawn every 2 minutes using syringe.
8. In Figure 3.5, 20 ml of 1 M sodium hydroxide was immediately added to the withdrawn sample to stop the oxidation process.

Fig. 3.5: Withdrawn sample with sodium hydroxide

9. Steps 7 and 8 were repeated until the experiment reached 30 minutes.
10. In Figure 3.6, the withdrawn samples were filtrated using filter paper to remove iron precipitate. The clear solutions were placed inside vials as shown in Figure 3.7.

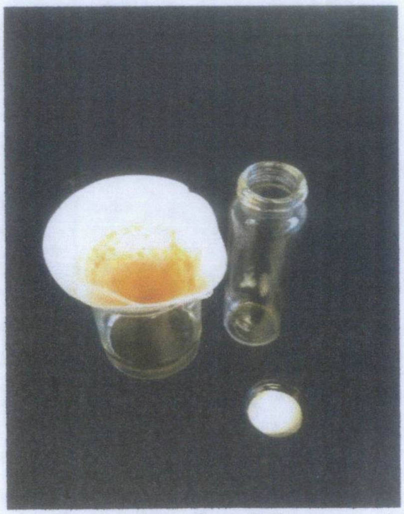

Fig. 3.6: Filtration of sample using Whatman 125mm filter paper

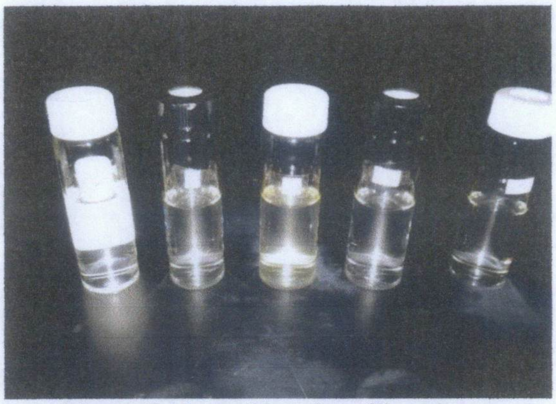

Fig. 3.7: Samples after filtration

11. The samples were analysed using Total Organic Carbon (TOC) analyser as shown in Figure 3.8 to get the TOC values.

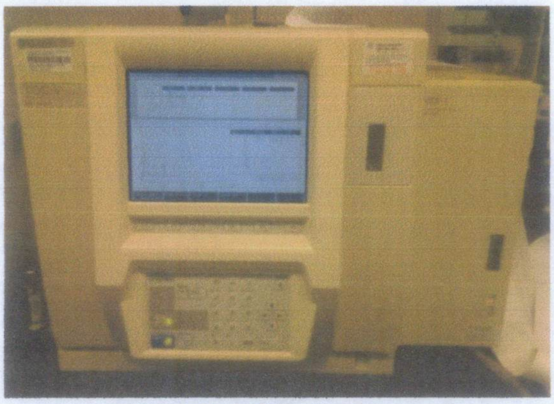

Fig. 3.8: TOC Analyser

12. Steps 3 to 11 were repeated using different variables; concentration of ferrous sulphate and concentration of hydrogen peroxide.

CHAPTER 4

RESULTS AND DISCUSSION

Experiments were conducted by manipulating the concentration of ferrous ion and hydrogen peroxide. Table 4.1 shows the results in percentage of TOC removal from varying the concentration of ferrous ion, while for hydrogen peroxide is shown in Table 4.2. The percentage of TOC removal without UV light was also observed and the results are presented in the respective tables.

Table 4.1: TOC Removal % for different Fe^{2+} concentration

Experiment Run	Variables	Fe^{2+} Concentration	TOC Removal %	Remarks
V1-Fe^{2+}	A2:B1	0.006 M	97.35	-
V2- Fe^{2+}	A2:B2	0.010 M	99.8	-
V3- Fe^{2+}	A2:B3	0.014 M	99.93	-
V4- Fe^{2+}	A2:B4	0.018 M	98.32	-
V5- Fe^{2+}	A2:B4	0.018 M	97.15	No UV
V6- Fe^{2+}	A2:B5	0.022 M	96.99	-

Table 4.2: TOC Removal % for different H_2O_2 concentration

Experiment Run	Variables	H_2O_2 Concentration	TOC Removal %	Remarks
V7- H_2O_2	A1:B3	0.6 M	92.38	-
V8- H_2O_2	A2:B3	1.6 M	99.93	-
V9- H_2O_2	A3:B3	2.6 M	94.47	-
V10- H_2O_2	A3:B3	2.6 M	93.15	No UV
V11- H_2O_2	A4:B3	3.6 M	96.82	-
V12- H_2O_2	A5:B3	4.6 M	97.99	-

4.1 Degradation of ME

From Table 4.1 and 4.2, all runs of experiment showed that there are TOC removals after being treated by the oxidation process. It proves that Fenton and photo-Fenton oxidation can be used to degrade MEA in wastewater. The hydroxyl radical from the oxidation process is able to react with organic substrate in MEA and reducing the wastewater organic compound.

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}OH + {}^{\cdot}OH \rightarrow \text{Degradation product} + H_2O \qquad (7)$$

Equation 7 shows the reaction of hydroxyl radical with MEA to produce the degradation product and water. Previous study found that the alcoholic group in MEA is oxidized and produce glycine ($C_2H_5NO_2$) as intermediate before further degradation (Harimurti et al., 2010). The degradation product is not identified yet, but from the result it is shown that the wastewater TOC values decrease, hence proving the decrease in the organic content.

4.2 Effect of UV Light Presence (Photo-Fenton)

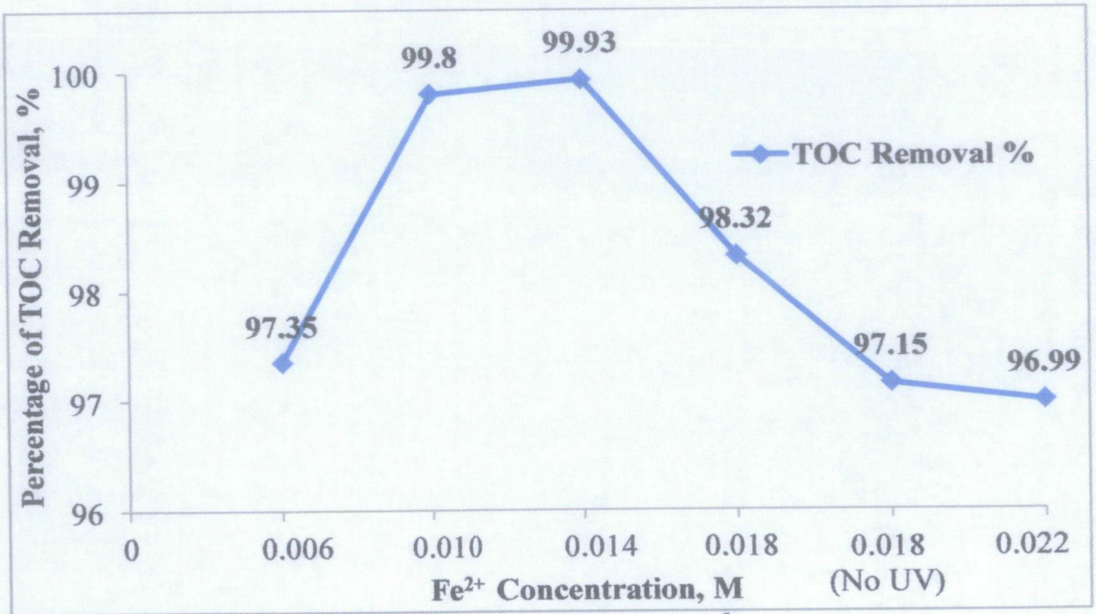

Fig. 4.1: TOC Removal % for different Fe^{2+} concentration

Figure 4.1 shows the graph of TOC removal percentage for different Fe^{2+} concentration based. At Experiment Run 4 and 5, the effect of UV light presence in the reaction is compared. In other word, it compares the rate of MEA degradation between Fenton and photo-Fenton reaction. We can see that the percentage of TOC removal with the presence of UV light is higher, which is 98.32% compared to without UV light which is 97.15%.

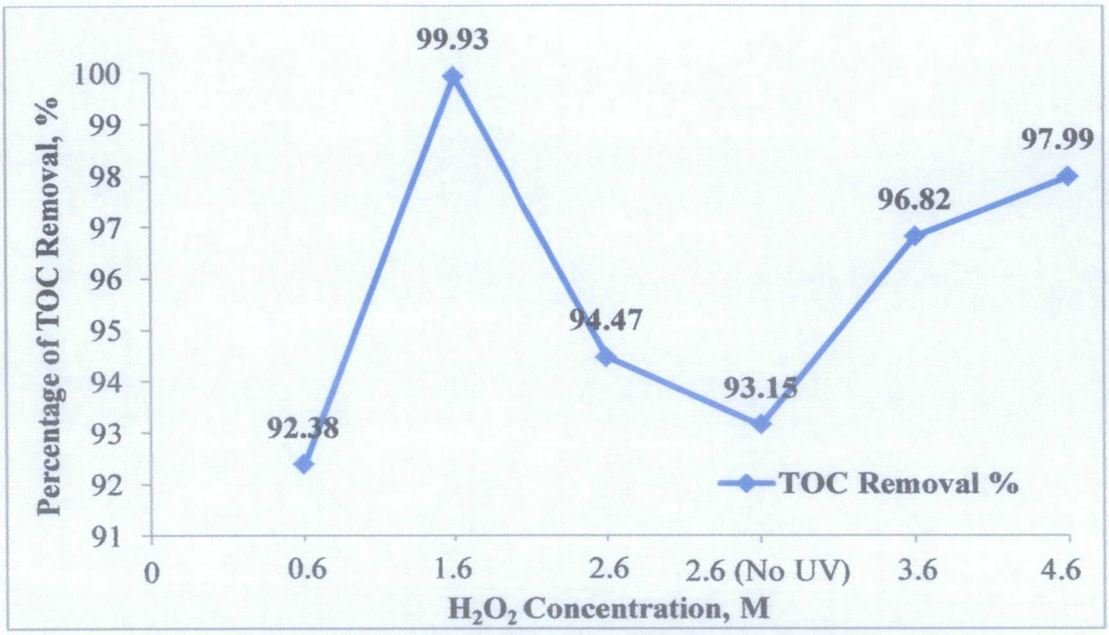

Fig. 4.2: TOC Removal % for different H_2O_2 concentration

The same trend is shown from Figure 4.2 which shows the graph of TOC removal percentage for different H_2O_2 concentration. For photo-Fenton, the removal percentage is 94.47% which is higher compared to Fenton at 93.15%. Thus, it can be concluded that the removal efficiency of MEA using photo-Fenton oxidation is higher than using normal Fenton oxidation. This is explained through the reaction equation below:

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + {}^{\cdot}OH + H^{+} \quad (7)$$

$$Fe(III)OH^{2+} \xrightarrow{hv} Fe^{2+} + {}^{\cdot}OH \quad (8)$$

Equation 7 and 8 shows the photoreduction effect promoting more hydroxyl radicals to be produced, hence speeding up the degradation of MEA in the wastewater.

4.3 Effect of Ferrous Ion Concentration

The experiments were conducted with different quantities of Fe^{2+} ranging from 0.006 M to 0.022 M while keeping the amount of H_2O_2 constant at 1.6 M. From Figure 4.1, we can see that at Fe^{2+} concentration of 0.014 M, the highest percentage of TOC removals is observed which is 99.93%. It can be said that the rate of degradation using 0.014 M is faster compared to others.

We can also see that after 0.014 M, addition of more Fe^{2+} causes the percentage TOC removals continue to decreases. It shows that high concentration of Fe^{2+} does not help in increasing the efficiency of photo-Fenton oxidation process. This is because of the scavenging effect as shown in Equation 9.

$$Fe^{2+} + .OH \rightarrow Fe^{3+} \qquad (9)$$

The hydroxyl radicals that supposed to react with MEA are reacting with ferrous ion producing ferric ion. This causes the decrease in available hydroxyl radicals for the mineralization. In addition, the ferric ion produced can also decompose hydrogen peroxide, causing disturbance in the oxidation process.

4.4 Effect of Hydrogen Peroxide Concentration

The experiments are conducted with different quantities of H_2O_2 ranging from 0.6 M to 4.6 M while keeping the amount of Fe^{2+} constant at 0.014 M. From Figure 4.2, we can see that at H_2O_2 concentration of 1.6 M, the highest percentage of TOC removals is observed which is 99.93%. It can be said that the rate of degradation using 1.6 M is faster compared to others.

Like Fe^{2+}, H_2O_2 also cause scavenging effect whereby the hydroxyl radicals react with hydrogen peroxide as shown in Equation 10. This is why the removal percentage is not observed at the higher concentration of hydrogen peroxide, as increasing the concentration will cause reduction in available hydroxyl radicals.

$$H_2O_2 + .OH \rightarrow .OOH + H_2O \qquad (10)$$

4.5 Limitations

There are several limitations faced during the experiments. These limitations might affect the accuracy of experimental results.

4.5.1 Estimation of Fe^{2+} and H_2O_2 concentration

Various literatures mentioned that the molar ratio of Fe^{2+}/H_2O_2 can affect the degradation process of MEA. Estimated range of values for Fe^{2+} and H_2O_2 concentration are taken based on the previous study to match the fixed parameters in this experiment. Therefore, the optimum values found are related to the estimated range used. If another range is used, the optimum values might be different.

4.5.2 Temperature Control

Literature stated that the optimum temperature for Fenton oxidation to occur is at 300K (Omar et al., 2010). However, due to limitation of equipment, the reactor cannot be cooled down as the exothermic reaction increase the temperature. It is observed that after 30 minutes of experiment, the temperature rose up to 313 K. Since there is no sufficient equipment to control this, the effect of temperature on the reaction is neglected.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

As a conclusion, this project is important as it deals with alternative ways of treating wastewater from industries. Photo-Fenton's oxidation is believed to be one of the effective ways to encounter the current problem with the conventional ways of treating the effluent with alkanolamine. The photoreduction knowledge is integrated in the Fenton's reaction in this project to enhance the rate of degradation of organic compound in the wastewater.

The results proves that the presence of UV light in photo-Fenton oxidation process have higher MEA removal efficiency compared to the normal Fenton oxidation. It is also found that for this project, the optimum concentration of ferrous ion is 0.014 M and for hydrogen peroxide is 1.6 M.

It is mentioned earlier that the photo-Fenton reaction can also be executed using sunlight as the source of light. As a recommendation, a future work may be done to study the effectiveness of solar Fenton reaction for the treatment of MEA wastewater.

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