STATUS OF THESIS

Title of thesis | **Degradation Kinetics of MEA and DEA by Fenton's Reagent with Biological Post-Treatment**

I, **SABTANTI HARIMURTI** hereby allow my thesis to be placed at the Information Resource Center (IRC) of Universiti Teknologi PETRONAS (UTP) with the following conditions:

1. The thesis becomes the property of UTP.
2. The IRC of UTP may make copies of the thesis for academic purposes only.
3. This thesis is classified as

☐ Confidential

☑ Non-confidential

If this thesis is confidential, please state the reason:

_____

_____

_____

The contents of the thesis will remain confidential for _____ years.

Remarks on disclosure:

_____

_____

_____

Endorsed by

Signature of Author

Permanent address : Jln. Deresan II No. 23 Depok, Sleman, Yogyakarta, Indonesia.

Date : 6/4/09

Signature of Supervisor

Department of Chemical Engineering
Universiti Teknologi PETRONAS
Malaysia

Date : 6/4/09

UNIVERSITI TEKNOLOGI PETRONAS

Approval by Supervisor

The undersigned certify that he has read, and recommend to the Postgraduate Studies Programme for acceptance, a thesis entitled

"Degradation Kinetics of MEA and DEA by Fenton's Reagent with Biological Post-Treatment"

submitted by

Sabtanti Harimurti

for the fulfillment of the requirements for the degree of

Master of Science in Chemical Engineering

Date: 6/4/09

Signature : _____

Supervisor : Prof. Binay K Dutta

Date : 6/4/09

UNIVERSITI TEKNOLOGI PETRONAS

"Degradation Kinetics of MEA and DEA by Fenton's Reagent with Biological Post-Treatment"

By

Sabtanti Harimurti

A THESIS

SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME

AS A REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE

IN CHEMICAL ENGINEERING

BANDAR SERI ISKANDAR,

PERAK

APRIL, 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Teknologi PETRONAS or other institutions.

Signature : 

Name : Sabtanti Harimurti

Date : 6/4/09

ACKNOWLEDGEMENT

First of all, this work could not be accomplished without Allah permission. Allah creates all knowledge in this universe we live in. If the ocean were ink (wherewith to write out) the words of Allah, sooner would the ocean be exhausted than would the words of my Lord, even if we added another ocean. Our knowledge is just as a small drop of water from the ocean. Therefore, all the contributions that I can provide in this work are for the shake of Allah only.

This work could not completed on time in two and half years without all valuable helps of my supervisor, Prof Dr. Binay K Dutta. I would not forget about his patience in guiding me to write the dissertation. I would like to thank Pn. Putri N Faizura Megat Khamaruddin for her helpful comments in course of my research work. I would like to thank Associate Prof Dr. Suzana Bt. Yusof for her support and wisdom as Head of Chemical Engineering Department, UTP.

Special thanks to my family (Ayok, Lutfi, and Qornain), for their love, patience and faith all the days throughout this two and half years of my master study in UTP.

I thank the financial support that has made this project possible. The Chemical Engineering Department and Postgraduate Studies Program, Universiti Teknologi PETRONAS have each provided me necessary means of support. Thanks to postgraduate office staff, especially Kak Norma, Pn. Kamaliah, En. Fadhil. I would like also express my gratitude to technicians at UTP, En. Zabaa, En. Jailani, En Fauzi, En. Yusuf, En. Firdaus, Asnizam, Khairul, Sahafizann, Fazli, Kak Lung and Kak Zimah for their effort in helping and providing me with the all chemicals and other experimental tools that I needed for this research.

I would also like to acknowledge with gratitude the many contributions of Raihan Mahirah, Idhzam Fauzi, Faizal Haris, Welly Herimurti, Kiki Adikurnia, Saepurahman, Merry Hastuti, Sominidevi, Nurul Huda, Kamaleshwaran, and Vicknesh, for their kind consideration and cooperation during research works of this study.

Special thanks go to Surya, Amelia, Nga, Ameer, Omer, Fauzan, Zulfan and Jody. Because all of you my GA works were colorful.

For all of you in the sport hall, especially Mbak Etik, Ari, Fitri, Inung and Afny thank you very much for partner sharing to play badminton and I would not like to forget anything in the swimming pool. Without all of that I am sure I could not sustain in the hard lab work.

To all that I mention above and to all that I can not list individually including all of my friends in Universiti Teknologi Petronas, surely your support cannot be repaid with everything, and may those only be rewarded by Allah.

ABSTRACT

Alkanolamines in aqueous solutions are commonly used for scrubbing of carbon dioxide from natural gas, synthesis gas and other gas mixtures. Large quantities of amines appear in the wastewater during cleaning and maintenance as well as shutdown of the absorption and desorption columns. The amines are not readily biodegradable and such wastewater cannot be treated in the conventional treatment facility. Advanced Oxidation Processes (AOP), 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 recalcitrant organics which are not readily amenable to conventional biological oxidation. Degradation of alkanolamines by Fenton's reagent has been investigated in this work. Mono- and di-ethanolamines have been selected as two model alkanolamines. Fenton's oxidation experiments were conducted in a jacketed glass reactor and the effects of process parameters such as dosing of the reagents (H_2O_2 and $FeSO_4;7H_2O$), pH, initial concentration of the amine as well as the mode of addition of the reagents have been studied in details. Since the degradation process involves a number of intermediates, not all of which could be identified, the chemical oxidation demand (COD) of the amine solution is selected as a measure of the extent of degradation. Determination of the COD was done by Hach 5000 spectrophotometer following the standard procedure. FTIR Spectrometer and HPLC were used for identification and analysis of the degradation fragments. Amine concentrations upto 20,000 ppm was used since it is characteristic of the effluents from a natural gas treating plant. It was observed that only a fraction of the COD

could be removed by using a moderate quantity of the reagents. Also, for a solution having a higher initial amine concentration, the degradation process was very fast. Most of the total COD removal was attained within a few minutes from the start of the reaction. This was followed by a very slow rate of COD removal. The reaction rate as well as the extent of reaction was most favored at a pH of 3. Also the rate of degradation passes through a maximum with increase of H_2O_2 dosing and the Fe^{2+}/H_2O_2 ratio. Continuous addition of the Fenton's reagent is much more effective with better utilization of the H_2O_2 than one-time addition. Besides COD, time evolution of the concentrations of the amine and hydrogen peroxide were measured to monitor the course of the reaction. A rapid fall of H_2O_2 concentration accompanied the fast COD reduction. But COD removal was less steep for continuous reagent addition experiments. The trends were very much similar for both MEA and DEA. They showed closely similar behavior.

Although it was not possible to identify all the degradation products of the amines, the formation of glycine as one of the intermediates was decisively established. This indicates that the alcohol group of an alkanolamine might be more vulnerable to electrophilic attack by the HO• radicals than the α-carbon atom with respect to the alcohol group. A plausible reaction pathway is suggested and a rate equation for MEA degradation was developed.

A high dose of Fenton's reagent was not of help to increase the COD reduction. With addition of the stoichiometric quantities of the regent, the degradation amounted to only about 60% COD removal even though about 98% of H_2O_2 as hydroxyl radical source was utilized. Oxidation of one of the degradation products

namely glycine using Fenton's oxidation was investigated separately. The degradation rate was slower than the pure substrate. Since 40-50% of the COD remains in the Fenton-treated solution, we explored the biodegradability of the organic fragments and oxidation products. The biodegradability test was carried out in an aerobic batch reactor prescribed by the materials and methods specifications in the Zahn-Wellens/EMPA Test according to the US Environmental Protection Agency (EPA) method OPPTS 835.3200. Partially degraded alkanolamines after about 40% COD removal by Fenton's oxidation was used to study the biodegradability. The biological oxidation of untreated alkanolamine was done in parallel. The COD in solution as well as the biomass concentration was monitored to follow the course of the reaction. The pH of the medium ranged between 6.5 – 8. No attempt to maintain a constant pH by buffering was made in order to ascertain the usefulness of the method under industrial operating conditions. 'Activated sludge' from the central wastewater treatment unit of this university was used for seeding the batch bioreactor. The results show that the acclimatization time for biological oxidation of a partially degraded amine sample was about the half of that of the 'pure' amine. The time of maximum COD removal was also shorter for the former sample. The kinetics of biomass growth could be fitted by the Monod equation. The kinetic constants were evaluated.

Emission of ammonia from the reactor was detected and an ammonia probe was used to monitor the formation of ammonia during the biodegradation process. It appears that ammonia formation per unit COD of the partially degraded sample was more than that of a 'pure' amine. This observation is compatible with the formation of more oxygenated degradation products such as amino-acids during Fenton's

oxidation. The results of this study are expected to be useful for developing a practical strategy of treatment of amine-laden wastewater in natural gas-treating plants.

Index terms: Monoethanolamine, Diethanolamine, Fenton's reagent, COD, Biodegradability, MLSS.

ABSTRAK

Alkanolamines adalah satu larutan yang selalu digunakan untuk tujuan menyingkirkan gas carbon dioxide daripada kandungan gas asli, gas sintesis dan juga gas-gas yang lain. Semasa penyelengaraan absorption dan desorption columns sejumlah besar kandungan amines ditemui dalam air kumbahan yang dikeluarkan melaluinya. Larutan amines sukar untuk dihuraikan secara biological dan ini menyebabkannya sukar dirawati melalui rawatan convensional. Advanced Oxidation Processes (AOP), seperti pengoxidaan dengan menggunakan Fenton reagent, UV-H_2O_2 dan UV-Ozone dapat membantu dalam penghuraian kandungan bahan buangan secara separa supaya ia dapat kemudiannya dirawati melalui rawatan biological. Kajian terhadap penghuraian Alkanolamines dilakukan dengan lebih terperinci dalam tugasan ini. Dalam kajian ini jenis alkanolamines yang digunakan adalah mono dan di-ethanolamines. Experimen ini dijalankan didalam sebuah kelalang dimana parameter seperti nilai pH, consentrasi amine, kandungan H_2O_2 dan $FeSO_4$, $7H_2O$ serta kandungan tambahan reagen lain telah dibuat kajian secara terperinci. Disebabkan tidak kesemua bahan huraian dapat dikesan atau dikaji, nilai COD digunakan sebagai kraiteria dalam menyukat tahap penghuraian. Tahap COD diukur dengan mengunakan sistem HACH 5000 spectrophotometer melalui langkah pengunaannya. FTIR Spectrometer dan HPLC dapat digunakan untuk mengkaji kandungan hasil penghuraian. Bagi menepati tahap konsentrasi kandungan yang dikeluarkan dari pusat pemerosesan gas asli, sebanyak 20,000ppm Amine digunakan dalam experiment ini. Didapati bahawa cuma sejumlah bahagian COD sahaja dapat

dikurangkan denngan pengunaan reagent yang berpatutan. Selain itu, kandungan konsentrasi amine yang tinggi membantu mempercepatkan riaksi pemerosesan. Didapati bahawa cuma beberapa minit sahaja diperlukan bagi meneutralkan kesemua kandungan COD dalam larutan yang digunakan. Selepas penurunan yang mendadak, penurunan COD akan kembali pelahan. Didapati bahawa pH yang sesuai bagi experiment ini adalah dalam lingkungan 3. Melalui experiment yang dijalankan didapati bahawa penghuraian yang maksima dapat diperolehi melalui penambahan kandungan H_2O_2 dan Fe^{2+}/H_2O_2 .Penambahan kandungan fenton yang berterusan didapati lebih efektif terutama sekali bagi H_2O_2 berbanding penambahan sekaligus. Selain kandungan COD, penglibatan masa juga dititikberatkan dalam experiment ini untik mengetahui bagaimana masa dapat memanupulasikan tindak balas kimia. Penurunan konsentrasi H_2O_2 yang mendadak menandakan perununan COD yang pantas. Didapati kadar kecerunan graph bagi penambahan reagent yang berterusan adalah rendah berbanding penambahan sekaligus. Trand yang sama diperolehi bagi MEA dan DEA.

Walaupun sukar bagi kita untuk mengenal pasti kesemua jenis bahan kimia yang terhasil daripada penghuraian amines, glycine adalah salah satu bahan persementaraan yang dapat dikesan dalam experiment ini. Ini menunjukkan bahawa serangan electrophilic daripada HO• radical terhadap alkanolamine adalah lebih tinggi berbanding atom carbon-α. Dengan ini satu formula reaksi bagi penghuraian telah dibentuk.

Pengunaan kandungan Fenton yang berlebihan tidak membantu dalam menurunkan tahap COD. Dengan penambahan Fenton secara stoichiometric, didapati bahawa kadar penghuraian cuma mencapai 60% penurunan COD walaupun

kandungan H_2O_2 yang telah berinteraksi sebagai hydroxyl radical adalah sebanyak 98%. Melalui proses pengoxidasian, salah satu hasil penghuraian daripada amine yalah glycine. Tahap penghuraiannya adalah lebih pelahan berbanding penghuraian kandungan yang tulin. Disebabkan kadar kandungan COD yang masih tertinggal dalam larutan Fenton yang telah dirawati, kami telah membuat kajian yang lebih terperinci tentang kadar penghuraian bahan organik serta produk oxidasinya. Experiment untuk mengetahui kadar penghuraian bahan organiknya dilakukan dalam sebuah reactor aerobic. Penjelasan bagi langkah pengunaannya dihuraikan dalam kajian Zahn-Wellens/EMPA yang menepati kritiria EPA, (US Environmental Protection Agency (EPA) method OPPTS 835.3200). Alkanolamines yang separa-terhurai (selepas 40% kandungan COD telah dikeluarkan melalui pengoxidaan melalui process Fenton) digunakan dalam mengkaji kadar penghuraian bahan organik. Pengoxidaan biological dilakukan secara separa keatas alkanolamine. Kandungan COD serta tahap kandungan Biomass diteliti untuk mengetahui langkah pemerosesannya. Tahap pH dalam larutan dikawal supaya berada dalam lingkungan 6.5 hingga 8. Buffer tidak ditambah bagi mengawal nilai pH untuk mengoptimalkan operasi didalam industry. 'Activated sludge' yang diambil daripada unit kumbahan universiti digunakan dalam bio reactor. Keputusan experiment menunjukkan bahawa masa bagi rawatan amine yang separa terhurai adalah separuh daripada masa yang diperlukan untuk merawati kandungan amine yang tulin. Masa yang diperlukan bagi penurunan COD secara maksimum adalah lebih singkat berbanding sempel yang sebelumnya. Perubahan kinatik biomass ini dapat dijelaskan melalui "Monod equation". Paramiter kinatik bagi kajian ini dikaji

Pengeluaran ammonia daripada reactor dapat dikesan. Ammonia probe digunakan bagi mengesan pembentukan ammonia semasa penghuraian secara biological dalam process. Didapati bahawa pembentukan ammonia per unit COD dalam sempel yang telah melalui penghuraian separa adalah lebih daripada amine yang tulin. Experiment menunjukkan bahawa banyak kandungan telah dioksidakan kepada amino-acid melalui pengoxidaan Fenton. Keputusan daripada kajian ini dapat member manafaat dalam membentuk langkah untuk marawati air kumbahan amineladen yang dikeluarkan daripada puast rawatan gas asli.

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION 1

1.1. Background of Research 1

1.1.1. Natural Gas Processing 2

1.1.2. CO_2 and H_2S Removal from Natural Gas 2

1.1.3. The Hybrid Process ─Advanced Oxidation followed by BiologicalTreatment─ 5

1.2. Problem Statement 6

1.3. Objectives 7

1.4. Scope of Work 7

CHAPTER 2: LITERATURE REVIEW 9

2.1. Industrial wastewater 9

2.1.1. Wastewater Characteristics 9

2.1.2. Wastewater Regulations 10

2.1.3. Wastewater Treatment Methods 11

2.2. Natural Gas Sweetening Process Waste 13

2.2.1. Source of Natural Gas Sweetening Process Waste 13

2.2.2. Characteristics of Natural Gas Sweetening Process Waste 15

2.3. Advanced Oxidation Processes 15

2.3.1. Fenton's Process 18

2.3.2. UV-based Processes 22

2.3.3. Ozone-based Processes 27

2.3.4. High Voltage Electrical Discharge Processes 29

2.3.5. Others AOPs....31

2.4. Degradation Intermediates....33

2.5. Biological Oxidation....33

2.5.1. Environmental Requirements....35

2.5.2. Bacterial Growth....36

2.5.3. Acclimatization....37

2.5.4. Biodegradation of Wastewater Containing Amines....38

CHAPTER 3: EXPERIMENTAL....39

3.1. Material....40

3.1.1. Chemical....40

3.1.2. Simulated Wastewater....41

3.1.3. Biomass Inoculums....41

3.1.4. Mineral Medium....41

3.1.5. Reagents Used....42

3.2. Experimental Set up....43

3.2.1. Fenton's Oxidation Processes....43

3.2.2. Biodegradability of Partially Degraded MEA and DEA....45

3.3. Analytical Method....47

3.3.1. COD (Chemical Oxigen Demand)....47

3.3.2. TOC (Total Organic Carbon)....48

3.3.3. Un-reacted Alkanolamine and Byproduct Identification using HPLC....49

3.3.4. Byproduct Functional Group Identification using FTIR....49

3.3.5. Un-reacted H_2O_2 determination....50

3.3.6. pH....50

3.3.7. DO (Dissolved Oxigent)....50

3.3.8. MLVSS (Mixed Liquor Volatile Suspended Solid) 51
3.3.9. MLSS (Mixed Liquor Suspended Solid) 52
3.3.10. Dissolved Ammonia (NH_3) 52

CHAPTER 4: RESULT AND DISCUSSION 53
4.1. Treatability Studies with Fenton's reagent 53
4.1.1. Effect of Initial Concentration 54
4.1.2. Effect of Hydrogen Peroxide Concentration 55
4.1.3. Effect of pH 57
4.1.4. Effect of $FeSO_4;7H_2O$ Dosing 60
4.1.5. Stoichiometric Amounts of H_2O_2 and $FeSO_4;7H_2O$ 61
4.1.6. Different Addition Mode of Fenton's Reagent 63
4.1.7. Degradation Rate of Amine by Fenton's Reagent 70
4.1.8. Comparison of COD and TOC 72
4.1.9. Degradation Intermediates after Fenton Oxidation 75
4.2 Biological Oxidation as Post-Treatment 78
4.2.1. Biological Oxidation 78
4.2.2. Kinetics of Biological Oxidation 83

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS 88
5.1. Conclusions 88
5.2. Recomendations 89
References 91
Publications 97
Appendices 98

LIST OF FIGURES

Figure 1.1: Structural formula of Monoethanolamine (MEA) and Diethanolamine (DEA)…… 3
Figure 1.2: Flow diagram amine treating process 4
Figure 1.3: The concept of coupling AOP-based pre-treatment with biological post-treatment.....6
Figure 2.1: Schematic of advanced oxidation processes classification.....16
Figure 2.2: Scheme of ozone decomposition in water 30
Figure 2.3: Reaction oxidation scheme of secondary amine by hydroxyl radical 34
Figure 2.4: Typical bacterial growth curves in term of numbers…….37
Figure 2.5: Complete biodegradation of alkanolamine..... 38
Figure 3.1: Flow diagram of experimental component.....39
Figure 3.2: Fenton's Process experimental set up.....44
Figure 3.3: Biodegradability test experimental set up.....47
Figure 4.1: Effect of initial concentration on MEA degradation 54
Figure 4.2: Effect of initial concentration on DEA degradation 55
Figure 4.3: Effect of Hydrogen peroxide concentration on MEA degradation.....57
Figure 4.4: Effect of Hydrogen peroxide concentration on DEA degradation 58
Figure 4.5: Effect of pH on MEA degradation….....59
Figure 4.6: Effect of pH on DEA degradation 59
Figure 4.7: Effect of $FeSO_4;7H_2O$ on MEA degradation 60
Figure 4.8: Effect of $FeSO_4;7H_2O$ on DEA degradation.....61
Figure 4.9: COD and H_2O_2 profile on equivalent concentration of DEA and Fenton's reagent with one time addition of Fenton's reagent.....62
Figure 4.10: Partially Degraded DEA with New Fenton Reagent (6050 mg/L COD)+ 26.5 ml H_2O_2 30 % + 1 gram $FeSO_4;7H_2O$ pH 3) 63
Figure 4.11: Degradation of Glycine compare to MEA.....64
Figure 4.12: COD and H_2O_2 profile on equivalent concentration of DEA and Fenton's reagent with continuous addition of $FeSO_4;7H_2O$ 65

Figure 4.13: COD and H_2O_2 profile when H_2O_2 and $FeSO_4;7H_2O$ continuous for 30 minute....66
Figure 4.14: COD and H_2O_2 profile when H_2O_2 one time addition in the beginning and $FeSO_4;7H_2O$ continuous for 30 minute....66
Figure 4.15: Effect of different addition mode of Fenton's reagent....67
Figure 4.16: Different addition model of Fenton's Reagent (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3) run 30 minute on COD profile....68
Figure 4.17: Continuous addition of H_2O_2 and $FeSO_4;7H_2O$(5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3)....69
Figure 4.18: Continuous addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm DEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3)....70
Figure 4.19: COD and TOC profile by Fenton's reagent on DEA degradation....71
Figure 4.20: Chromatogram....73
Figure 4.21: Infrared spectra of Glycine....73
Figure 4.22: Infrared spectra of partially degraded MEA....74
Figure 4.23: Infrared spectra of partially degraded DEA....74
Figure 4.24: Plot of Y vs X, Eq 4.15....77
Figure 4.25: Biodegradability profile....79
Figure 4.26: COD degradation and MLSS profile (MEA/Par. Deg. MEA)....80
Figure 4.27: COD degradation and MLSS profile (DEA/Par. Deg. DEA)....81
Figure 4.28: COD degradation and NH_3 profile(MEA/Par. Deg. MEA)....82
Figure 4.29: COD degradation and NH3 profile(DEA/Par. Deg. DEA)....82
Figure 4.30: Plots of $1/\mu$ vs. $1/S$ on MEA degradation....85
Figure 4.31: Plots of $1/\mu$ vs. $1/S$ on partially degraded MEA degradation....85
Figure 4.32: Plots of $1/\mu$ vs. $1/S$ on DEA degradation....86
Figure 4.33: Plots of $1/\mu$ vs. $1/S$ on partially degraded DEA degradation....86
Figure Plot of Calibration Curve (MEA vs. Area)....116
Figure Plot of One time addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3)....118
Figure Plot of One time addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm DEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3)....121
Figure Plot of Calibration Curve (DEA vs. Area)....123

Figure Infrared Spectra of “pure” DEA 125
Figure Infrared Spectra of “pure” MEA.....125

LIST OF TABLES

Table 2.1 Malaysian effluent standard regulation for sewage and industrial effluents, environmental quality act 1974 11
Table 2.2 Redox potential standards of some oxidant species 17
Table 2.3 Chemical species those are able to be oxidized by hydroxyl radical 18
Table 2.4 Radiation type and pertaining energy 23
Table 3.1 List of chemicals were used in the present work 40
Table 3.2 List of biodegradability test run condition 46
Table 4.1 Estimated biological kinetic coefficients for untreated alkanolamines and partially degraded alkanolamines 87
Table Raw data of figure 4.1 98
Table Raw data of figure 4.2 99
Table Raw data of figure 4.3 100
Table Raw data of figure 4.4 102
Table Raw data of figure 4.5 102
Table Raw data of figure 4.6 103
Table Raw data of figure 4.7 104
Table Raw data of figure 4.8 105
Table Raw data of figure 4.9 106
Table Raw data of figure 4.10 107
Table Raw data of figure 4.11 108
Table Raw data of figure 4.12 109
Table Raw data of figure 4.13 110
Table Raw data of figure 4.14 111
Table Raw data of figure 4.15 112
Table Raw data of figure 4.16 113
Table Raw data of figure 4.17 114
Table Raw data of MEA Calibration Curve 115
Raw data One time addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3) 117

Table Raw data of figure 4.18 119
Raw data One time addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm DEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3) 120
Table Raw data of DEA Calibration Curve 122
Table Raw data of figure 4.19 124
Table Raw data of figure 4.25 126
Table Raw data of figure 4.26 128
Table Raw data of figure 4.27 129
Table Raw data of figure 4.28 130
Table Raw data of figure 4.29 131
Table Raw data of figure 4.30 132
Table Raw data of figure 4.31 132
Table Raw data of figure 4.32 133
Table Raw data of figure 4.33 133

LIST OF SYMBOLS

eV	Electron Volt
Hz	Hertz (frecuency)
nm	Nano meter
t	Time
kJ	Kilo Joule
CODt	COD value of test compound at sampling time
CODbt	COD value of blank at sampling time
COD3h±30	COD value of test compound at 3hours±30 minute sampling
CODb3h±30	COD value of blank at 3hours±30 minute sampling
$COD_{removal\ 30}$	Percentage of COD removal at 30 minute
COD_0	COD value at 0 minute
COD_{30}	COD value at 30 minute
k	Rate constant
k_{max}	maximum substrate utilisation rate
K_S	Half saturation coefficient
M	Molar
μ	Specific growth rate
μ_{max}	Maximum specific growth rate
NTU	Turbidity
r	Degradation rate
s	second
S	Substrate concentation
$TOC_{removal\ 30}$	Percentage of TOC removal at 30 minute
TOC_0	TOC value at 0 minute
TOC_{30}	TOC value at 30 minute
$Y_{X/S}$	Biomass yield

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Alkanolamines in aqueous solution are extensively used for scrubbing certain acidic gases. The most utilized alkanolamines for scrubbing acidic gases are monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA) and di-isopropanolamine (DIPA). The amines are regenerated in stripping tower for recycling back to the absorber. During shutdown and maintenance of these facilities, high concentrations of residual alkanolamine may be carried over into the wastewater, whereupon they can disturb the biological treatment system of the plant. Advanced oxidation processes (AOP's) have proved to be extremely effective in the degradation of high concentrations of organics which may be difficult to treat in a conventional biological oxidation unit. The more common AOP's use either H_2O_2 or O_3 as the source materials for the generation of strongly oxidizing radicals such as hydroxyl (HO•) and hydroperoxyl (HO_2•) in solution. Ultraviolet radiation or ferrous sulfate, separately or in combination, are used to initiate the process of generation of the oxidizing radicals. Fenton's reagent, a mixture of hydrogen peroxide and ferrous sulfate in aqueous solution, has proved to be more effective than UV-H_2O_2 or UV-O_3 for most of the recalcitrant organics (Walling, C. 1975).

Fenton's treatment of two model alkanolamines ─namely, MEA and DEA ─ is reported in this thesis. Only partial degradation of the amines could be achieved with a reasonable quantity of reagents. Biological post treatment following Fenton's oxidation was conducted for testing the practical application of the hybrid strategy.

1.1.1 Natural Gas Processing

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

Raw natural gas typically consists primarily of methane (CH_4), the shortest and lightest hydrocarbon molecule. It also contains varying amounts of ethane (C_2H_6), propane (C_3H_8), normal butane (n-C_4H_{10}), isobutane (i-C_4H_{10}), pentanes and even higher molecular weight hydrocarbons. Other impurities such as acidic gases ─carbon dioxide (CO_2), hydrogen sulfide (H_2S) and mercaptans such as methanethiol (CH_3SH) and ethanethiol (C_2H_5SH)─ and water vapor and also some nitrogen(N_2) and helium(He) are present (Kohl and Nielsen, 1997) in natural gas.

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

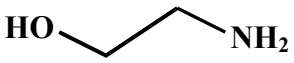
1.1.2 H_2S andCO_2 Removal from Natural Gas

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

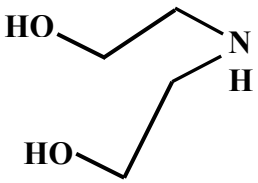
1. Absorption into a liquid
2. Adsorption on a solid
3. Permeation through a membrane
4. Chemical conversion to another compound
5. Condensation

Absorption is undoubtedly the single most important operation of gas purification processes. Aqueous alkanolamine is the most generally accepted and widely used solvent for capturing H_2S and CO_2 from natural gas (Kohl and Nielsen, 1997). The amines that have proved to be of principal commercial interest for gas purification are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and di-isopropanolamine (DIPA).

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



Monoethanolamine (MEA)



Diethanolamine (DEA)

Figure 1.1 Structural formula of Monoethanolamine (MEA) and Diethanolamine (DEA).

The principal reactions of acidic gas purification represented as (Kohl and Nielsen, 1997):

Ionization of water:

$$H_2O \leftrightarrow H^+ + OH^- \quad (1.1)$$

Ionization of dissolved H_2S:

$$H_2S \leftrightarrow H^+ + HS^- \quad (1.2)$$

Hydrolysis and ionization of dissolved CO_2:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad (1.3)$$

Protonation of alkanaolamine:

$$RNH_2 + H^+ \leftrightarrow RNH_3^+ \quad (1.4)$$

Carbamate formation:

$$2RNH_2 + CO_2 \leftrightarrow R_1NHCOO^- {}^+H_3NR_2 \quad (1.5)$$

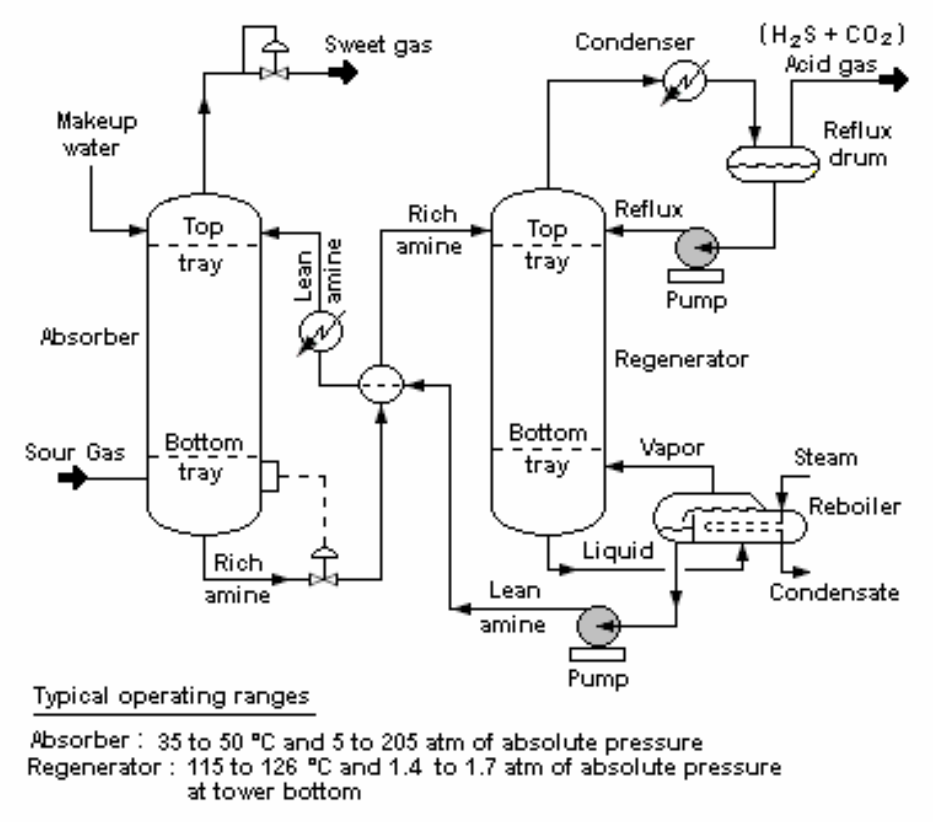


Figure 1.2 Flow diagram of a typical amine treating process (Wikipedia, the free encyclopedia**)**

The basic flow arrangement of the alkanolamine acid gas absorption process is shown in Figure 1.2. Amine gas treating process includes an absorber unit and a regenerator unit as well as accessory equipment. In the absorber, the down flowing amine solution absorbs H_2S and CO_2 from the up-flowing sour gas to produce a sweetened gas stream (i.e., an H_2S-free gas) as a product and an amine solution rich in the absorbed acid gases. The resultant "rich" amine solution is then routed into the regenerator (a stripper with a reboiler) to produce regenerated or "lean" amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H_2S and CO_2. This H_2S-rich stripped gas stream is then usually routed into a Claus process to convert it into elemental sulfur (Kohl and Nielsen, 1997). The CO_2 generated during desorption may be put to a number of uses including enhanced oil recovery (EOR).

1.1.3 The Hybrid Process ─Advanced Oxidation followed by Biological Treatment─

Periodic cleaning of absorption and stripping towers in a natural gas processing plant will generate wastewater with a large portion of alkanolamine. High concentration of alkanolamine thus generated has low biodegradability or is often toxic to the bacteria and can not be treated in the conventional biological oxidation. An alternative technique is to partially degrade the amine by an advanced oxidation process (AOP's) such Fenton's reagent's (Fe^{2+} + H_2O_2) to generate smaller fragments of degradation products which are amenable to biological oxidation.

Coupling of chemical oxidation (AOP or wet air oxidation, WAO) as pre-treatment before biological oxidation as post-treatment is conceptually beneficial as it can lead to increased overall treatment efficiency (Mantzavinos, 2007; Jones, 1999; Koprivanac and Kusic, 2007). The concept is illustrated in Figure 1.3.

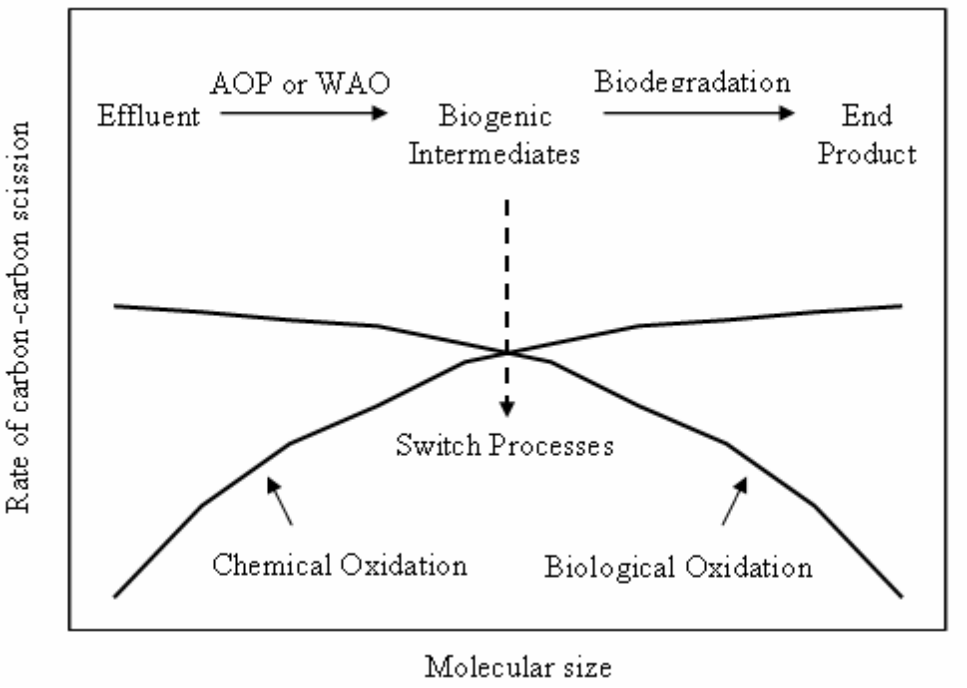


Figure 1.3 The concept of coupling AOP-based pre-treatment with biological post-treatment (Mantzavinos, 2007).

1.2 Problem Statement

In the above context, this work has been undertaken to experimentally investigate the degradability of alkanolamines using Fenton's reagent for advanced oxidation. Monoethanolamine (MEA) and diethanolamine (DEA) are selected as the model compounds for the study. Effects of different process parameters such as the initial concentration of the amine, the dosage of Fenton's reagent, pH and the mode of addition of the reagent (one time or continuous) are to be studied. In order to explore the advantage of the hybrid strategy of combined AOP and biological oxidation, the biodegradability of the partially degraded amines as well as 'pure' amines will be investigated following standard procedure and using locally available activated sludge.

1.3 Objectives

In the above context, the objectives of the present work are as follows:

1. Fenton's oxidation of two model alkanolamines (MEA and DEA),
2. To investigate the effect of various process parameters on the rate and extent of degradation of the amines,
3. To identify the optimum process condition within the range of parameters studied,
4. To identify the degradation intermediates and reaction pathway,
5. To develop a simplified rate equation and to estimate the kinetic constants,
6. To compare the rate and extent of degradation for different modes of addition of the reagents (H_2O_2 and $FeSO_4;7H_2O$) to the reaction medium,
7. To study the biodegradability of the partially degraded amines and compare with that of the 'pure' amines,
8. To fit the data on biological oxidation with a kinetic equation.

1.4 Scope of Work

The waste water generated during cleaning and maintenance of the absorption and stripping towers heat exchangers, and reboilers in a natural gas processing plant contains a substantially high concentration of amine to the tune of 20,000 ppm or more. In this prospective we have used in the degradation experiments synthetic wastewater containing similar high concentrations of the amine down to several hundred ppm. This is one the major parameter studied in this work. The variation of pH was confined to the acidic range only since rapid decomposition of hydrogen peroxide to water and oxygen occurs at a high pH particularly in the presence of

suspended iron oxide particles that act as decomposition catalyst. On the lower side, pH up to 2 was used although, as it will be detailed later, vigorous reaction with foaming and gas liberation occurs at such a low pH. The ratio of H_2O_2 and Fe^{2+} was varied over a wide ranges. Studies were confined to nearly ambient temperature since a higher temperature promotes H_2O_2 decomposition and reduce the utilization of the oxidizing capacity of the reagent. The mode of the addition of the reagents was well within the scope of this study because of its significantly better performance.

So far as the biological post-treatment is concerned, we used a diluted solution of the degraded amines. The COD was around 1000mg/L. This was done in consideration of the fact that in the event of pumping in the real partially degraded wastewater to the conventional biological treatment unit in a plant, its concentration would be greatly lowered after mixing with all other effluents from different units of the plant. The activated sludge locally available in the wastewater treatment facility of the university, in consideration of avoiding exotic strains, was used.

CHAPTER 2

LITERATURE REVIEW

2.1 Industrial wastewater

Metcalf and Eddy (1991) defined wastewater as a combination of liquid and water which carry the wastes that are removed from residence, institution and industry, together with such ground water, surface water, and storm water. When untreated wastewater is allowed to accumulate, the decomposition of organic material lead to the production of malodorous gases. Wastewater also contains numerous pathogenic or disease-causing microorganisms. The nutrient rich wastewater that enters the aqueous ecosystem leads to eutropication, which still causes oxygen depletion. It is also toxic to the aquatic life and responsible for methemoglobinemia when it is contaminated to the drinking water.

2.1.1 Wastewater characteristics

Industrial wastewater is characterized in term of physical, chemical and biological constituents. The important physical properties are color, odor and dissolved substances. While the chemical constituents may include organic compounds such as carbohydrates, phenol, pesticides, etc, gases such as hydrogen sulfide, methane, and oxygen; and inorganic such alkalinity, heavy metals, nitrogenous substances, pH, etc, the biological constituents may contain various species, protista, virus, etc (Metcalf and Eddy, 1991).

Organic chemicals are important constituents in municipal as well as industrial wastewater. This characteristic has become one of the important concerns in determining the quality of wastewater. Moreover, the organic chemicals usually are not specific and consist of mixture of many different carbonaceous materials. As a consequence, test for organic content of such wastewater is not specific. The most commonly test used biochemical oxygen demand (BOD) and chemical oxygen demand (COD). However, much attention is also focused on nutrients especially nitrogen and phosphorous that are contained in the wastewater (Eckenfelder and Musterman, 1995).

2.1.2 Wastewater Regulation

Wastewater treatment is primary developed in response to the concern for public health and adverse condition caused by the discharge of wastewater to the environment (Metcalf and Eddy, 1991). The purpose of the treatment process is to remove suspended and floatable material, treatment of biodegradable organics and other contaminants, as well as elimination of pathogenic organism.

In order to maintain an acceptable quality of wastewater in terms of its characteristics, different countries have enacted their respective regulation specifying the maximum admissible values of the parameters. The Malaysian standard for industrial effluent is presented in Table 2.1. Some more strict standards have been developed recently to deal with the removal of nutrients and priority pollutants. When the wastewater is to be reused, standards normally include requirements for removal of refractory organic, heavy metals, and in some cases dissolved solids (Metcalf and Eddy, 1991). Consequently to achieve the effluent standard regulation, industries have to treat the wastewater appropriately before disposal. Alternatively, industries are able to arrange a contract with third party for treatment the wastewater.

Table 2.1 Malaysian effluent standard regulation for sewage and industrial effluents, environmental quality act 1974 [Laws of Malaysia; (act 127). 1999]

Parameters	Unit	Standard (A)	Standard (B)
Temperature	˚C	40	40
pH value	-	6.0 – 9.0	5.5– 9.0
BOD5 at 20˚C	mg/L	20	50
COD	mg/L	50	100
Suspended Solids	mg/L	50	100
Phenol	mg/L	0.001	1.0
Free chlorine	mg/L	1.0	2.0
Sulphide	mg/L	0.50	0.05
Oil and grease	mg/L	Non detectable	10.0

2.1.3 Wastewater treatment Methods

Essentially, contaminants in the waste water are removed by three major methods –physical, chemical and biological–. The removal methods are usually classified as physical unit operations, chemical unit operations, and biological unit operations (Metcalf and Eddy, 1991). However, wastewater treatment in a centralized wastewater plant (WWTP), rarely uses any individual treatment method in isolation. The WWTP consists of several treatment techniques in combination:

a. Physical Unit Operations: The physical unit operations include screening, mixing, flocculation, sedimentation, flotation, filtration, and gas transfer. These methods are generally first to be utilized in the wastewater treatment. Physical treatment is predominantly used to remove the suspended materials (Metcalf and Eddy, 1991).
b. Chemical Unit Processes: Removal of contaminants from wastewater by addition of chemicals or by other chemical reactions is known as chemical

unit processes. Precipitation, adsorption, and disinfections are the common examples used in the wastewater treatment. The chemicals that are added to the wastewater directly react with the pollutants to form more stable chemical or act as flocculants or coagulant that change the configuration of pollutant. In other instances the chemical reagents break down or decompose the pollutant compounds to harmless end products.

c. Biological Unit Processes: These constitute removal processes of contaminants from wastewater by biological activity. Biological unit processes is used primarily to remove the biodegradable organic substances (colloidal or dissolved) in wastewater.

In industrial applications, treatment units involve several steps depending on the characteristic of wastewater and specific treated wastewater objectives. Since each method is effective in a particular situation, the process of selection is very important to obtain the best performance and to reduce operational cost as well as investment cost.

As mentioned above, unit operations and processes are grouped together to provide various levels of treatment. Historically, the term “preliminary” and/or “primary” referred to physical unit operation; “secondary” referred to chemical and biological unit processes; and “advanced” or “tertiary“ referred to combination of all three unit processes. However, a more rational approach is first to establish the level of contaminant removal (treatment) required before the wastewater can be made fit for reuse or discharge to the environment. The required unit operations and processes necessary to achieve that required level of treatment can then grouped on the basic fundamental consideration (Metcalf and Eddy, 1991).

2.2 Natural Gas Sweetening Process Waste

Natural gas production has increased to meet the rising demand. Meanwhile, raw natural gas consists of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) that is known to be pollutants in significant level. These gases must be removed before piping or shipping because it causes corrosion, reduces the heating value and thus decreases the sales value of the gas (Arnold and Stewart, 1989; Kohl, and Nielsen, 1997). Natural gas sweetening processes based on amine absorption have become common in practical application (Arnold and Stewart, 1989). This amines solution combined with anti-corrosive agents are used to absorb acid gases. During shutdown process, the amine waste is generated. Such amine wastes require appropriate treatment before disposal.

2.2.1 Source of Natural Gas Sweetening Process Wastewater

During gas sweetening process, non reclaimable contaminants tend to accumulate in the system and cause the reduction of efficiency and operational problems (Arnold and Stewart, 1989; Kohl, and Nielsen, 1997). The problem may be partially overcome by a number of strategies: (a) purging a part of the solution and replacing it with fresh absorbent; (b) replace the entire volume of contaminated solution; (c) inject caustic solution to free amine bond up as heat stable salts and more CO_2 induced degradation product; and (d) reclaim the entire solution.

Wastewater from the sweetening process units is exposed to the environment during process operation and turn-around. Periodically turn-around process is performed to maintain satisfactory process performance. This step produces large quantity of amine waste. The general sources of amine wastewater during process operation are (Arnold and Stewart, 1989):

a. The reclaimer: The normal generation temperature in the stripping tower will not regenerate heat-stable salt or compounds such as azodazole-2. Therefore, a reclaimer is usually included to remove these contaminants. A side stream of from amine circulation is drawn from the bottom of the stripping column. This stream is than heated to boil the water and amine overhead while the heat-stable salts and azodazole-2 are retained in the reclaimer. This reclaimer is periodically shut down and collected contaminants are cleaned and removed from the system. The amine bound to contaminant is introduced to the wastewater stream.
b. Foaming problem in absorption tower: Amine systems foam rather easily, resulting in excessive amine carried over from the absorber. Foaming can be caused by a number of foreign materials such as condensed hydrocarbon, degradation product, valve grease, etc.
c. Degraded amine: Since the sweetening process is operated in a close loop system, the used amines will be degraded during the process. The degradation products are removed through reclaimer. Degraded amine is remediated by injection of fresh amine to stripping column.
d. Production of heat stable salt and other solids: Some solid contaminants may present in the system. These solid contaminants can be produced from heat stable salt or solid. The cake that remains in the filter has to be backwashed to maintain the operation pressure of the filter. The used water for backwash of the filter becomes wastewater. The amine bonded to the cake will also go to wastewater.
e. Contamination of hydrocarbon: The liquid hydrocarbon comes from the bottom of absorption tower and inlet separator. At low pressure some hydrocarbons condense and form liquid. This hydrocarbon mixed with the water in absorption tower gets introduced to the wastewater stream.
f. Several others source of amine wastewater are from: water used to washed the vessel and others plant equipments i.e. heat exchanger, pumps, and etc; valve leakage and operational upset.

On the whole, the wastewater from sweetening process units may be combination of raw amine-solution, amine degradation product, thermally stable salts, heavy hydrocarbon and particulates.

2.2.2 Characteristics of Natural Gas Sweetening Process waste

Natural gas sweetening process generates high COD value waste due to the high concentration amine that is used. The concentration may be as high as 15 – 30 % by weight in the practice (Kohl, and Nielsen, 1997). Consequently, the wastewaters from that process become the main concern according to the critical impact. It is known that amine is detrimental to good operation of a biological treatment plant (Stephenson and Blackburn, 1998; Russel, 2006).

Because of the high COD of the wastewater from the sweetening plant, preliminary treatment is preferable. It is worth to explain that the pretreatment would maintain the feed properties of influent in the wastewater treatment plant.

2.3 Advanced Oxidation Processes

Advanced Oxidation Processes (AOP's) are novel chemical processes in the wastewater treatment methods. Those are methods based on generating of very reactive species, such as hydroxyl radical, capable of degrading a wide range of organic contaminants in the waste water. The processes include UV irradiation [either direct irradiation of contaminant or photolytic oxidation mediated by hydrogen peroxide (UV/H_2O_2) and/or ozone (UV/O_3)], heterogeneous photo catalysis using semi conductor catalysts (UV/TiO_2), electron beam irradiation, X-ray, γ-ray radiolysis, non-thermal electrical discharge, supercritical water and ultrasonic irradiation (Jones, 1999).

The most common AOP's are Fenton's treatment, UV/H_2O_2, O_3/H_2O_2 and combinations thereof. Hydroxyl radicals are produced from hydrogen peroxide via different pathways and to different efficiencies depending on the nature of the catalyst (AOP system) involved. Figure 2.1 demonstrates hydroxyl radical production from the advanced oxidation processes.

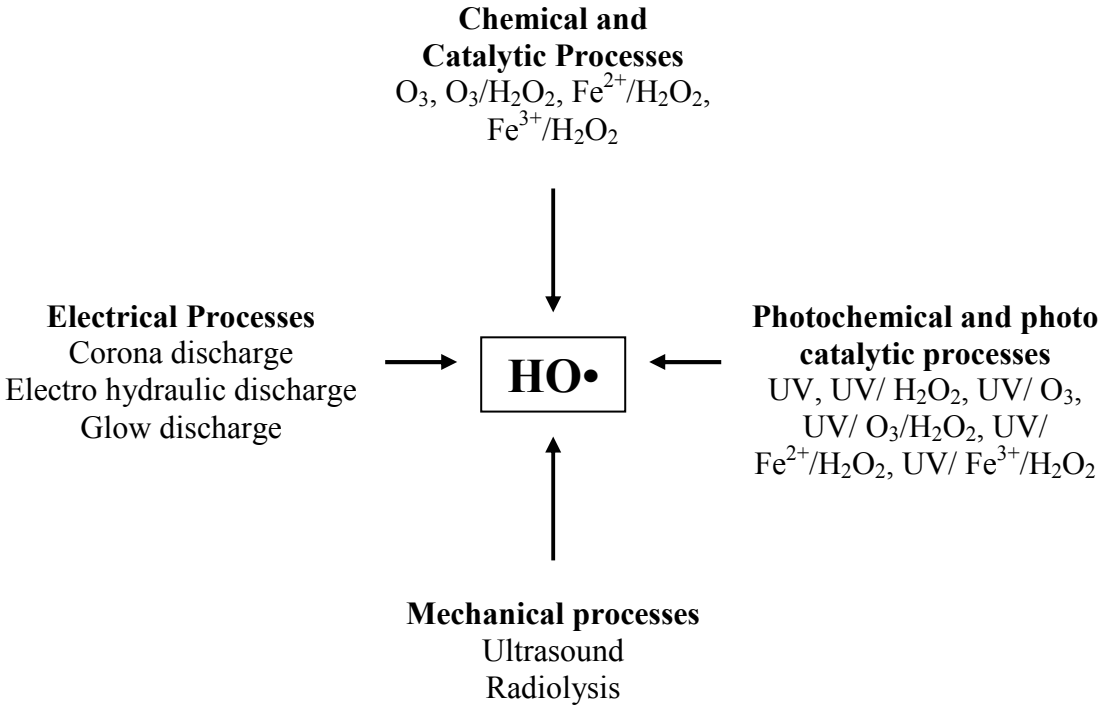


Figure 2.1 Schematic of advanced oxidation processes classification (Koprivanac and Kusic, 2007)

AOP's can be classified by chemical and catalytic, photochemical and photo catalytic, mechanical and electrical processes (Figure 2.1). Chemical processes involve the application of ozone/or hydrogen peroxide, while a subcategory of this type of AOP's can be named catalytic processes that involve usage of some powerful catalyst (e.g. iron or cupper ion) in combination with hydrogen peroxide to produce hydroxyl radical, so called Fenton type processes. Photochemical and photo catalytic processes involve application of UV or solar irradiation in combination with some powerful oxidants (ozone and/or hydrogen peroxide) or photo catalyst (e.g. TiO_2, ZnO, etc). Hydroxyl radicals can also be produced under the influence of mechanical

(e.g. ultrasound process, radiolysis) or electrical (e.g. electro hydraulic discharge and non thermal plasma processes) energy (Koprivanac and Kusic, 2007).

A list of some oxidant species is given in Table 2.2. Hydroxyl radical is placed in the second place after fluorine. AOP's are promising for the treatment of hazardous toxic organic pollutants in aqueous solution. Chemical species those can be oxidized by hydroxyl radical listed in Table 2.3. However some simple organic compounds can not be readily oxidized using hydroxyl radical, such as acetic, maleic and oxalic acid, as well as acetone, chloroform and tetrachloroethane (Koprivanac and Kusic, 2007). However, they degrade slowly. The process may be enhanced considerably by selecting conducive process condition.

Table 2.2 Redox potential standards of some oxidant species (Koprivanac and Kusic, 2007).

Oxidant	**Redox Potential, E°, V**
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Permanganate ion	1.67
Chlorine	1.36
Chlorine dioxide	1.27

Table 2.3 Chemical species oxidizable by hydroxyl radicals (Koprivanac and Kusic, 2007).

Group	Details
Acids:	formic, gluconic, lactic, malic, propionic, tartaric.
Alcohols:	benzyl, *tert*-butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes:	acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutyraldehyde, tricholraldehyde
Aromates:	benzene, chlorobenzene, chlorophenol, PCBs, phenol, catecol, benzoquinone, hydroquinone, *p*-nitrophenol, toluene, xylene, trinitrotoluene
Amines:	aniline, cyclic amines, diethylamine, dimethylformine, EDTA, propanediamine, *n*-propylamine
Dyes:	azo, anthraquinone, triphenylmethane
Ethers:	tetrahydrofuran
Ketones:	dihydroxyacetone, methylethylketone

2.3.1 Fenton's Process

Technology of Fenton's treatment dates back over a hundred years to 1894 when M.J.H. Fenton reported that ferrous ion promoted the oxidation of tartaric acid with aqueous hydrogen peroxide. Ferrous–catalyzed oxidation by hydrogen peroxide at acidic pH has since come to be known as Fenton's reagent (Jones, 1999). However 40 years later, Haber and Weiss proposed that the hydroxyl radical is the oxidant specie in the Fenton's system. There are six steps of Fenton's reagent oxidation that Walling (1974) modeled. The equations are shown below [Eq (2.1) – (2.6)].

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet$ $k = 76.5\ M^{-1}s^{-1}$ (2.1)

$HO\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^-$ $k = 3 \times 10^8\ M^{-1}s^{-1}$ (2.2)

$HO\bullet + RH \rightarrow H_2O + R\bullet$ $k = 10^7 - 10^{10}\ M^{-1}s^{-1}$ (2.3)

$R\bullet + Fe^{3+} \rightarrow Fe^{2+} + \text{product}$ (2.4)

$2R\bullet \rightarrow \text{product (dimmer)}$ (2.5)

$R\bullet + Fe^{2+} + H^+ \rightarrow Fe^{3+} + RH$ (2.6)

The overall oxidation reaction rate is normally controlled by the rate of generation of HO• radicals which in turn depends upon the concentrations of H_2O_2 and $FeSO_4$ and the competing reaction that may lead to loss of the oxidation power in the system as suggested by Laat and Gallard (1999).

$HO\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$ $k = 3.3 \times 10^7\ M^{-1}s^{-1}$ (2.7)

$HO_2\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+}$ $k = 1.2 \times 10^6\ M^{-1}s^{-1}$ (2.8)

$HO_2\bullet + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+$ $k < 2 \times 10^3\ M^{-1}s^{-1}$ (2.9)

The use of Fenton's treatment of wastewater is relatively new, but it is attractive due to the fact that iron is a highly abundant and non-toxic element (Buzzi, 1992), and hydrogen peroxide is easy to handle and breaks to environmentally benign products. Moreover, the Fenton treatment is able to convert a broad range of pollutants to harmless or biodegradable product (Koprivanac and Kusic, 2007).

Many researchers have reported the effectiveness of Fenton's reagent for the degradation of organic contaminants in the wastewater. These include aromatic hydrocarbons and other compounds such as amines, phenol and substituted phenols, polycyclic aromatics, chlorinated hydrocarbons and more complex molecules like dyes, pharmaceuticals, amines, alcohols, mineral oils, etc. Lou and Lee (1995) used Fenton's reagent to destroy benzene, toluene and xylene (BTX). Almost complete removal was claimed to have been achieved within a short time of ten minutes. A very fast degradation rate was also reported by Ray et al. (2003) for the removal of MTBE-contaminated water from 1,300 g/L to regulatory level of 20 g/L using Fenton's reagent with 10 minute reaction. Degradation of aromatic amines (aniline

and a few substituted anilines) was studied by Casero et al (1996). They identified the intermediates by mass spectrometry. Complete mineralization was achieved within one to three hours. Mineralization of aniline was also studied by Brillas et al (1997) by using a few advanced oxidation techniques – such as anodic oxidation, photo-catalysis, electro-Fenton and photo-Fenton techniques. UV irradiation was found to accelerate each of the processes. De et al. (2006) studied degradation of phenol and chlorinated phenols. Quite a few studies were reported on degradation of residual dyes or dyeing wastewater using the Fenton's reagent. Up to 95% of COD removal from carpet dyeing wastewater was reported by Gulkaya et al (2006) by suitably adjusting the ratio of H_2O_2/Fe^{2+} concentration. A comparison of UV-H_2O_2 and Fenton's reagent was reported by Alshamsi et al. (2006) who studied efficiencies of degradation of Crystal Violet and also by Alnuaimi et al (2007) who studied about decolorations of Neutral Red. Fenton's reagent proved to be more effective than the photo-chemical route but pH in the Alshamsi study was found to have little effect in the range of parameters studied. Oturan et al. (2000) used the Fenton's reagent to degrade pentachlorophenol which is often found to be present in effluents from pesticide industries. These authors used a novel technique of electrochemically generating hydroxyl radicals in situ thereby reducing the consumption of H_2O_2. The technique is called electro-Fenton process. Qiang et al. (2003) studied optimizing the process conditions for minimization of iron sludge in Fenton oxidation processes by electro-regenerating Fe^{2+} with constant potential or constant current mode. They reported that regeneration would be effective under pH 2.5. Xu et al (2007) reported that solar photo-Fenton has a potential to effectively remove TOC from the paper and pulp industry effluent on large scale. Nesheiwat (2000) discussed application of the Fenton's technique for destruction of contaminated soil washings that contained a spectrum of refractory organics. Alaton and Teksoy (2005) studied the effectiveness of Fenton's reagent to pre-treat acid dye-bath effluents of a textile industry before conventional biological treatment. Gotvajn and Zagorc-Konca (2005) combined Fenton's reagent and biological oxidation for heavily polluted fermentation broth waste. Solozhenko et al. (1995) could successfully degrade the contaminants in wastewater from dyeing and finishing industries. Biodegradation of a pharmaceutical wastewater was greatly improved by Fenton's treatment as reported by Tekin et al.

(2006) since of breakdown of the organics into smaller fragments makes it amenable to normal biological oxidation.

Besides the conventional Fenton process (Fe^{2+}/H_2O_2), that involves the application of ferrous salt (mostly ferrous sulphates) as a source of iron catalyst for Fenton reaction, there is a number studies that investigated the application of so-called Fenton "like" processes for degradation of organics pollutant in the wastewater. There are three types of Fenton "like" processes. The first group process considers the use of ferric salts instead of ferrous salt as catalyst for the incitation of Fenton reaction (Ali et al, 1996). Next group of process considers the use of heterogeneous Fenton type catalyst such iron powder, iron-oxides, iron-ligands, or iron ions doped in zeolites, pillared clays or resin, instead of homogeneous ferrous ions obtained from the dissolution of added ferrous salts. Last group of processes use other metal ions such as copper, manganese or cobalt, as a replacement for ferrous ions in Fenton reaction (Koprivanac and Kusic, 2007).

Even though the Fenton system offers a cost effective source of hydroxyl radical, their efficiency is limited by a couple of disadvantages: a) the need for the removal of remaining iron ions and oxides after treatment and b) a limited yield in the reaction process due to the formation of stable Fe^{3+}-complexes. These limitations can be overcome by the usage of heterogeneous Fenton-type catalyst which can lower the final concentration of iron in the bulk after the treatment and also by the assistance of UV irradiation the formed Fe^{3+}-complexes, thus allowing the Fe^{3+} ions to participate in the Fenton catalytic cycle (Koprivanac and Kusic, 2007).

The presence of UV in the Fenton-type processes could give some benefit. First benefit is additional of hydroxyl radical source beside the primary source throughout Fenton mechanism. Consequently, hydroxyl radical could be generated in photo-Fenton processes from the photolysis of hydrogen peroxide (Equation 2.10) and from the reduction of ferric ions to ferrous ions (Equation 2.11). In addition, UV light could provide the avoidance of breaking the Fenton catalytic cycle due to the

formation of stable Fe^{3+}-complexes between free Fe^{3+} ions and some aliphatic acid formed as byproducts of degradation (Equation 2.12).

$$H_2O_2 + h\nu \rightarrow 2\ HO\bullet \quad (2.10)$$

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + HO\bullet \quad (2.11)$$

$$Fe^{3+}(L^-) + h\nu \rightarrow Fe^{2+} + L\bullet \quad (2.12)$$

Second benefit of the presence UV light in the photo-Fenton Processes is to achieve the complete mineralization due to the degradation of some hydroxyl radical persistent byproduct, such oxalic acid and acetic acid, by UV light.

2.3.2 UV-based Processes

The "UV-based Processes" are considered as all processes that apply UV light either for degradation of organic pollutant or for the initiation of oxidation mechanisms by the irradiation of some powerful oxidants or photo-catalyst. UV-based processes could be classified into UV photolysis, photochemical processes and photocatalytic.

A. UV Photolysis

Investigations regarding UV light were begun since Isaac Newton observed the diffraction of white beam when passing through a prism. At the beginning of 19^{th} century, the radiant energy beyond two ends of spectra of visible light was discovered. One of those is identified as infrared and another as ultraviolet region. Furthermore, it was shown that invisible chemically active irradiation beyond violet end of spectrum were the subject of laws of interference. Further investigation

indicated the fact that irradiation with visible (VIS), infrared (IR) or ultraviolet (UV) light has characteristic of the same electromagnetic irradiation, but they differ in respect of its frequency, and what was discovered latter, pertaining to energy.

Table 2.4 Radiation type and pertaining energy; 1 Einstein = 1 mol of photons.

Radiation	Wavelength (nm)	Energy range (kJ Einstein-1)
IC	>780	<155
VIS	780 – 400	155 – 300
UV-A	400 – 315	300 – 377
UV-B	315 – 280	377 – 425
UV-C	280 – 100	425 – 1198

.

The primary usage of UV radiation in the earlier period was for disinfection, but with the development of reaction mechanism, UV radiation nowadays establishes the usage for oxidation purpose as well. UV-C is mostly used for oxidation processes. While the most common UV-C wavelength is 254 nm that could be achieved by low-pressure vapor mercury lamp invented by Hewith at 1901.

At room temperature, most molecules reside in their lowest-energy electronic state, i.e. “ground state”. When molecules are exposed to UV radiation, they get transferred to a state with higher energy, i.e. “exited state”. The molecules in the “exited state” have very short lifetime (10^{-9} – 10^{-8} s), after which it returns to “ground state” by one or several mechanism (fluorescence phosphorescence) or decompose to yield a different molecule. The mechanism of direct photolysis is expressed below:

$$M + h\upsilon \rightarrow M^* \quad (2.13)$$

$$M^* \rightarrow M \quad (2.14)$$

$$M^* \rightarrow \text{Product} \quad (2.15)$$

UV radiation is generally used in combination with some powerful oxidant or photocatalyst. The efficiency of its separate use depends on limitations such as:

a. Water solution should be treated in a way to achieve the highest possible UV transmission, i.e. turbidity should be as low as possible.
b. Very high concentration of hydroxyl radical could inhibit mineralization reaction of organic contaminant present in water.
c. Water solution should be free of heavy metals and oil.
d. Costs of UV radiation are higher than Fenton dark process.

B. Photochemical Processes

Photochemical processes use combination of UV light and some powerful oxidant such hydrogen peroxide (H_2O_2) and /or Ozone (O_3). Application of UV/ H_2O_2 has been investigated for water purification. This purification involves hydroxyl radical generation through direct photolysis of H_2O_2. It is well known that hydroxyl radical is a very reactive species that could degrade the organic contaminant. Success of this application depends on the initial concentration of organic contaminant in water and presence of "scavenger" such organic or inorganic compound which could inhibit or even stop the treatment process. UV/H_2O_2 process is in use:

a. Removal of micro- and macro- pollutants from drinking water.
b. Treatment of low concentration organic toxic compounds present in ground water.
c. Treatment of smaller volume of highly recalcitrant pollutants in order to achieve their detoxification and faster degradation.
d. To control of exhaust gases in the case of volatile organic compound.

Quantity of energy required for direct photolysis of hydrogen peroxide is very high, and theoretically two hydroxyl radicals could be generated per absorbed energy quantum. In practice, the highest quantum yield for generation of hydroxyl radical is 0.5 mol of H_2O_2 per Einstein. Generation of hydroxyl radical by UV radiation can be expressed as follows:

$$H_2O_2 + h\upsilon \rightarrow 2\ HO\bullet \qquad (2.16)$$

While the scavenger mechanism of H_2O_2 and hydroxyl radical which influences the overall process efficiency can be expressed as shown below:

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \qquad (2.17)$$

$$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \qquad (2.18)$$

$$HO\bullet + HO_2^- \rightarrow HO_2\bullet + HO^- \qquad (2.19)$$

$$HO_2\bullet + HO\bullet \rightarrow H_2O + O_2 \qquad (2.20)$$

Important parameters of the UV/H_2O_2 process are UV lamp characteristic, reactor configuration, pH of solution and initial concentration of H_2O_2. While some limitation on UV/ H_2O_2 process which should be taken is the presence of iron and potassium salts in treated water resulting with reduction of UV radiation. This salt could be avoided by adjusting pH solution to the value where those salts can precipitate. Furthermore another limitation is related to the large quantities of suspended particle resulting with increased turbidity. This problem could be solved by filtration as pretreatment of such wastewater.

Like hydrogen peroxide, ozone is also widely used as an oxidant in the photochemical process. In addition, ozone is even better oxidant than hydrogen peroxide due to the significantly higher value of molar absorption coefficient at 254 nm, typically the wave length for UV-C radiation. Moreover, the rate of ozone photolysis is almost 1000 time higher than hydrogen peroxide.

The UV/O_3 process is based on the fact that by the decomposition of ozone under UV radiation two hydroxyl radicals are generated which rather form hydrogen peroxide than react with organic matter present in the water, shown by the equation below:

$$O_3 + H_2O + h\upsilon \rightarrow H_2O_2 + O_2 \qquad (2.21)$$

Furthermore, the H_2O_2 formed can decompose under UV radiation to hydroxyl radicals that react with organic matter presence in the water, equation (2.13). There are several mechanisms for the degradation of organic pollutant in water: direct photolysis, hydroxyl radical attack generated from different source, and direct ozone attack. There is also combination of these two binary systems (UV/H_2O_2 and UV/O_3) as called $UV/ H_2O_2/ O_3$). Furthermore the process could enable complete mineralization of organics presence in water.

C. Photocatalytic Process

Photocatalitic process uses UV light for the irradiation of some powerful photocatalys such as TiO_2, ZnO etc. Photocatalytic activity of TiO_2 is based on its semiconductor properties. Radiation of photons, which have higher transfer energy, of such semiconductor leads to generation of electron-hole pair:

$$TiO_2 + h\upsilon \rightarrow h_{vb}^{+} + e_{cb}^{-} \qquad (2.22)$$

Holes in valence band (h_{vb}^{+}) are very strong oxidant. While electrons in conductance band (e_{cb}^{-}) take action as reductants. Further holes in the valence band react with hydroxyl ions or water (H_2O) on the surface producing hydroxyl radical:

$$H_2O + h_{vb}^{+} \rightarrow HO\bullet + H^{+} \qquad (2.23)$$

$$HO^{-} + h_{vb}^{+} \rightarrow HO\bullet \qquad (2.24)$$

Electrons react with dissolved oxygen producing superoxide radical (O_2•) or its protonated form, perhydroxyl radical (HO_2•):

$$O_2 + e_{cb}^- \rightarrow O_2\bullet \quad (2.25)$$

$$O_2\bullet + 2H^+ \rightarrow 2HO_2\bullet \quad (2.26)$$

In water, two HO_2• can recombine if their concentration allow them to react significantly yielding hydrogen peroxide (H_2O_2) and oxygen (O_2). It follows photocatalytic reduction of hydrogen peroxide by scavenging an electron band where hydroxyl radical generated:

$$H_2O_2 + e_{cb}^- \rightarrow HO\bullet + HO^- \quad (2.27)$$

The efficiency of TiO_2 photocatalysis could be improved by addition of hydrogen peroxide, but the optimal dosage of addition should be taken an account. When it is excess, it decrease process effectiveness.

Photocatalyst such semiconductor are comprised of microcrystalline or microcrystalline particles and they are used in a form of thin layer or as powder dispersion. Like TiO_2, alternative photocatalysts used are ZnO, CdS and SnO_2.

2.3.3 Ozone-based Processes

Ozone is an inorganic molecule constituted by three atoms of oxygen. It is present in the atmospheric layer around the earth, and it is formed by the photolysis of diatomic oxygen and further recombination of atomic and diatomic oxygen:

$$O_2 + h\upsilon \rightarrow 2O\bullet \quad (2.28)$$

$$O\bullet + O_2 \rightarrow O_3 \quad (2.29)$$

Under the term of ozone –based processes, ozone is the main component in many oxidation processes. In this process, ozone is applied either alone or with combination of an oxidant such as hydrogen peroxide (H_2O_2/O_3 processes), UV radiation (UV/ O_3 processes), catalyst, activated carbon, ultrasound, etc.

Ozone can be generated artificially in an ozone generator. There are two ways of generating ozone:

a. the cleavage of oxygen molecules under the influence of a strong electrical field
b. the photolysis of oxygen by the same mechanism as in the nature, but induced artificially.

The first use of ozone is as a disinfectant in many water treatment processes and in hospitals. Ozone application as oxidant for water purification was retained through 20^{th} century, and its significant increase was noticed in 1970s when the production of trihalomethanes and other organohalogenated carbon were identified during the water treatment by chlorine. Reactivity of ozone is very high with a redox potential 2.07 V, either in liquid or in gas. Its high reactivity owes to electronic configuration; ozone can be presented as a hybrid in four different molecular resonance structures that give ozone characteristics of an electrophilic, dipolar or even nucleophilic agent. Furthermore, ozone molecule could react with an organic compound under two mechanisms: direct or indirect. Direct mechanism involves organic compound degradation by molecular ozone and occurs in acidic pH range. While the main reaction involving indirect mechanism are reactions of addition to unsaturated part of hydrocarbon molecule and electron transfer. Rather high oxidation/reduction potential enables ozone to react with many organics, and also inorganic compounds.

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad (2.30)$$

Reaction of ozone and hydroxyl ions present in water by indirect ozone mechanism at basic condition generate hydroxyl radical, which further reacts with an organic compound present in water.

$$O_3 + H_2O + OH^- \rightarrow HO\bullet + O_2 + HO_2\bullet \quad (2.31)$$

Mechanism of ozone decomposition in water depends on the presence of chemical species that can initiate, promote or inhibit its decomposition. The most accepted ozone decomposition mechanism is expressed in Figure 2.2.

According to the presented mechanism of ozone decomposition in water, it can be shown that ozonation can classified in AOPs when the degradation of organics occur by indirect mechanism. While classified as classical chemical treatment method when direct mechanism method is dominant in the degradation of organics in water (Koprivanac and Kusic, 2007; Lenntech, 2008; Russel, 2006).

Among the new alternative O_3 processes, either direct or indirect, the one that has been widely investigated is O_3/H_2O_2. This process is named peroxone process or perozonation. In this process, hydroxyl radical is generated by reaction of ozone and perhydroxyl ion (HO_2^-), which present in water by dissociation of H_2O_2. Overall mechanism of reaction expressed below:

$$H_2O_2 + O_3 \rightarrow 2\ HO\bullet + 3O_2 \quad (2.32)$$

2.3.4 High Voltage Electrical Discharge Processes

The high voltage electrical discharge processes, called corona discharge causes chemical and physical processes induced by strong electrical field. It is proved that by applying electrical discharge in liquid phase intensive UV irradiation and various active species (HO•, •H, •O, HO_2^-, O_2•-, H_2O_2, etc) are produced. By the

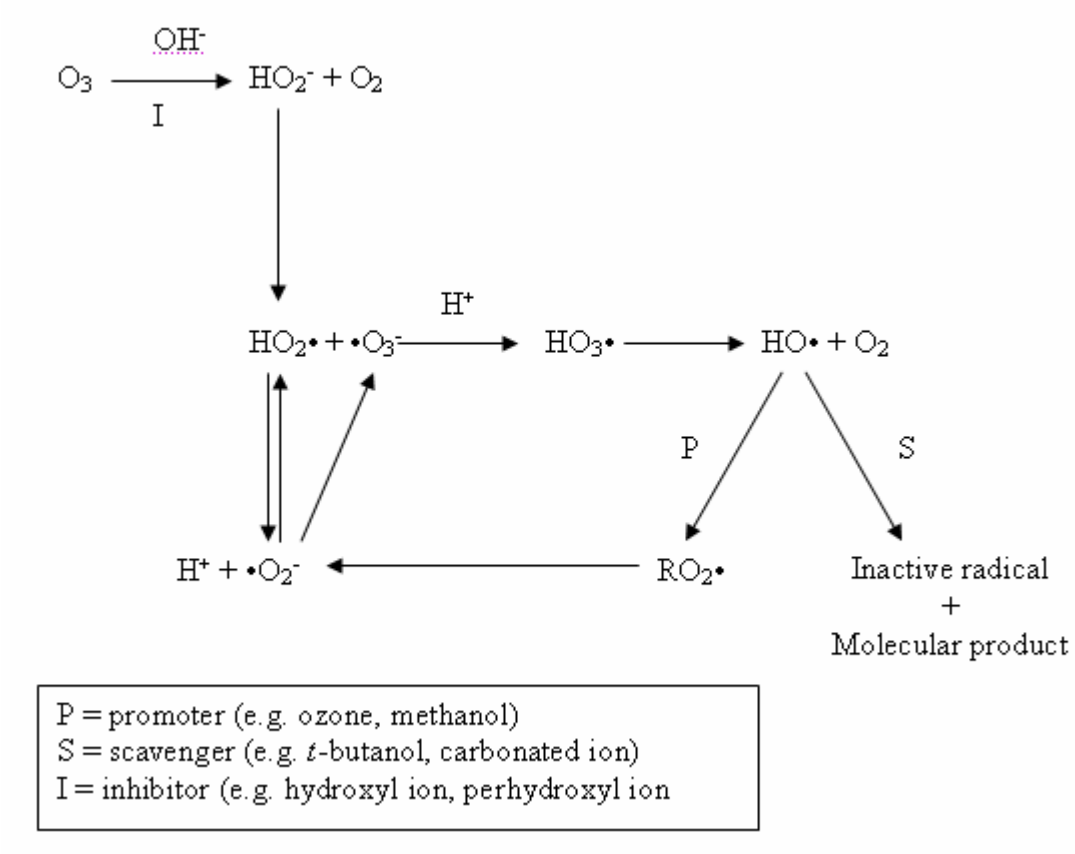


Figure 2.2 Scheme of ozone decomposition in water (Beltran, 2003)

presence of oxygen in the system, ozone and its ozone-related radical species can be formed, Equation (2.30) and Equation (2.32). This process can be effective for treatment of biological microorganism and dissolved chemicals in liquid phase.

Pulsed corona discharge produces repetitive (60Hz), fast raising high voltage pulses with short lifetime (μs). Application of short high voltage pulse (200 – 100 ns) consider presence of non-thermal condition, hence electrons having a higher mean energy (T_e >> 1 eV) compare with the other constituent in liquid (T_{H2O} < 0.1 eV). In this way, the chemical with less mobility than electrons and which have no influent to generation of radicals because of losing energy for the migration of ions is minimized as high as possible. Among all radical species generated in corona when electrons with high energy collide with water molecules, hydroxyl radicals are the main species responsible for degradation organics.

$$H_2O + e^{-}* \rightarrow HO\bullet + \bullet H + e^{-} \quad (2.33)$$

$$H_2O + e^{-}* \rightarrow H_2O^{+} + 2\ e^{-}* \quad (2.34)$$

$$H_2O + H_2O^{+} \rightarrow H_2O^{+} + HO\bullet \quad (2.35)$$

Such radicals could react between themselves resulting in the production of H_2O_2, H_2 or H_2O.

$$HO\bullet + HO\bullet \rightarrow H_2O_2 \quad (2.36)$$

$$H\bullet + H\bullet \rightarrow H_2 \quad (2.37)$$

$$HO\bullet + H\bullet \rightarrow H_2O \quad (2.38)$$

Furthermore, the degradation of organic compounds could be performed by: a) direct reactions with highly reactive species (HO•), b) indirect reaction over radicals formed from stable molecules (H_2O_2), and c) direct reactions with stable molecules.

2.3.5 Others AOPs

This subchapter contains review of other AOPs, such as: ultrasound or ultrasonic irradiation, radiolysis of water and electrochemical processes.

A. Ultrasound.

Ultrasonic processes as wastewater treatment method generate free radicals (such hydroxyl radical) upon the action of ultrasonic waves on liquid. The applied frequency ranges from 20 – 40 kHz. Ultrasound produces the chemical effect through several different physical mechanisms and the most important nonlinear acoustic process for sonochemistry is cavitation.

Water irradiation using ultrasound causes decomposision of the water molecules in to extremely reactive radical HO• and H•, shown in equation below:

$$H_2O + \textit{ultrasound} \rightarrow HO\bullet + H\bullet \quad (2.39)$$

Further the reactive radical species could react with organic pollutant present in the water through oxidation or reduction.

B. Water Radiolysis

Water radiolysis processes involve high energy ionizing radiation ranged from keV to MeV to irradiate of dilute aqueous solution resulting in the excitation and ionization of water molecules. It is well known that radical species are very reactive to degrade organic pollutants present in water.

C. Electrochemical Processes

The electrochemical processes can occur by direct electron transfer reaction of reduction or oxidation of organic pollutant, or by chemical reaction of the pollutant with previously electrogenerated species. Mechanism of the reaction generally viewed as a direct anodic oxidation of organic pollutant involving its reduction by direct electron transfer from organic molecule to the electrode to form a radical cation that readily deprotonates.

$$RH + \textit{electrolysis} \rightarrow R\bullet + H^+ + e^- \quad (2.40)$$

2.4 Degradation Intermediate

Oxidation of an organic compounds such as amines by hydroxyl radical may proceed through abstraction of hydrogen atoms leading to the formation of carboxylic acids which are further degraded to smaller fragments and eventually to CO_2 and H_2O when enough hydroxyl radicals are generated in the reaction medium.

The electrophilic attack of the hydroxyl radical may also cause a cleavage of C-N bond. Under neutral or acid condition the amino functional group is protonated to a certain extent, which might deactivate the α-CH bond. Hence, a further located C-atom of the amine is oxidized. In contrast with this, in alkaline condition a competitive direct electrophilic attack at the free electron pair of the nitrogen atom also can take place. This is due to the fact that the amino function is unprotonated. As a result, steric screening affects the direct electrophilic attack of the hydroxyl radical at the free electron pair of the nitrogen. Reaction scheme for degradation of a secondary amine by hydroxyl radical is showed in Figure 2.3. It is based on the electrophilic attack of hydroxyl radical which leads to hydrogen abstraction inducing a cleavage of the C-N bond. Subsequently, the organic nitrogen is transformed to CO_2, NH_4^+, NO_2^- and NO_3^-.

2.5 Biological Oxidation

Biological treatment is a method to remove contaminants in the wastewater by biological activity. Primarily, biological treatment is used to remove biodegradable organic substances (colloidal or dissolved) in the wastewater. These substances are absorbed, fragmented and metabolized by the bacteria leading to biomass growth as formation of metabolic product. Pretreatment may be required for contaminants which are toxic to the microorganism. Biological treatment can also remove nutrients (nitrogen and phosphorous) in the wastewater. The removal of carbonaceous biochemical oxygen demand is accomplished biologically using a variety of

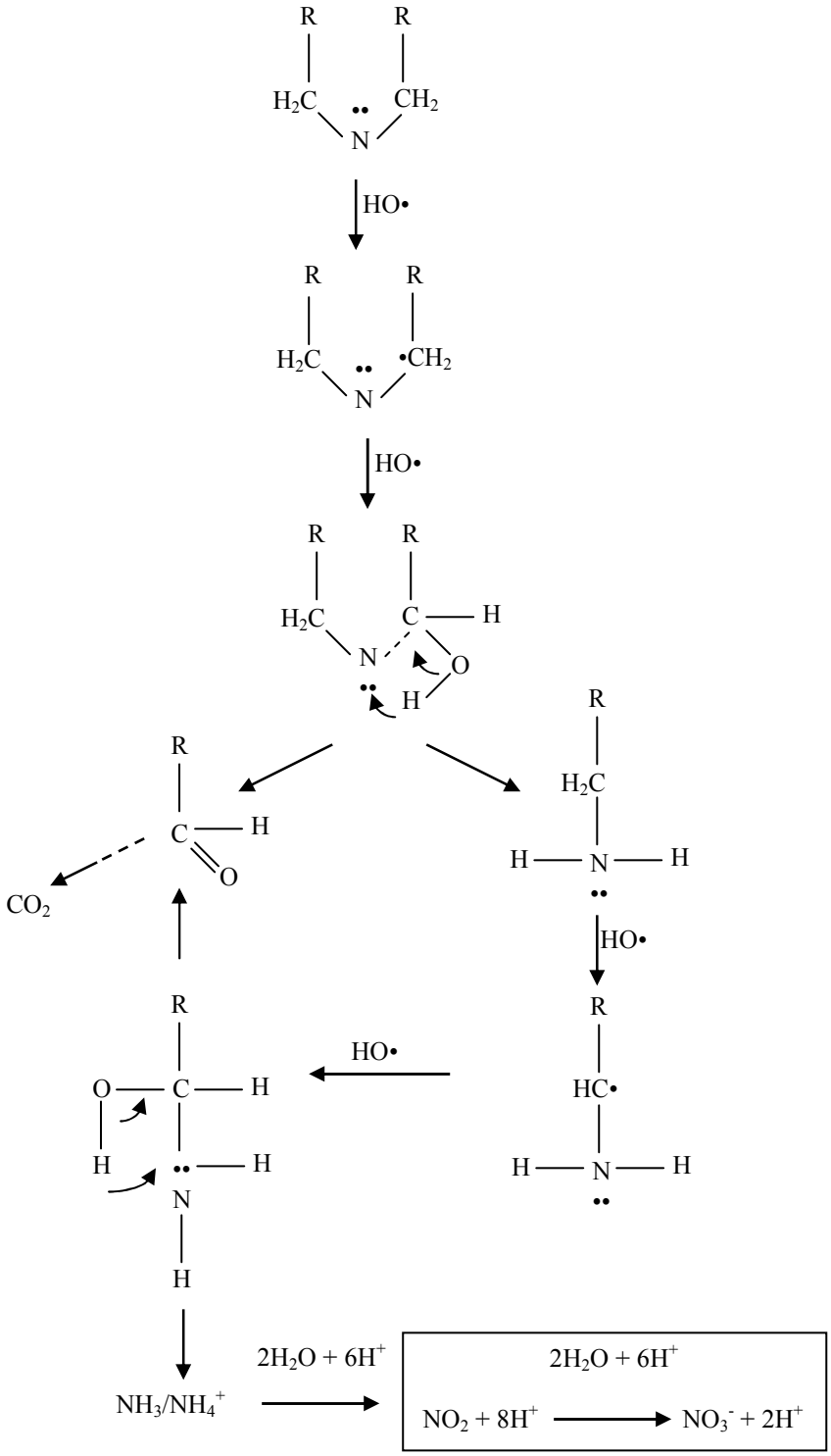


Figure 2.3 Reaction oxidation scheme of secondary amine by hydroxyl radical (Klare et al, 2000)

microorganism, principally bacteria. A proper environmental control such as pH and temperature should be provided, so that the process can operate effectively (Metcalf and Eddy, 1991).

The following general guidelines can be applied for the relationship between biodegradability and molecular structure (Eckenfelder and Musterman, 1995):

a. Nontoxic aliphatic compound containing carboxyl (R─COOH), ester (R─COO─R), or hydroxyl (R─OH) groups are readily biodegradable. Compound with dicarboxylic (HOOC─R─COOH) groups require longer acclimatization than those with a single carboxyl groups.
b. Compound with carbonyl (R─R═O) groups or double bonds (R═R) are moderately degradable and slow to acclimatize.
c. The biodegradability of compounds with amino ($R─NH_2$) or hydroxyl groups (R─OH) decreases, depending on the degree of saturation as follows: primary > secondary > tertiary carbon atom of attachment.
d. The biodegradability of halogenated (R─X) compounds decreases with increasing degree of halogen substitution.

2.5.1 Environmental Requirements

The environmental requirements such as pH and temperature have an important effect on the survival and growth of bacteria. Generally optimal growth occurs within a fairly narrow range of pH and temperature, although some bacteria may able to survive and grow within much border limits. Temperature lower than optimum has more significant effect on growth rate than temperature above the optimum. It has been observed that growth rate doubled with approximately every 10˚C in temperature until the optimum temperature is reached. Based on the temperature range bacteria classified as psychrophilic (cryophilic), mesophilic and thermophilic.

The pH environment is also the importance factor growth of organism. Most of bacteria can not tolerate into pH level above 9.5 or below 4.0. Optimum pH for bacterial growth lies at 6.5 – 7.5 (Metcalf and Eddy, 1991).

2.5.2 Bacterial Growth

Bacteria usually reproduce by binary fission. Binary fission is a reproduction by dividing the original cell into two new organisms. Generation time can vary from days to less than 20 minutes (Metcalf and Eddy, 1991). Various environmental conditions such as substrate concentration, nutrient concentration, and even system size have important effects on bacterial reproduction.

Bacterial growth in term of number count against time follows four phases as bellow:

1. *The lag phase*. This phase is the time required for the bacteria to acclimatize. Addition of a new inoculum into the culture media is a new environment. In this phase bacteria begin to divide.
2. *The log-growth phase*. During this period the cells divide at a rate of generation time and their ability to process the food.
3. *The stationary phase*. In this phase the population remains stationery. There are two advanced reason for this phenomena: (a) the cells have exhausted the substrate or nutrient necessary for growth and (b) the growth of new cells is offset by the death of old cells.
4. *The log-death phase*. During this phase, the bacterial death rate exceeds the rate of production of new cells. In some cases, the log-death phase is the inverse of the log-growth phase.

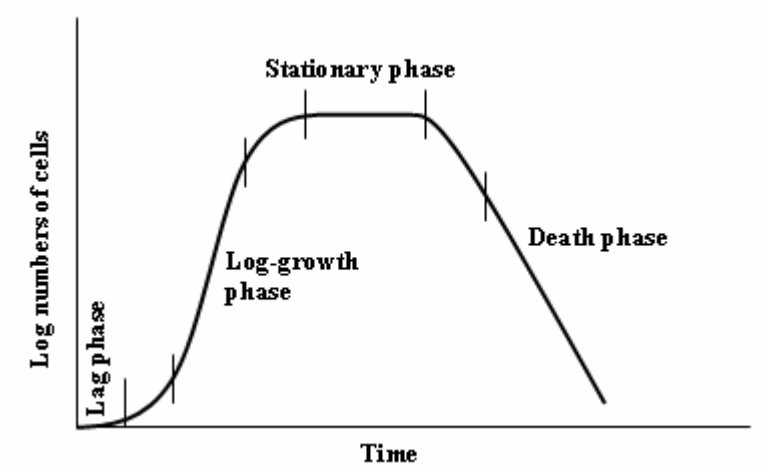


Figure 2.4 Typical bacterial growth curves in term of numbers.

The bacterial growth pattern can also be expressed in term of change bacterial mass with time. This pattern consists four phases as follow:

1. *The lag phase*. During this phase bacterial mass increases very slowly and the bacteria require time to acclimatize to their new nutritional environment.
2. *The log-growth phase*. The rate of growth and metabolism are functions of the ability of the microorganism to process the food that is available in excess in the surroundings of microorganism.
3. *Declining growth phase*. The rate of increase of bacterial mass decreases because of limitation of food supply.
4. *Endogenous phase*. During this phase, the microorganism is forced to metabolize their own protoplasm without replacement because of the concentration of food is at minimum. This phenomenon is known as *lysis* or *cryptic growth*.

2.5.3 Acclimatization

Acclimatization is the rapid adaptation of microorganism to consume the pollutants in the wastewater. Some corresponding supplemental substrates can be

added to enhance the biodegradability of wastewater constituents, if nutrient deficiency occurred in bioreactor. In certain cases, the low acclimatization process may occur due to low adaptability the biomass or low biodegradability of wastewater constituents (Eckenfelder and Musterman, 1995).

2.5.4 Biodegradation of wastewater containing amines

An alkanolamine is a compound containing C, H, O, and N elements. A series of biochemical reactions is required to achieve complete degradation of wastewater containing amine. Carbon oxidation, nitrification, and denitrification are needed for total biodegradation. The complete biodegradation of amine compound is schematically shown in Figure 2.5.

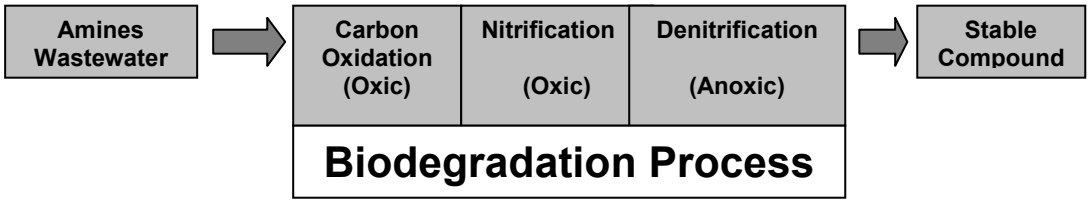


Figure 2.5 Complete biodegradation of alkanolamine.

Carbon oxidation and nitrification occur in oxic condition. Heterotrophic groups are responsible for carbon oxidation to form water (H_2O) and CO_2. While autotrophic groups are responsible for nitrification to form H^+, H_2O, and NO_3. Meanwhile, denitrification forms N_2 by changing operation condition to anoxic.

Limited report available on treatment of wastewater containing alkanolamine, especially for treatment of wastewater from sweetening process. Bilad MR (2007) found that by using sequencing batch reactor (SBR) and sequencing batch membrane bioreactor (SBMBR) system was able to treat the artificial wastewater containing MEA up to 3600 mg/L. The system showed fast acclimatization, high adaptability subject to sudden change in concentration and good settling of sludge.

CHAPTER 3

EXPERIMENTAL

This chapter wills detail out the experimental part of the present work, as well as description on the material, set-up of equipment, procedure and operation of the experiment and analytical methods. The details of each experiment are also elaborated in this chapter. Basically, the experiment is divided in three main activities. Those activities are Fenton's treatment of simulated waste containing MEA or DEA, analysis of the degradation product and biodegradability test. The outline of these experimental methods is shown in Figure 3.1.

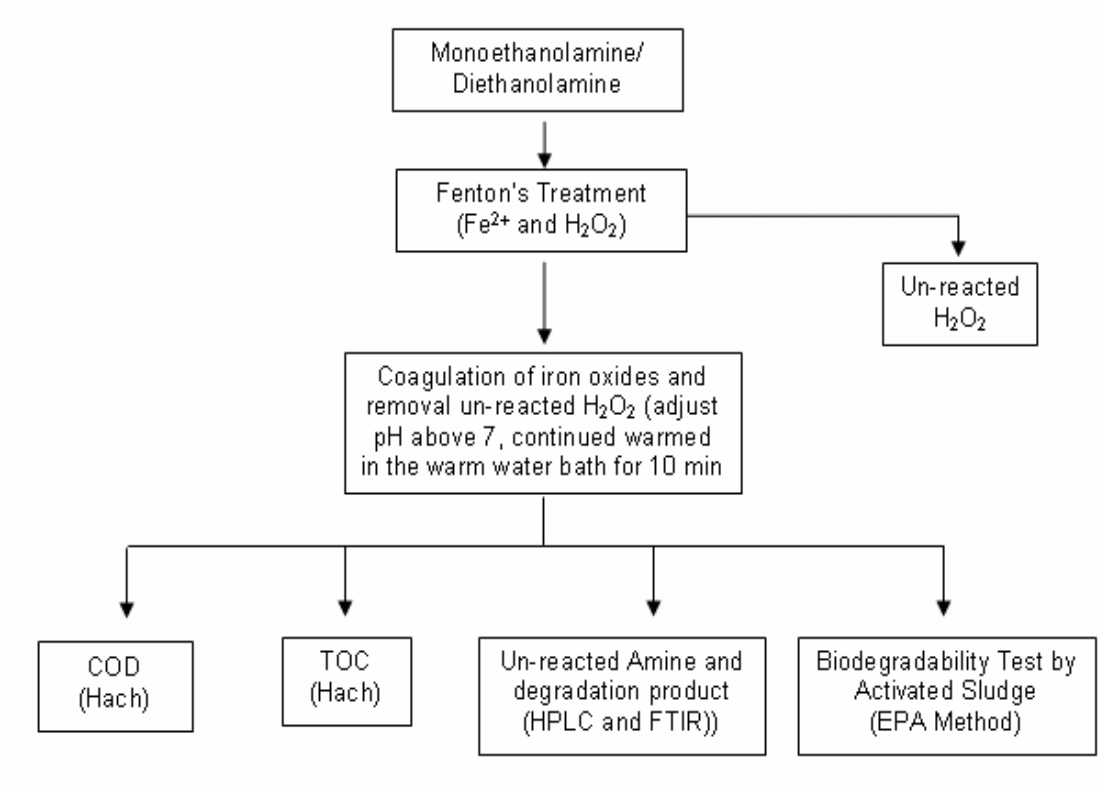
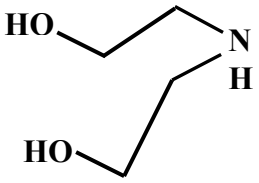


Figure 3.1 Flow diagram of experimental components.

3.1 Material

3.1.1 Chemicals

Table 3.1 Chemicals used in the present work

Chemicals	Supplier	MW g·mol^{-1}	T_m °C	T_b °C	$\rho(T = 25\ °C)$ g·cm^{-3}
MEA 99.8 % 	Merk	61.08	10.3	170	1.012
DEA 98.0 % 	R & M Chemical	105.14	28.0	217	1.090
Hydrogen Peroxide (H_2O_2) 30% by weight	Merk	34	-	-	1.11
Iron (II) Sulfate 7- hydrate ($FeSO_4;7H_2O$) 99.5 – 104.5 %	HmbG Chemicals	278.2	-	-	1.04
Potassium Permanganate ($KMnO_4$)	Merk				
Sulfuric Acid (H_2SO_4)	Systerm	98.08	-15	330	1.84
Sodium Hydroxide (NaOH)	R & M Chemical	40	-	-	-

3.1.2 Simulated Wastewater

Simulated wastewater for Fenton's treatment was prepared by dissolving a requisite quantity of the amine in distilled water. The lowest concentration (by volume) of amine was 800 ppm and higher concentrations were 5000 ppm, 10000 ppm and 16000 ppm, respectively. The lowest concentration 800 ppm amine had a COD reading of about 1400 mg/l. And the highest concentration 16000 ppm had a COD reading more than 20000 mg/l which is similar to the COD value of wastewater from the natural gas processing industries coming out of washing and cleaning of the absorption and stripping towers.

3.1.3 Biomass inoculum

The biomass inoculum was prepared from activated sludge seed taken from the existing WWTP at Universiti Teknologi PETRONAS (Malaysia). The sludge was taken from the center of clarifier using sludge trapper. The sludge trapper was submerged into the clarifier whereby due to the nature of its design, the sludge entered the trapper. The sludge was than brought to the lab and directly aerated for 1 day while determining the MLVSS (dry matter) and thereafter placed in the bioreactor to start the biodegradability test.

3.1.4 Mineral Medium

The preparation of mineral medium is done separately in four stocks. Those are stock A, stock B, stock C and stock D.

Stock A is prepared by dissolving of components listed below in 1 liter aqueous solution. The pH of the solution should be 7.4.

KH_2PO_4	8.5 g
K_2HPO_4	21.75 g

Na_2HPO_4, $2H_2O$	33.4 g
NH_4Cl	0.5 g

While stock B, C and D had the recipes below:

Stock B: 1 liter contain,

$CaCl_2$, $2H_2O$	36.4 g

Stock C: 1 liter contain,

$MgSO_4$, $7H_2O$	22.5 g

Stock D: 1 liter contain,

$FeCl_3$ anhydrous	0.15 g

A fresh mineral medium was prepared by mixing of 10 ml stock A and 1 ml each stock B, C and D per liter solution and was prepared fresh before each biodegradability test (US EPA Method, 1998).

3.1.5 Reagents used

A. Starch Indicator

Starch indicator for iodometry was prepared by dissolving 1 g starch powder in the 100 ml distilled water with heating on a hot plate until getting a clear solution. The cool clear solution was used as the indicator for standardization of potassium permanganate solution that used for determination of un-reacted hydrogen peroxide after Fenton's treatment.

B. HPLC mobile phase

The HPLC mobile phase is a mixture of 0.1 M Na_2HPO_4 and 0.1 M NaOH solution in water at a ratio 60% Na_2HPO_4 to 40% NaOH, pH 12. Filtration of the mobile phase stock is necessary before used. This is to eliminate any solid present in the stock which will create problems in the process of HPLC analysis.

C. Distilled Water

The distilled water was prepared in the laboratory. It is prepared by distilling tap water using Merit W4000 distillation set. The distilled water was used to prevent any additional constituent that may be present in tap water.

3.2 Experimental set up

3.2.1 Fenton's Oxidation Process

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

Un-reacted H_2O_2 present in a sample seriously interferes with COD measurement (Talinli and Anderson, 1992). Removal of the H_2O_2 was done by warming the sample in a boiling water bath for 10 minutes after addition of 2 ml of 1(M) NaOH solution to 8 ml sample. The precipitated hydrated ferric oxide was removed by filtration using 0.45µm filter and the COD of the sample was measured. The change of volume of a sample at different stages was taken into account during COD calculation.

Figure 3.2 Fenton's Process experimental set up

3.2.2 Biodegradability Test of Partial Degraded MEA and DEA

Biodegradation studies were conducted in an aerobic batch bioreactor according to the materials and methods specifications in the Zahn-Wellens/EMPA Test as par the US Environmental Protection Agency (EPA) method OPPTS 835.3200 (US EPA Method, 1998). Partially degraded MEA and untreated MEA were added in separate reactors to achieve an initial COD of approximately 1000 mg/L and seed bacteria from the activated sludge sewage treatment plant in Universiti Teknologi PETRONAS (Malaysia) was added to the reactors to achieve initial biomass concentration of approximately 100 mg/L MLSS. To ensure sufficient micronutrients and suitable growth conditions, a mineral medium as described in the US EPA Method mentioned above was added and the pH of the liquid was maintained at 7. Aeration was done by bubbling compressed air through the wastewater using wet cotton placed in the perforated plastic tubing. Samples were withdrawn every 6 hours and analysed for COD, NH_3, and mixed-liquor suspended solids (MLSS). The experiment was conducted for a 5-day period. In a different experiment set up, about 1000 mg/L MLVSS of biomass was used to study the biodegradability of untreated alkanolamine and partially degraded alkanolamine via Fenton's process in order to compare the standard compound suggested in the US EPA method. Di-ethylene glycol was used as the standard compound. At around 1000 mg/L COD of test compound was added in the activated sludge. Samples were withdrawn everyday and the biodegradation study was characterized by measuring COD and oxygen uptake rate (OUR). Observation was started at 3hours±30 minute after addition of the test compound in the sludge at 0 minute observation. Sampling continued till COD reading was constant. A blank reactor which was activated sludge and mineral medium was also provided. Biodegradability of each compound was showed by COD evolution versus time. The COD removal was calculated by:

$$CODremoval = \left[1 - \frac{CODt - CODbt}{COD3h \pm 30 - CODb3h \pm 30}\right] x100\% \qquad (3.1)$$

Where:

CODt = COD value of test compound at sampling time, t

CODbt = COD value of blank at sampling time, t

COD3h±30 = COD value of test compound at 3hours±30 minute sampling

CODb3h±30 = COD value of blank at 3hours±30 minute sampling

Table 3.2 Biodegradability test run conditions following the Zahn-Wellens/EMPA Test as par the US Environmental Protection Agency (EPA) method OPPTS 835.3200 (US EPA Method, 1998).

Period of test	Normally for up to 28 days
Temperature	20 - 25 °C
Light	No Light (dark place or diffuse light)
Aeration	Purified and humidified air (pass through wet cotton)
DO	Not less than 2 mg/L
pH	Adjusted to 6.5 – 8.0 (using NaOH or H_2SO_4)
0 minute sampling	3 $\pm$ 30 minute after addition of the test compound
Volume of experiment	1 – 5 liter
Ratio inoculum to test compound	2.5: 1 or 4: 1
Degradation test	COD measurement

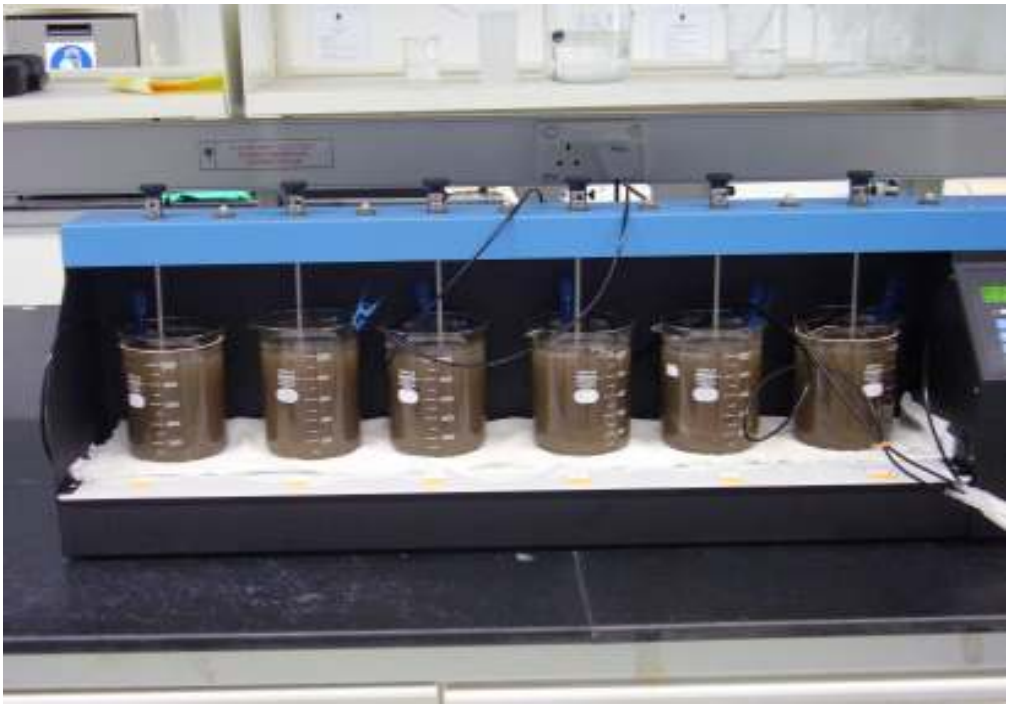


Figure 3.3 Biodegradability test experimental set up

3.3 Analytical Methods

3.3.1 COD (Chemical Oxygen Demand) determination

Chemical oxygen demand determination was performed using HACH analytical equipment Method 8000 that was approved by Standard Method for the Wastewater Analysis, USEPA. This parameter is very important to monitor the degradation of alkanolamine and the concentration of the test compound in bioreactor. Two ml of sample was oxidized using the standard chemical from HACH and digested at 150 ˚C for two hours on the DRB HACH digester. The COD reading was obtained by using HACH DR 5000 spectrophotometer. The range of COD measurement is 0 – 1500 mg/L COD. Furthermore, COD removal at 30 minute was calculated by:

$$COD_{removal30} = \frac{COD_0 - COD_{30}}{COD_0} x100\% \quad (3.2)$$

where: $COD_{removal\ 30}$ = percentage of COD removal at 30 minute,
COD_0 = COD value at 0 minute, and
COD_{30} = COD value at 30 minute

3.3.2 TOC (Total Organic Carbon) determination

Total organic carbon determination was conducted using HACH analytical equipment Method 10128 that was approved by Standard Method for the Wastewater and Industrial Waters Analysis, USEPA. Measurement of this parameter was done to compare the profile of COD reduction and TOC reduction in the Fenton's process. 0.3 ml sample was digested using the standard reagent from HACH at 105 ˚C for two hours on the DRB HACH digester, and the TOC was measured using HACH spectrophotometer DR 5000. The range of TOC measurement was 100 – 700 mg/L C. Further, TOC removal at 30 minute was calculated by:

$$TOCremoval_{30} = \frac{TOC_0 - TOC_{30}}{TOC_0} x100\% \quad (3.3)$$

where: $TOC_{removal\ 30}$ = percentage of TOC removal at 30 minute,
TOC_0 = TOC value at 0 minute, and
TOC_{30} = TOC value at 30 minute

3.3.3 Un-reacted alkanolamine and identification of degradation product using HPLC

An Agilent series 1100 brand of HPLC was used to monitor the degradation products and un-reacted alkanolamine after Fenton's treatment. YMC-Pack PolymerC18 reverse phase column was used with 100mM Na_2HPO_4/100mM NaOH (60/40, pH 12) as eluent and UV (215 nm and 253nm) detector. Flow rate of the eluent was 1 ml/minute. Degradation product determination was performed by comparison of the sample with the standard compound which was assumed. Qualitative analysis was based on the retention time of each compound in the chromatogram, while quantitative un-reacted alkanolamine analysis was based on the calibration curve prepared using standard alkanolamine. The calibration curve for MEA and DEA are expressed below:

MEA : $$\text{Area} = 0.210[\text{MEA}] - 2.267 \quad (3.4)$$

DEA : $$\text{Area} = 0.443[\text{DEA}] + 10.076 \quad (3.5)$$

3.3.4 Identification of the functional groups using FTIR

The method to characterize the functional groups of the degradation product after Fenton's treatment was done by infrared spectroscopy. A Perkin Elmer Spectrum One Fourier Transform Infrared Spectrometer was used to obtain the spectra.

3.3.5 Un-reacted H_2O_2 determination

Determination of the un-reacted H_2O_2 in the Fenton's process was performed using 0.05 $KMnO_4$ solutions. Titration of acidified sample after filtration from Fenton's process was conducted. Change color from colorless to light pink is the end point of titration. Sodium thiosulphate (NaS_2O_3) was used to standardize the $KMnO_4$ by iodometry with 1% starch solution as indicator (Mendham, 2000).

3.3.6 pH

The pH of the mixed liquor was measured using pH probe of HACH sens ion 1 pH meter. This pH meter was calibrated regularly. The pH of Fenton's process was used to monitor the oxidation process in the reactor, while pH of bioreactor to monitor the activity of microorganism in the bioreactor. The range of pH measurement was 2-5 on Fenton oxidation and 6.5-8 on biological oxidation.

3.3.7 DO (Dissolved Oxygen)

Dissolved oxygen was measured using HQ30d flexi HACH DO meter. LD0101 DO Probe was used for measurement of the dissolved oxygen in the bioreactor during the biodegradability test. The rate of oxygen consumption also can be monitored by this parameter.

3.3.8 MLVSS (Mixed liquor volatile suspended solid)

Total suspended solid was measured using method 2540-E that has been approved by APHA (2001). An increase in the MLVSS in the bioreactor represented the growth of microorganism and yield of biomass. The residue from method 2540-E was ignited to a constant weight at 550°C. The remaining solid represent the fixed suspended solid while the weight lost on ignition was the volatile suspended solid. Further, the MLVSS was calculated by:

$$\text{mg volatile solid/L} = \frac{(A - B) \times 1000}{\text{sample volume (ml)}} \qquad (3.6)$$

$$\text{mg fixed solid/L} = \frac{(B - C) \times 1000}{\text{sample volume (ml)}} \qquad (3.7)$$

Where: A = weight of residue + dish before ignition, mg
B = weight of residue + dish or paper filter after ignition, mg, and
C = weight of dish or paper filter, mg

3.3.9 MLSS (Mixed liquor suspended solid)

MLSS was measured using a HACH turbidimeter based on this calibration curve prepared using the seed sludge: Turbidity (NTU) = 0.6618[MLSS] – 1.964, with coefficient of correlation $R^2 = 0.9988$.

3.3.10 NH_3

Ammonia (NH_3) was measured using ion selective electrode for dissolved ammonia Sens ion 4. This ammonia meter was calibrated every week. 25 ml sample was collected and after added with ionic strength adjustor the measurement was performed.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Treatability studies with Fenton's reagent.

Oxidation of an organic compound by Fenton's reagent occurs in the acidic pH range. The oxidation rate is controlled by the generation rate of HO• radicals. The rate of HO• radical production in turn depends upon the H_2O_2 concentration, $FeSO_4$, and the competing reactions. These competing reactions may also be responsible for loss of the oxidation power in the system by a series of side reaction (Laat and Gallard, 1999). Equations (2.1) till equation (2.6) describe the major reactions in the Fenton's oxidation. While the equation (2.7) till equation (2.9) explain the competing reactions. In this study, relatively mild conditions of Fenton treatment were selected to enhance biodegradability of MEA and DEA. The effects of initial concentration of alkanaolamine, pH, concentration of H_2O_2, and concentration of $FeSO_4$ were studied separately. The ranges of values of these variables performed in the experiment are: (1) MEA concentration: 800 – 16000 ppm; pH: 2 – 5; H_2O_2: 50 – 250 ml (30% w/w) in 800 ml solution and $FeSO_4;7H_2O$: 4 – 16 gram in 800 ml solution. (2) DEA concentration: 800 – 16000 ppm; pH: 1 – 4; H_2O_2: 50 – 250 ml (30% w/w) in 800 ml solution and $FeSO_4;7H_2O$: 4 – 16 gram in 800 ml solution.

4.1.1 Effect of Initial Concentration

The study of the effect of initial alkanolamine concentration was performed at four initial concentrations of alkanolamine. The concentration was varied from 800

ppm to 16000 ppm maintaining constant of volume, pH and ratio between alkanolamines concentration to Fenton's reagent. Figures 4.1 and 4.2 show that the rate of COD degradation of MEA and DEA solution was strongly dependent on the initial concentration. The COD removal was low at a low concentration of amine. It was 14.2% for MEA and 17.2% for DEA at the end of 30 minute for 800 ppm initial concentration. More than 40% COD removal was achieved within 5 minutes when the initial concentration was 16000 ppm. Fenton oxidation was vigorous in the high concentration of reactant. Hence, the COD removal was higher compared in the low concentration. It is also seen that reaction was very fast at the initial time and then slowed down.

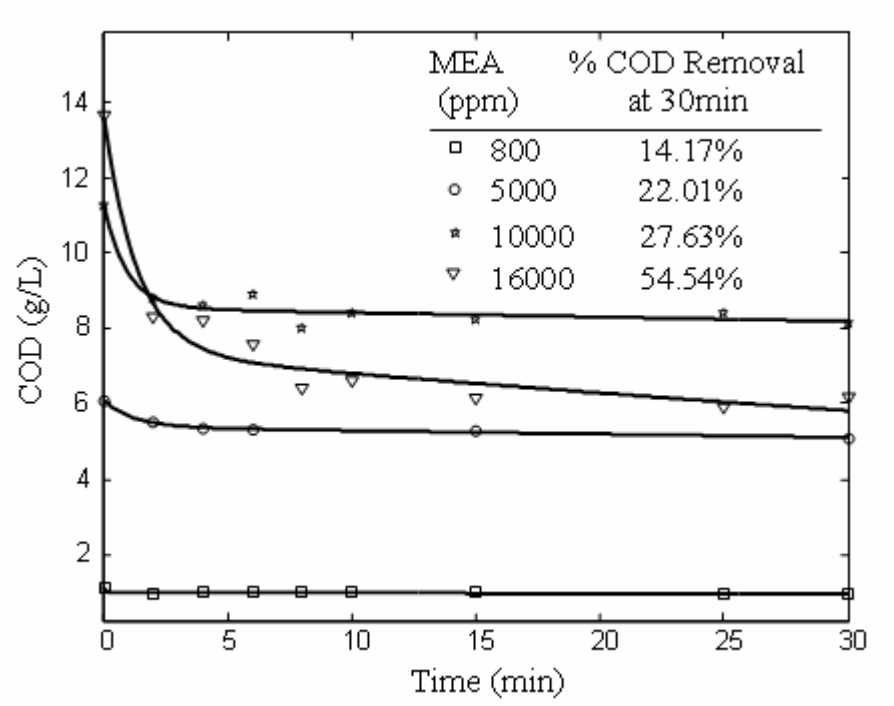


Figure 4.1 Effect of initial concentration on MEA degradation. {(800 ppm MEA: 0.4 g $FeSO_4$;$7H_2O$, 9.3ml H_2O_2 30%; 5000 ppm MEA: 2.5 g $FeSO_4$;$7H_2O$, 54.8 ml H_2O_2 30%; 10000 ppm MEA: 5 g $FeSO_4$;$7H_2O$, 106.67 ml H_2O_2 30%; and 16000 ppm MEA: 8 g $FeSO_4$;$7H_2O$, 175 ml H_2O_2 30%) at pH 3.

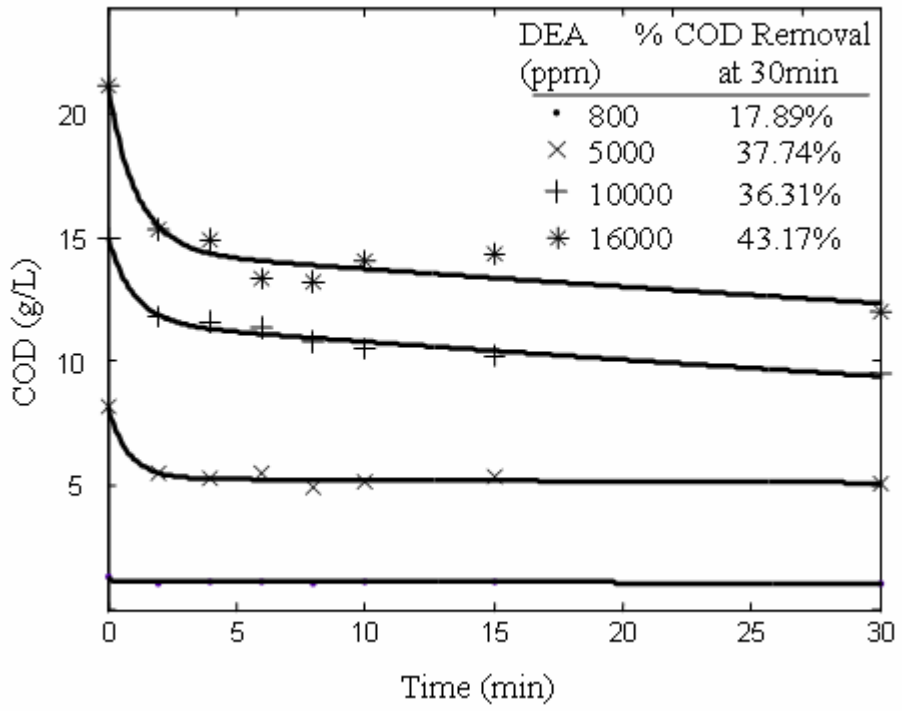


Figure 4.2 Effect of initial concentration of DEA degradation. {(800 ppm DEA: 0.4 g $FeSO_4;7H_2O$, 9.3ml H_2O_2 30%; 5000 ppm DEA: 2.5 g $FeSO_4;7H_2O$, 54.8 ml H_2O_2 30%; 10000 ppm DEA: 5 g $FeSO_4;7H_2O$, 106.67 ml H_2O_2 30%; and 16000 ppm DEA: 8 g $FeSO_4;7H_2O$, 175 ml H_2O_2 30%) at pH 3.

4.1.2 Effect of Hydrogen Peroxide Concentration

Four different H_2O_2 concentrations were tested in order to investigate the effect of its concentration. The volume of liquid, amine concentration (16000 ppm), $FeSO_4;7H_2O$ concentration (8 gram) and pH at 3 were maintained at constant values.

The hydroxyl radical causes the degradation reaction. This radical would degrade an organic matter to simpler molecules. The hydroxyl radical is generated from reaction between H_2O_2 and Fe^{2+} in the acidic pH (see Equation 2.1). A higher H_2O_2 concentration generates more hydroxyl radical enhancing the COD removal. In this study, the maximum COD removal was achieved at 175 ml H_2O_2 (30% by weight) for both MEA and DEA. A still higher hydrogen peroxide concentration

would not increase the COD removal. It is well known that hydrogen peroxide acts as a scavenger of hydroxyl radicals (see Equation 2.7). Hydroperoxil radicals are generated from that reaction. It is also well known that hydroperoxil as well oxidizes the organic matter, but the reactivity of hydroperoxyl is less compared with hydroxyl radical. Hence, the COD removal was less in the upper limit of H_2O_2 concentration.

The probable reason for less reactivity of hydroperoxyl is that in the first stage when the degradation was very fast, the Fe^{2+} ions react with H_2O_2 to produce hydroxyl radical (HO•) according with the following reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \quad (4.1)$$

Further the second stage when the degradation slow down, the Fe^{3+} ions produced in the first stage react with H_2O_2 to produce hydroperoxyl radicals ($HO_2\bullet$) and Fe^{2+} according with the following reaction:

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \quad (4.2)$$

$$FeOOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \quad (4.3)$$

As well in this stage, hydroxyl radical (HO•) produced from the first stage react with H_2O_2 to produce hydroperoxyl radical ($HO_2\bullet$) and water (H_2O) according with following reaction:

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \quad (4.4)$$

Thus hydroxyl radical (HO•) and hydroperoxyl radical ($HO_2\bullet$) are formed in the first stage and second stage of Fenton oxidation respectively. Oxidation capability of hydroxyl radical is much more than the hydroperoxyl radical.

The decrease of removal due to the scavenging effect of hydrogen peroxide is also reported by Lodha B and Chaudhari S (2007) on degradation of dye using

Fenton's reagent and Xu et al (2007) on removal of organic carbon from wastepaper pulp effluent by lab-scale solar photo-Fenton process.

The COD degradation profile at the different H_2O_2 concentrations is depicted in Figure 4.3 for MEA and Figure 4.4 for DEA. From both the figures it is seen that increasing H_2O_2 concentrations followed increasing COD removal until the certain limit and decreasing thereafter.

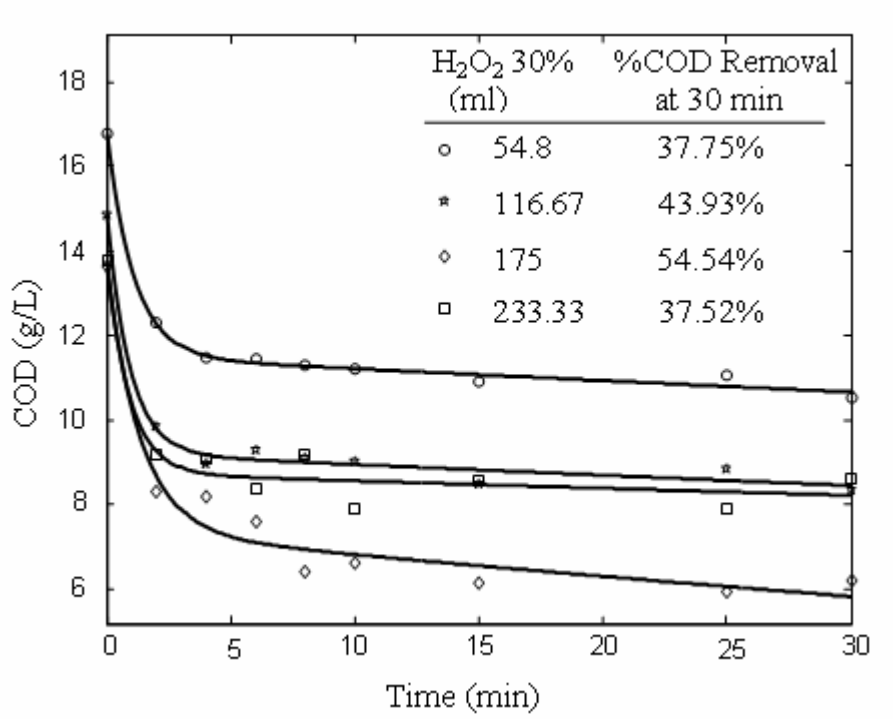


Figure 4.3 Effect of Hydrogen peroxide concentration on MEA degradation {16000 ppm MEA, 8 g $FeSO_4;7H_2O$ at pH 3 at four different H_2O_2 concentration }.

4.1.3 Effect of pH

Given below are the results on the effect of pH on the MEA and DEA degradation using Fenton's reagent. The experiments were carried out at four different pH values while maintaining the same volume of liquid, same amine concentration (16000 ppm), same H_2O_2 concentration (175 ml 30% by weight) and

same $FeSO_4;7H_2O$ concentration (8 g). Range pH studied for MEA was 2 – 5 and for DEA was 1 – 4.

The $Fe^{2+}/Fe^{3+} – H_2O_2$ system has its maximum catalytic activity at pH 2.8 – 3 (Jones, 1999). A higher or lower pH sharply reduces the effectiveness of the Fenton's reagent. At low pH, the complexation of the Fe^{3+} with hydrogen peroxide is inhibited, while at a high pH ferric ion precipitates as ferric hydroxide catalyzing decomposition of hydrogen peroxide.

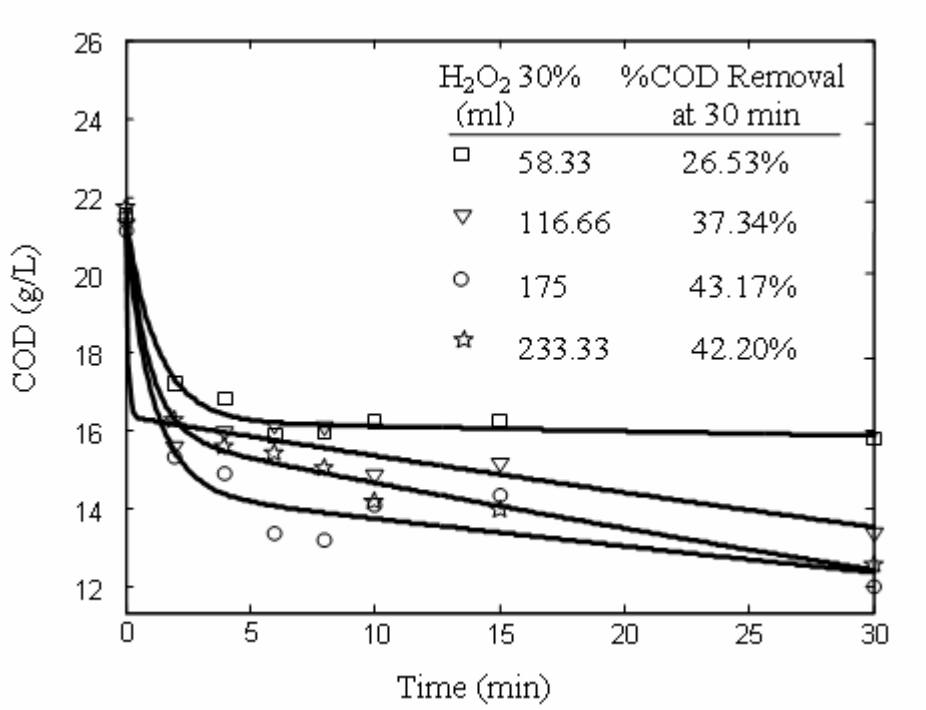


Figure 4.4 Effect of Hydrogen peroxide concentration on DEA degradation {16000 ppm DEA, 8 g $FeSO_4;7H_2O$ at pH 3 at four different H_2O_2 concentration }.

Zhang et al (2006) reported that optimum pH of the treatment of landfill leachate by Fenton's reagent was 2 – 3.5. The removal efficiency decreased in the pH higher than 3.5. Hickey et al. (1995) found the optimum pH of 3.0 in their work on degradation of atrazine using Fenton's reagent.

In this study, the best pH for MEA and DEA was 3. The influence of pH on MEA and DEA degradation using Fenton's reagent is presented in Figure 4.5 and Figure 4.6, respectively.

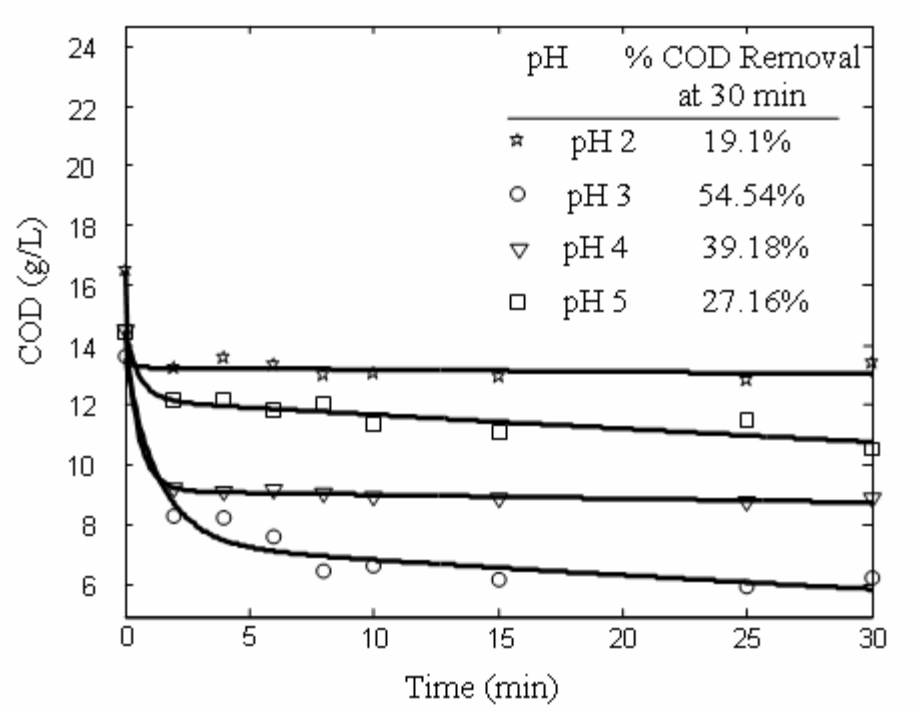


Figure 4.5 Effect of pH on MEA degradation {(16000 ppm MEA: 8 g $FeSO_4$;$7H_2O$, 175 ml H_2O_2 30% at different pH: 2 - 5)}

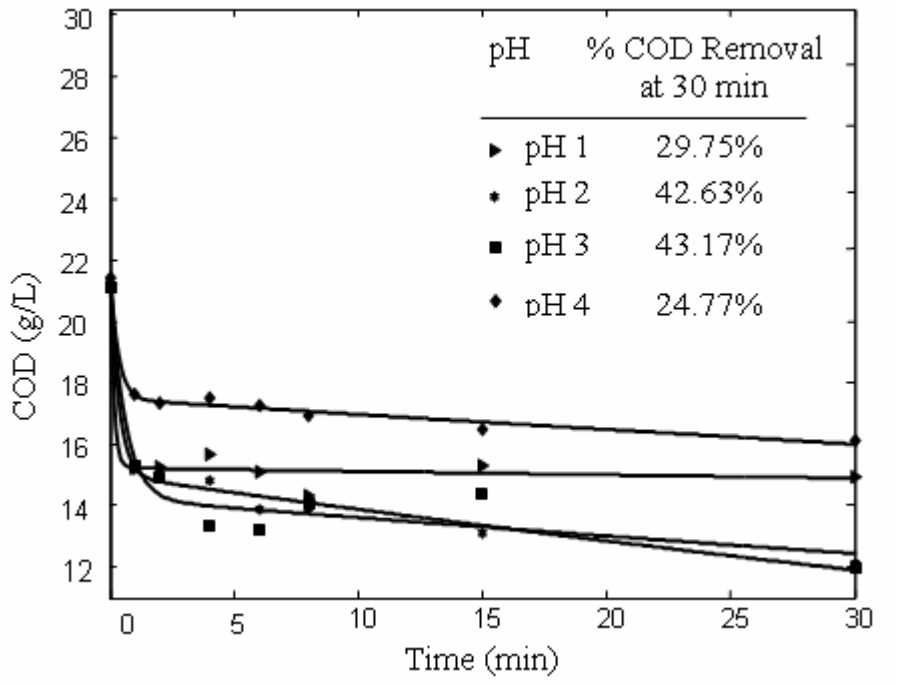


Figure 4.6 Effect of pH on DEA degradation {(16000 ppm DEA: 8 g $FeSO_4$;$7H_2O$, 175 ml H_2O_2 30% at different pH: 1-4)}

4.1.4 Effect of $FeSO_4;7H_2O$ Dosing

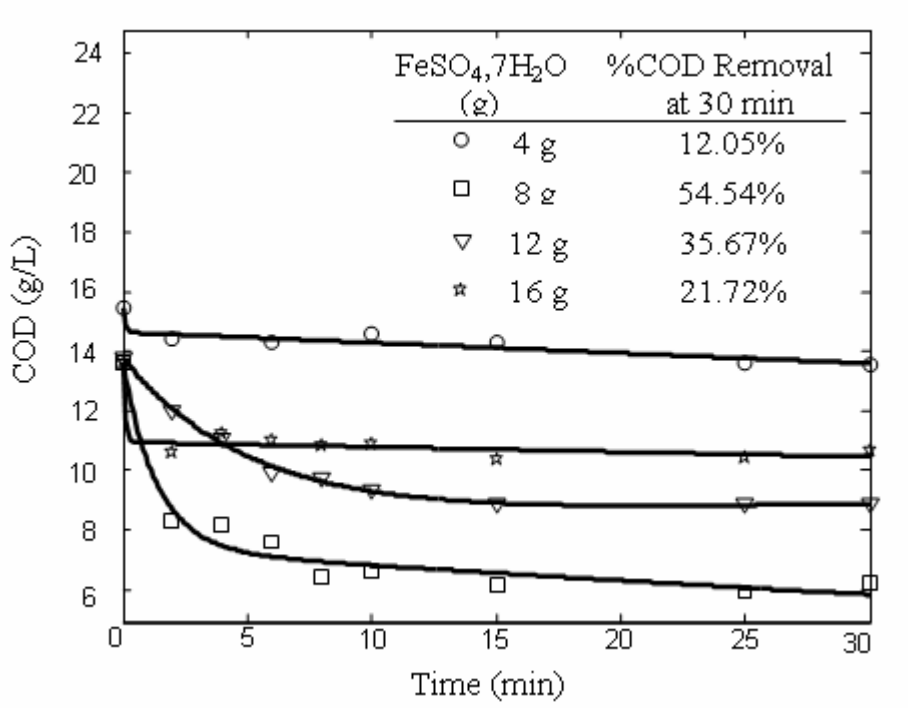


Figure 4.7 Effect of $FeSO_4;7H_2O$ on MEA degradation{(16000 ppm DEA: 175 ml H_2O_2 30% at pH 3) at different amount of $FeSO_4;7H_2O$: 4g, 8g, 12g and 16g, respectively)}

The effect of $FeSO_4;7H_2O$ dosing was studied at four concentrations of $FeSO_4;7H_2O$. The experiment was performed at an initial amine concentration of 16000 ppm and constant H_2O_2 addition of 175 ml at pH 3. Low dosage of 4 gram $FeSO_4;7H_2O$ caused a low COD removal. It was 12% for MEA and 34.4% for DEA. Increasing the amount to 8 gram, COD removal increased to 54.5% for MEA and 43.2% for DEA. However, a still higher $FeSO_4;7H_2O$ dosage more than 8 gram (12 and 16 gram) was not of help to increase the COD removal. It is well identified that a high concentration of $FeSO_4;7H_2O$ also has scavenging action on the hydroxyl radical (see Equation 2.2). The change of COD degradation at different $FeSO_4;7H_2O$ versus time is depicted in Figure 4.7 for MEA and Figure 4.8 for DEA.

Although an optimum $FeSO_4;7H_2O$ dosage on DEA degradation was 8 gram, but the COD removal at 30 minute almost constant for both experiment (see Figure 4.8). An intensive work to study this effect may need for extent work from this study.

Lodha B and Chaudary S (2007) reported the same result that the degradation of dye by Fenton's reagent had critical concentration. Low ferrous ion gave low removal and a still higher ferrous ions concentration after the critical concentration would decrease the removal of dye.

4.1.5 Stoichiometric amounts of H_2O_2 and $FeSO_4;7H_2O$

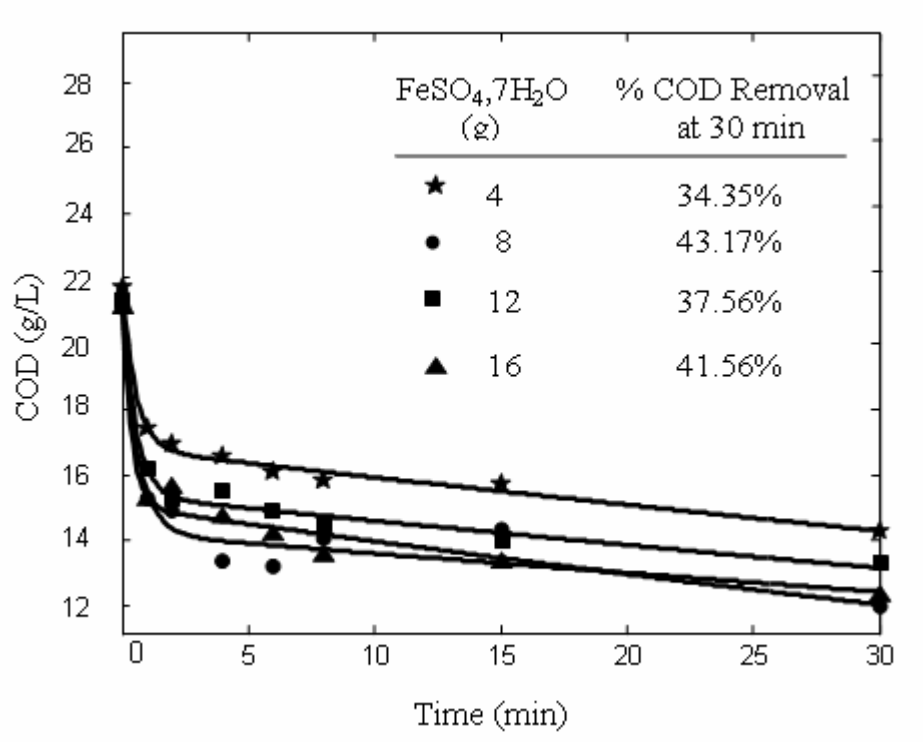


Figure 4.8 Effect of $FeSO_4;7H_2O$ on DEA degradation{(16000 ppm DEA: 175 ml H_2O_2 30% at pH 3) at different amount of $FeSO_4;7H_2O$: 4g, 8g, 12g and 16g, respectively)}

The degradation of alkanolamine was not complete even in excess of H_2O_2 which is the source of hydroxyl radical. An experiment was conducted to study the

behavior if stoichiometric amount of reagent is used. The stoichiomentic amount of reagent was calculated based on theoretical amount of hydroxyl radicals enough to remove the COD on the feed solution. In the 5000 mg/L COD (700 ml) of DEA needs 44.7 ml H_2O_2 30% and 121.6 g $FeSO_4;7H_2O$. The experiment was performed at pH 3.

Figure 4.9 shows that only 60% COD was removed. As in other cases, the degradation was completed in a few minutes. The reaction consumes about 98% of H_2O_2. Only traces of un-decomposed H_2O_2 were remaining. This shows that the hydroxyl radicals form very fast in the initial time of reaction and then a part of it is lost without taking part in the oxidation process. In addition, the partially degraded product like organic acid degrade slower even in strongly oxidizing environment (Jones, 1999).

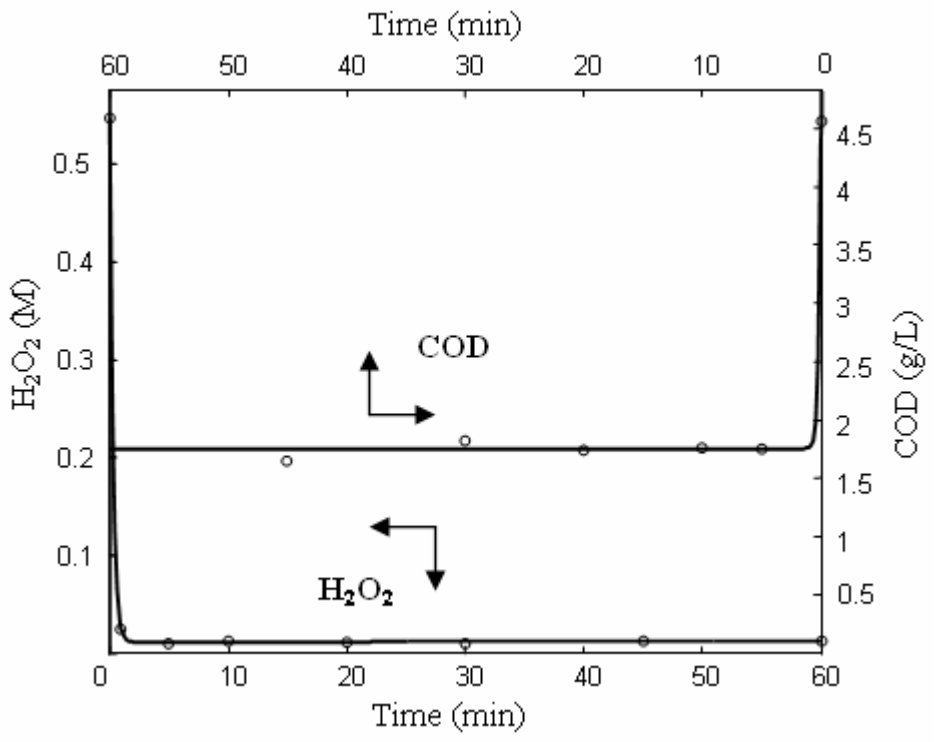


Figure 4.9 COD and H_2O_2 profile on equivalent concentration of DEA and Fenton's reagent with one time addition of Fenton's reagent (5000 COD (700 ml) + 44.7 ml H_2O_2 30% + 121.6 g $FeSO_4;7H_2O$ pH 3).

Oxidation of partially degraded DEA using Fenton's reagent was also observed. Fresh Fenton's reagent was added and COD concentration by time was measured. Degradation of partially degraded DEA by hydroxyl radical (Fenton's reagent) is less than that for 'pure' DEA. Only 17.02% COD removal achieved from about 5700 mg/L COD. Figure 4.10 shows the COD evolution vs. time for this experiment.

In a different experiment, degradation of glycine (one of byproducts which was identified) oxidation using Fenton's regent was as well preformed. Figure 4.11 shows the glycine degradation by Fenton's reagent. It was observed that glycine removal was lower compared to the MEA.

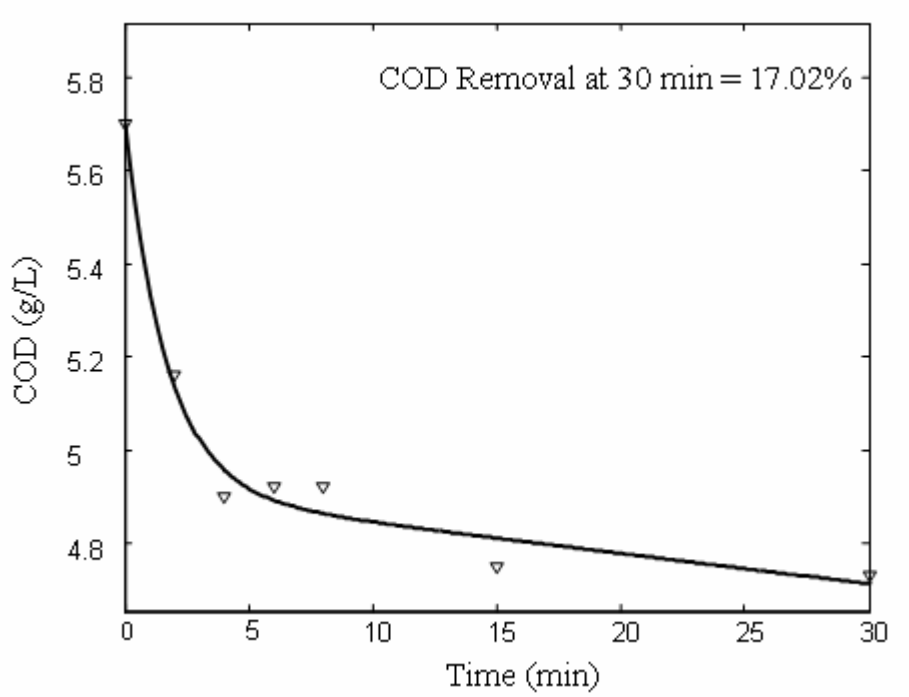


Figure 4.10 Partially Degraded DEA with Fresh Fenton's Reagent (6050 mg/L COD)+ 26.5 ml H_2O_2 30 % + 1 gram $FeSO_4;7H_2O$ pH 3)

4.1.6 Different Modes of Addition of Fenton's Reagent

A few of experiments on Fenton's degradation with different modes of addition of the reagents were conducted to study the profile of COD degradation and

H_2O_2 concentration in the liquid versus time. The modes of addition are one time addition, continuous addition, and semi continuous addition. In one time addition, $FeSO_4;7H_2O$ and H_2O_2 are charged together at the beginning. While in continuous addition, $FeSO_4;7H_2O$ and H_2O_2 together added over the reaction time. In the semi continuous addition either of $FeSO_4;7H_2O$ or H_2O_2 was added continuously and the other one was added at the initial time. Flow rate of all reagents added continuously was depending on the total designed volume of reagent divided by total oxidation time.

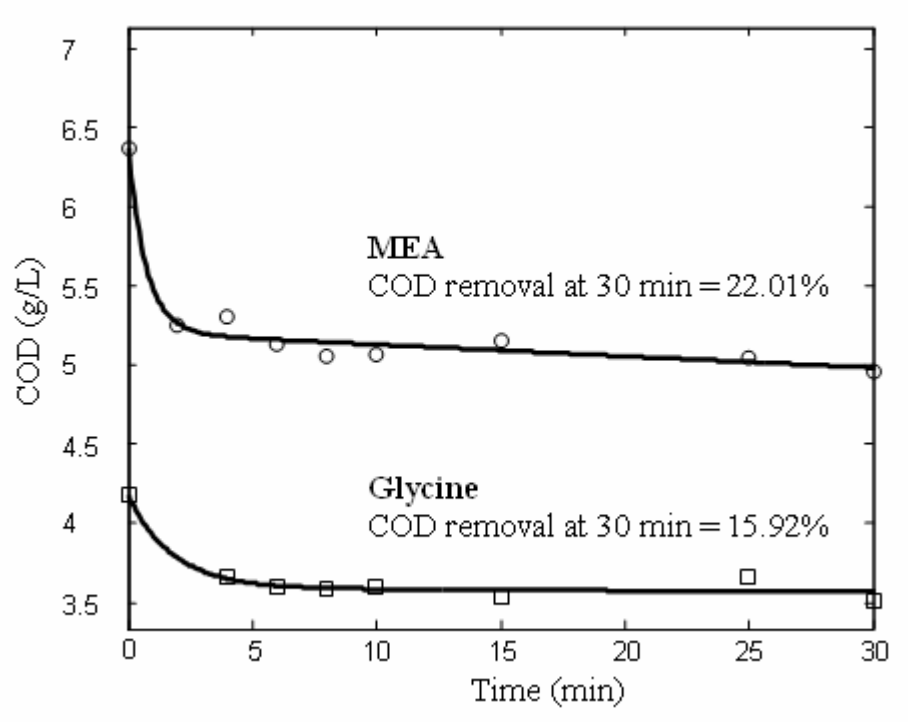


Figure 4.11 Degradation of Glycine compared to MEA {(5000 ppm Glycine + 54.8 ml H_20_2 30% + 2,5 g $FeSO_4,7H_20$ pH 3) and (5000 ppm MEA + 54.8 ml H_20_2 30% + 2,5 g $FeSO_4,7H_20$ pH 3)

In this study, one time addition of Fenton's reagent having COD and H_2O_2 shows very fast decrease in COD at the initial time of reaction and then slows down. Reaction was complete only in a few minute. An exponential profile follows the

degradation of COD and H_2O_2. The one time addition profiles are shown in Figure 4.9. Meanwhile for continuous addition of Fenton's reagent, the COD behavior follows an exponential profile and H_2O_2 profile follows a quadratic shape. The continuous addition patterns of COD and H_2O_2 against time are depicted in Figure 4.12, 4.13, 4.14 and 4.15. A different pattern for COD was identified when the reagent was stoichiometric. The degradation of COD follows a linear pattern, Figure 4.12. For semi continuous addition of Fenton reagent, the COD and H_2O_2 behavior follows an exponential shape. It was similar to the pattern for one time addition, but the degradation rate was slower.

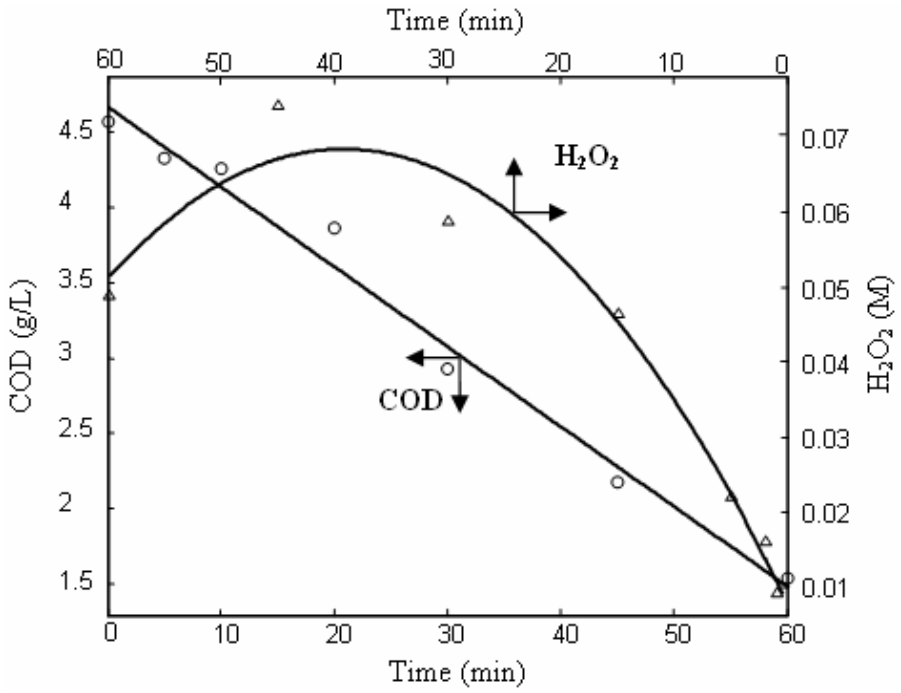


Figure 4.12 COD and H_2O_2 profile on equivalent concentration of DEA and Fenton's reagent with continuous addition of $FeSO_4;7H_2O$ (5000 COD (700 ml) + 44.667 ml H_2O_2 30% + 121.633 g $FeSO_4;7H_2O$ pH 3).

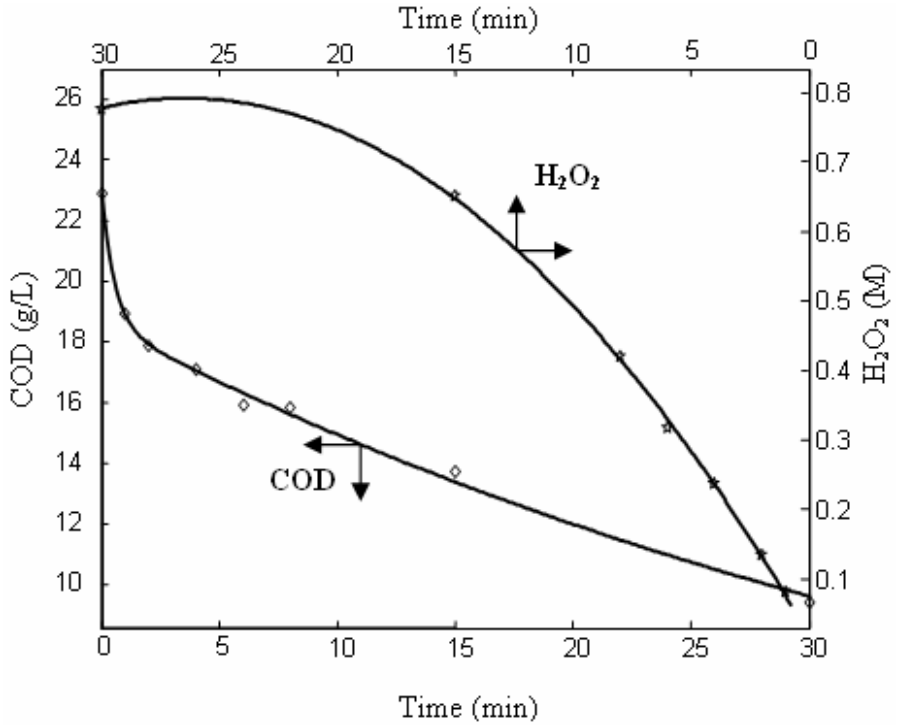


Figure 4.13 COD and H_2O_2 profile when H_2O_2 and $FeSO_4;7H_2O$ continuous for 30 minute (16000 ppm DEA; 175 ml H_2O_2 30% ; 16 g $FeSO_4;7H_2O$ pH 3)

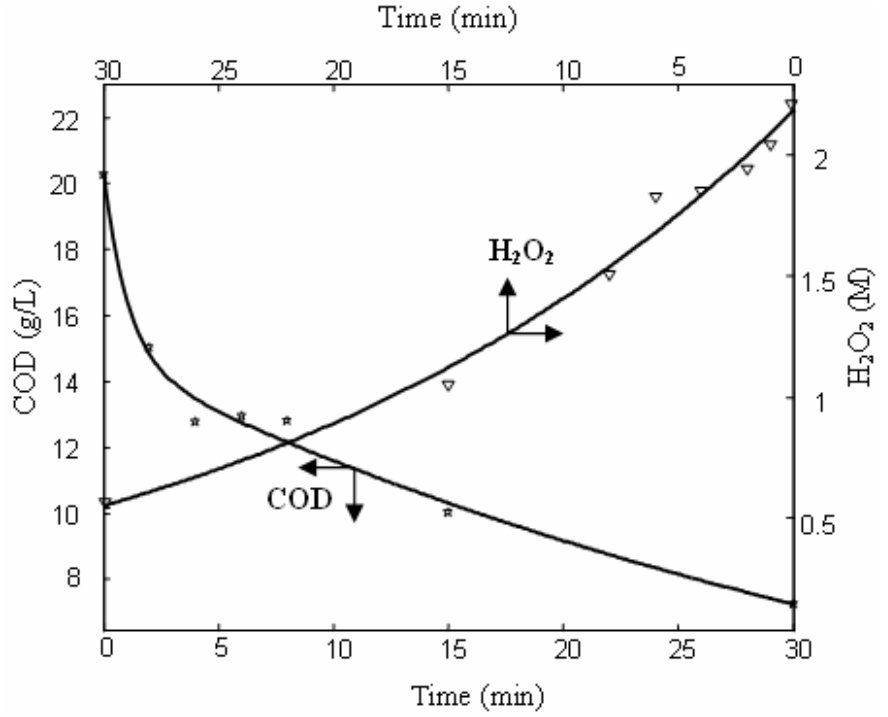


Figure 4.14 COD and H_2O_2 profile when H_2O_2 one time addition in the beginning and $FeSO_4;7H_2O$ continuous for 30 minute (16000 ppm DEA; 175 ml H_2O_2 30% ; 16 g $FeSO_4;7H_2O$ pH 3)

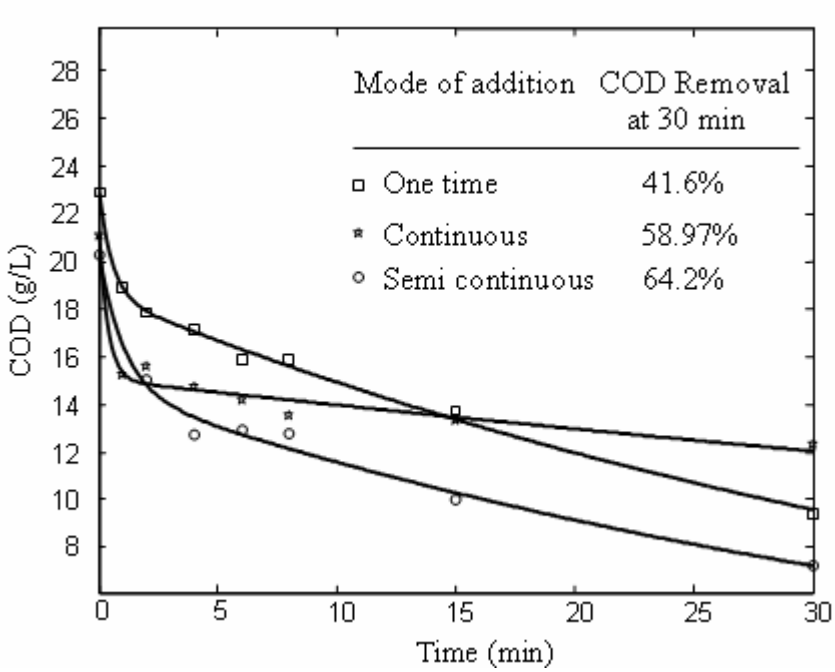


Figure 4.15 Effect of different addition mode of Fenton's reagent (16000 ppm DEA; 175 ml H_2O_2 30%; 16 g $FeSO_4;7H_2O$ pH 3)

The continuous and semi continuous modes of addition gave better removal. In the identical experimental conditions (16000 ppm DEA; 175 ml H_2O_2 30%; 16 g $FeSO_4;7H_2O$ pH 3), COD removal for semi continuous addition was 64.2%, while continuous addition was 59% and one time addition was 41.6 (Figure 4.15).

Under similar condition with the MEA experiment, continuous addition of Fenton's reagent was better removal compared with the one time addition. Figure 4.16 shows the degradation course of MEA in different modes of addition of Fenton's reagent.

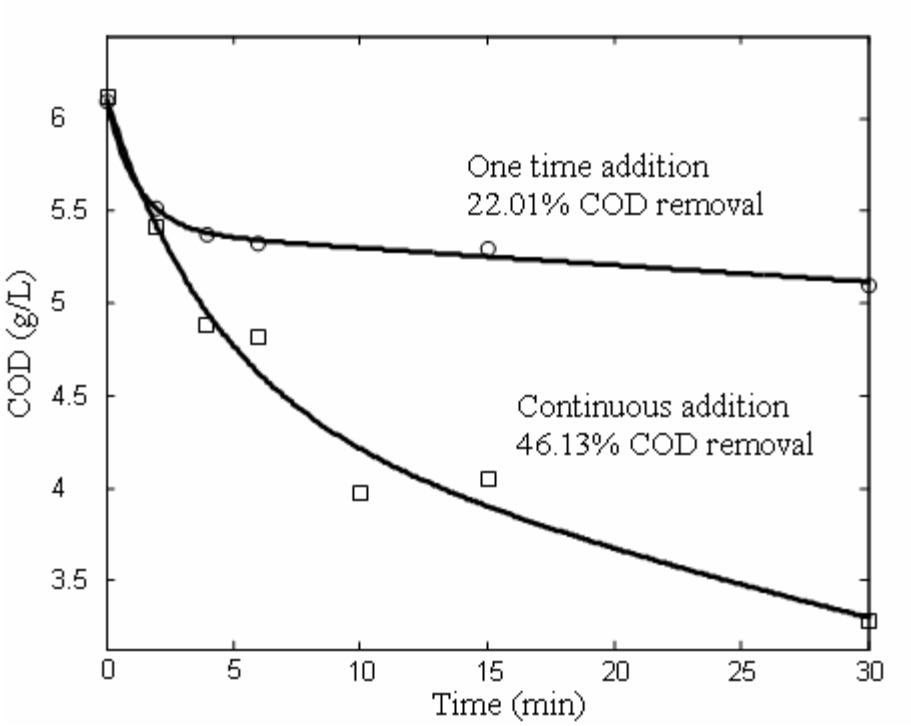


Figure 4.16 Different addition model of Fenton's Reagent (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3) run 30 minute on COD profile.

As pointed out by Casero et al (1997) adding peroxide slowly would minimize the side reaction. By this way, conversion of hydroxyl radical HO• to the much less reactive hydroperoxyl HO_2• is diminished. Therefore, effectiveness of hydroxyl radical utilization is increased. Mean while the side reactions which involve HO• or H_2O_2 and HO• scavenging usually occurs through reaction of the radical with Fe^{2+}, hydrogen peroxide or other HO• radical, according to:

$$HO\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (4.5)$$

$$HO\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet \quad (4.6)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (4.7)$$

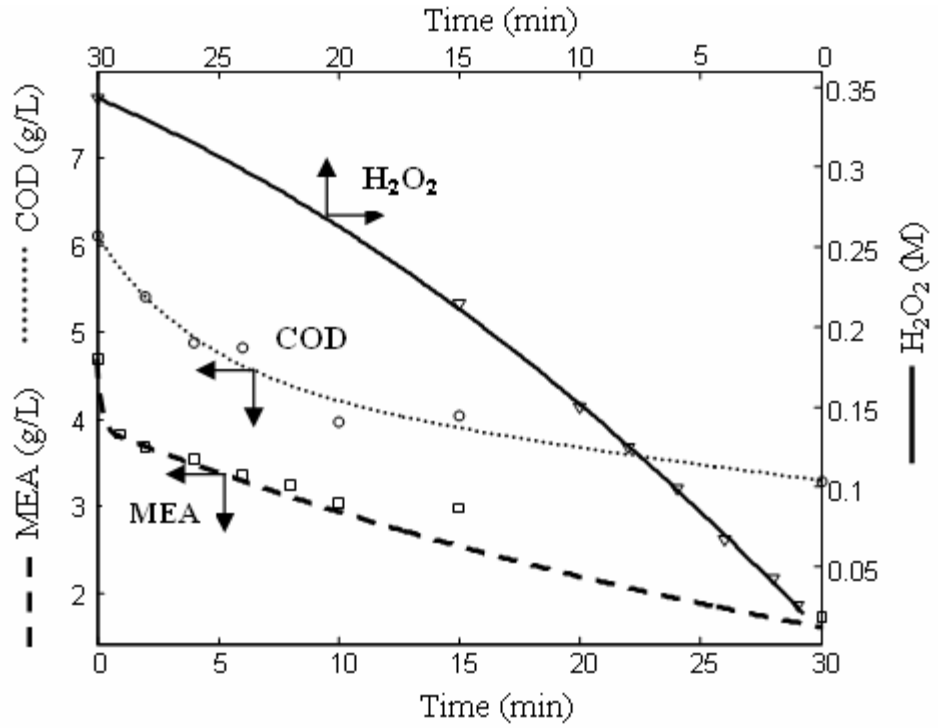


Figure 4.17 Continuous addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3)

The removal patterns of the amines for continuous addition of reagents are shown in Figure 4.17 (for MEA) and Figure 4.18 (for DEA). The patterns of COD removal and the profiles of H_2O_2 consumption are also shown along with. The initial amine concentrations and the reagent dosing are the same for both. The changes in MEA and DEA concentrations show a distinct difference –DEA disappears faster and to a larger extent than MEA–. This shows that DEA reacts faster than MEA perhaps because of the availability two α-carbons with two ethanol-amine groups in the former. COD removal is also higher for DEA. Consumption of H_2O_2 is slightly higher for MEA degradation. The disappearance pattern of DEA looks like that of a first order reaction.

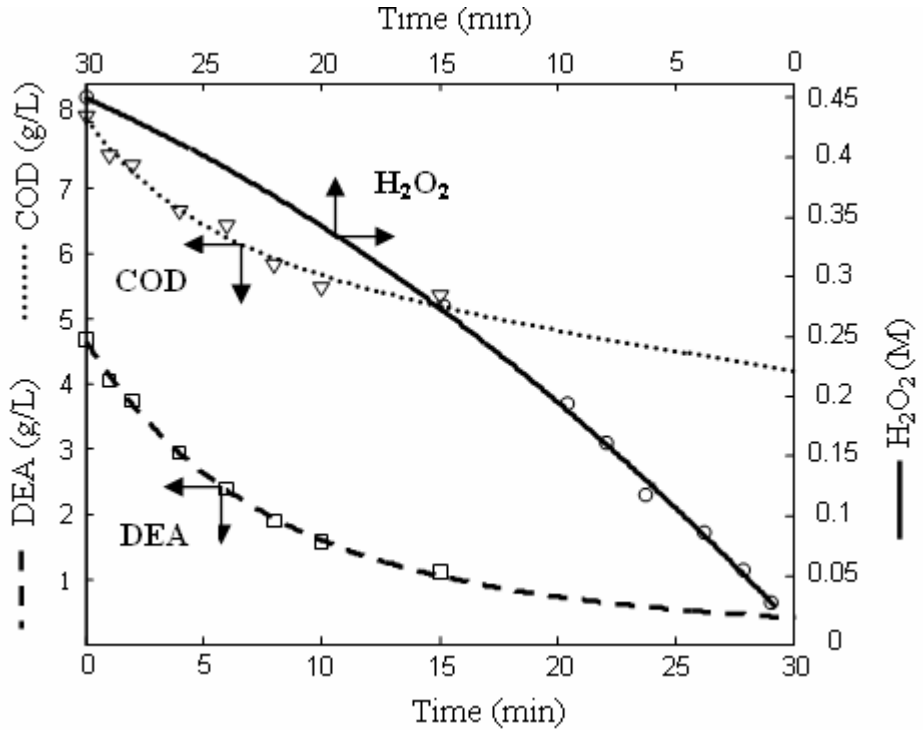


Figure 4.18 Continuous addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm DEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3)

4.1.7 Comparison of COD and TOC

The reduction profile of COD and TOC on DEA oxidation by Fenton's reagent was similar. Degradation of COD and TOC decreased fast in the initial time of reaction and than slower down. Figure 4.19 shows the corresponding of COD and TOC progress.

Oxidation of an organic compound by hydroxyl radical possibly proceed through abstraction of hydrogen atoms principal to formation of carboxylic acid. Further degradation eventually leads to CO_2 and H_2O. The presence of an organic acid such glycine has been identified in this study. The carboxylic acids are well known react slowly with hydroxyl radical. Consequently it is predictable that degradation of COD should be faster than reduction of TOC.

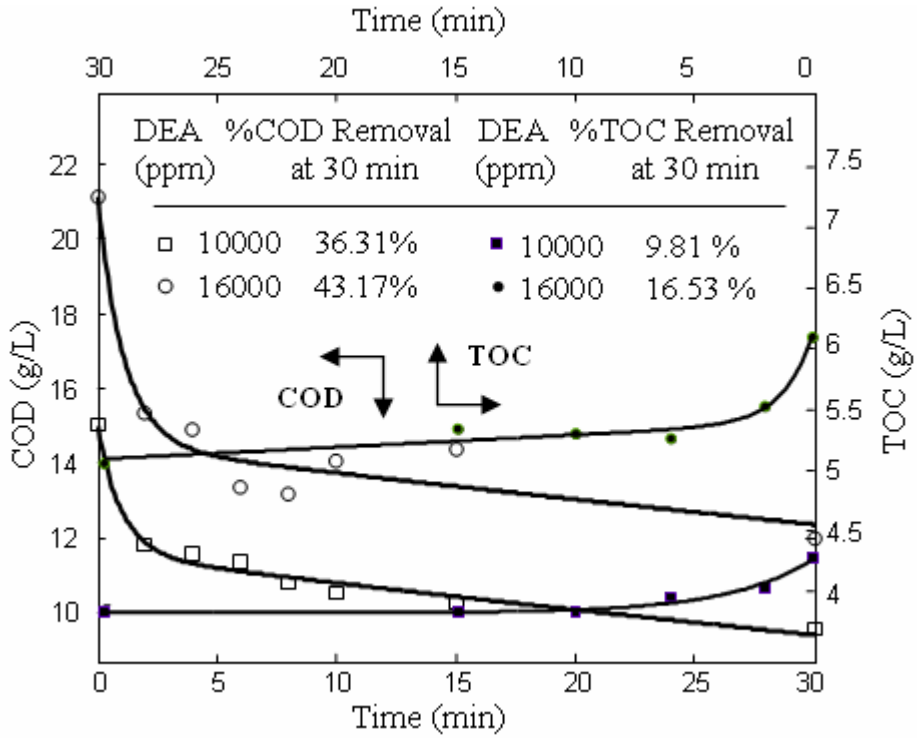


Figure 4.19 COD and TOC profile by Fenton's reagent on DEA degradation {10000 ppm and 16000 ppm DEA initial concentration}.

The measurement was conducted in two different initial concentrations of DEA. Those are 10000 ppm and 16000 ppm of DEA under identical condition. The reductions of COD were 36.3% and 43.2% respectively. While the TOC reductions were 9.8% and 16.53% respectively.

Since the COD removed by Fenton treatment mostly oxidize H atoms and the C atoms is slow to remove by Fenton's reagent, hence the biological oxidation is to be exploited in order to achieve of COD standard on wastewater effluent.

4.1.8 Degradation Intermediates after Fenton Oxidation

Oxidation of an organic compound such as MEA and DEA by hydroxyl radical may proceed through abstraction of hydrogen atoms or lead to the formation of carboxylic acids which are further degraded to smaller fragment and eventually to CO_2 and H_2O when enough hydroxyl radical is available. Under the acidic pH conditions, the amino group is protonated to certain level, which might deactivate the α-CH bond. Consequently, a further located C- atom of the amine is oxidized. Thus an amino-acid is a possible product.

An attempt to identify the degradation intermediate products after Fenton's treatment was made. HPLC and FTIR were used to characterize the intermediates. The chromatogram (Figure 4.20) shows a few peaks. One of the peaks is of glycine that appears at 4 minute. Peak for MEA appears at 5.1 minute, while peak for DEA appears at 5.4 minute. FTIR spectrums give stronger evidence about functional group of partially degraded alkanolamine. Infrared spectra of glycine and partially degraded alkanolamine were similar. The infrared spectra of partially degraded amine (DEA) also gave a similar output. It indicates the presence of a common component. A carbonyl (C = O) peak appears around 1620 - cm^{-1} [(C = O) as carboxylic acid] and bonding between C and N appear on the center of peak 1080cm^{-1}[(C – N) as aliphatic amine]. The sample was in aqueous solution and therefore a broad peak of water (H_2O) appears in the region between 3000 – 3700 cm^{-1} and covering many peaks for N – H (amine), O – H (carboxylic acid) and O – H (alcohol) that should be appear on that region. In addition, peaks with center 2090 cm^{-1} appear as interaction of COO^- from carboxylic group and N^+ from ammonium group [Silverstein et al (2005); Coates (2000)]. Infrared spectra of partially degraded MEA and DEA depicted in Figure 4.22 and 4.23.

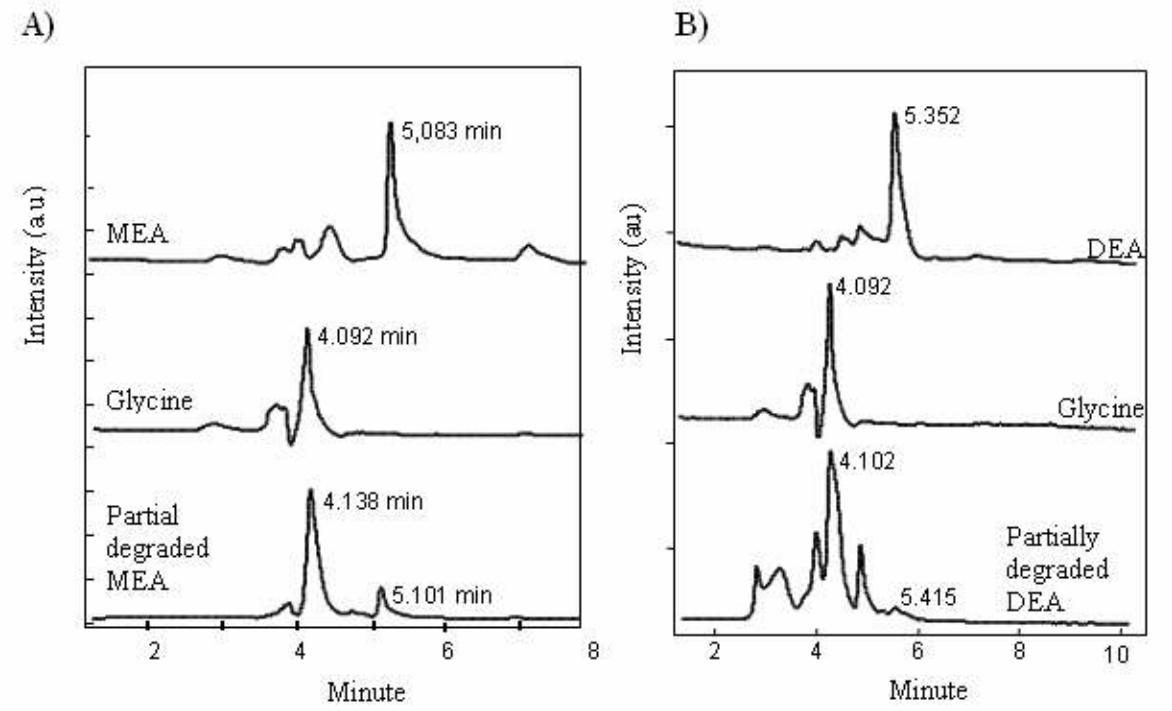


Figure 4.20 A) Chromatogram of MEA, partially degraded MEA and Glycine.
B) Chromatogram of DEA, partially degraded DEA and Glycine.

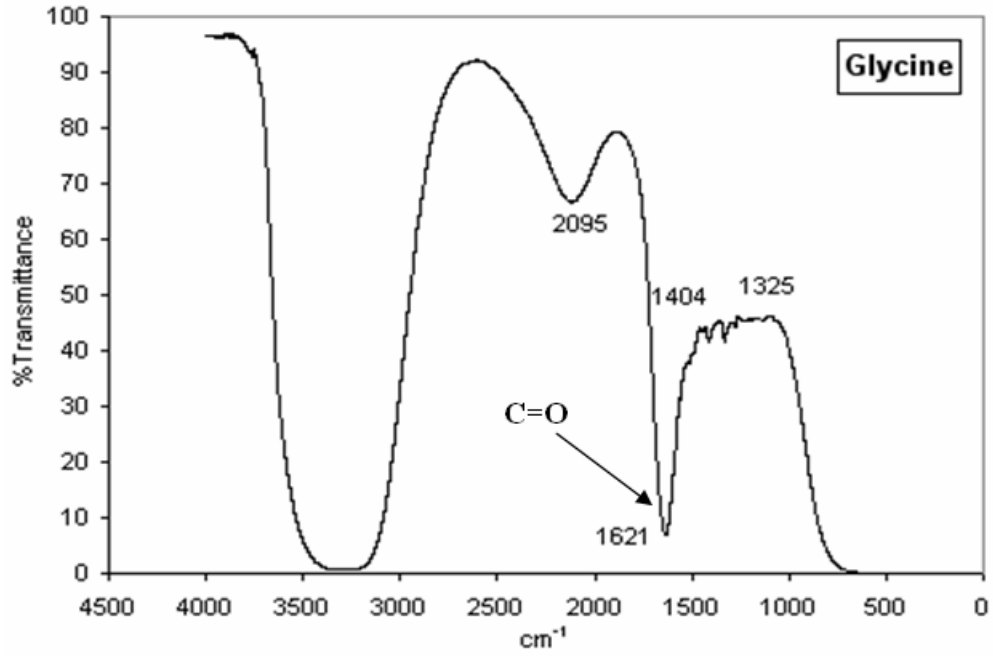


Figure 4.21 Infrared spectra of Glycine

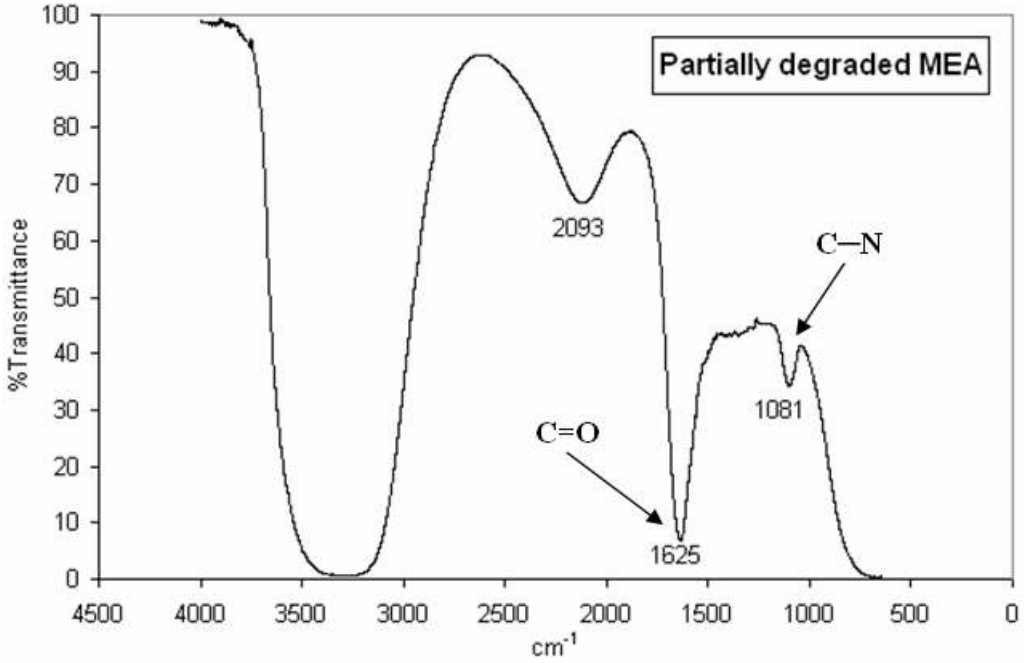


Figure 4.22 Infrared spectra of partially degraded MEA

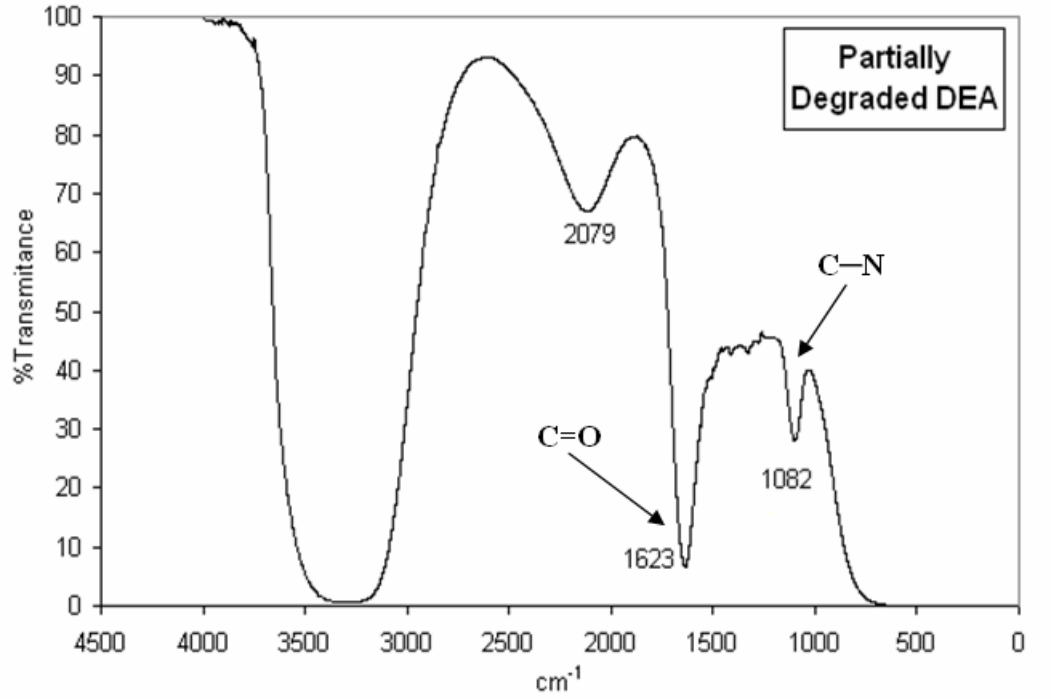


Figure 4.23 Infrared spectra of partially degraded DEA

4.1.9 A simplified Rate Model for Mineralization

In order to develop a rate equation we propose the following steps of generation and reaction of HO• groups. Here S stands for the substrate.

$$H_2O_2 + Fe^{2+} \xrightarrow{k_1} HO\bullet + Fe(OH)^{2+} \quad (4.8)$$

$$H_2O_2 + Fe^{3+} \xrightarrow{k_2} HO_2\bullet + Fe^{2+} + H^+ \quad (4.9)$$

$$H_2O_2 + HO\bullet \xrightarrow{k_3} HO_2\bullet + H_2O \quad (4.10)$$

$$Fe^{3+} + HO_2\bullet \xrightarrow{k_4} O_2 + Fe^{2+} + H^+ \quad (4.11)$$

$$S + HO\bullet \xrightarrow{k_5} \text{degradation products} \quad (4.12)$$

$$HO\bullet + Fe^{2+} \xrightarrow{k_6} Fe^{3+} + OH^- \quad (4.13)$$

$$S + HO_2\bullet \xrightarrow{k_7} \text{degradation products} \quad (4.14)$$

Since the degradation rate is very fast in the beginning and most of the Fenton mineralization occurs within a few minutes of addition of the reagents, determination of the initial rate constant assumes greater practical importance. Also quite a few species involved in the above reaction scheme are not present at the beginning and since HO• is the primary oxidizing species in the overall process, we consider the reactions (4.8), (4.10), (4.12) and (4.13) only in this simplified analysis. ‘A pseudo-steady state’ balance of the rates of generation and disappearance of the HO• radicals leads to following expression for its concentration.

$$[HO\bullet] = \frac{k_1[H_2O_2][Fe^{2+}]}{k_3[H_2O_2] + k_5[S] + k_6[Fe^{2+}]} \tag{4.15}$$

where k_1, k_3, k_5 and k_6 are the rate constants for reaction (4.8), (4.10), (4.12) and (4.13) respectively. The initial rate of mineralization of the substrate can be written as

$$[r_s]_0 = k_5[S]_0[HO\bullet]_0 = k_5[S]_0 \frac{k_1[H_2O_2]_0[Fe^{2+}]_0}{k_3[H_2O_2]_0 + k_5[S]_0 + k_6[Fe^{2+}]_0} \tag{4.16}$$

where the subscript 0 denotes zero time. The equation can be rearranged to

$$\left\{\frac{k_1[H_2O_2]_0[Fe^{2+}]_0[S]_0}{[r_s]_0} - [S]_0\right\} = \frac{1}{k_5}\left\{k_3[H_2O_2]_0 + k_6[Fe^{2+}]_0\right\} \tag{4.17}$$

$$\Rightarrow \qquad Y = \frac{1}{k_5}X \tag{4.18}$$

The above equation can be used to determine the degradation rate constant k_5 using the experimental data on the initial rate of degradation when only the concentration of added H_2O_2 is varied keeping constant those of substrate (S) and of Fe^{2+}. The rate constant k_1, k_3 and k_6 for the reaction (4.8), (4.10) and (4.13) respectively are available in the literature (Burbano et al., 2005; Neyens and Baeyens, 2003; Kang et al., 2002). We have taken the following values of the above rate constants: k_1 = 70, k_3 = 3×10^7 and k_6 = 3×10^8 $M^{-1}s^{-1}$ respectively. A plot of the quantity Y against X [see Eq(4.18)] should produce a straight line passing through the origin with a slope equal to the inverse of the constant, k_5. The plot of the experimental data in the form of equation (4.18) gives a straight line shows in Figure4.24. From the slope of the line, the rate constant for mineralization is estimated to be k_5 = 2.9×10^6 $M^{-1}min^{-1}$ = 4.8×10^4 $M^{-1}s^{-1}$. It is to be noted that we have taken the calculated rate of degradation as the rate of removal of COD or, in other words, the rate of complete oxidation of the substrate. It may be considered to be a

lumped representation of the process of degradation of the substrate as well as the intermediates. As a comparison, consider that the second-order rate constant with HO• of the similar compound ethylamine is around 5×10^9 $M^{-1}s^{-1}$ (Buxton et al., 1988), which additionally suggests that the measured k_7 is not the rate constant of the reaction between the Fenton's reactive species and MEA. Although the degradation data on MEA fitted reasonable well in the above model, our attempt to do that was not quite successful in the case of DEA. This may be due to a difference in mechanism of attack of the substrate by the HO• radical. Development of a model suitable for both the amines may perhaps be taken up as an extension of this work.

The experimental data on COD removal for same initial amine concentration (16000 ppm) and ferrous sulfate dose (8g) in 800 ml reaction mixture but with different H_2O_2 dose [54.8, 116.67, 175 and 233.33 ml; 30% w/w) as shown in Figure 4.3 are used to calculate the initial rate of degradation. The reduction of COD over first two minutes was used for calculation of r_0.

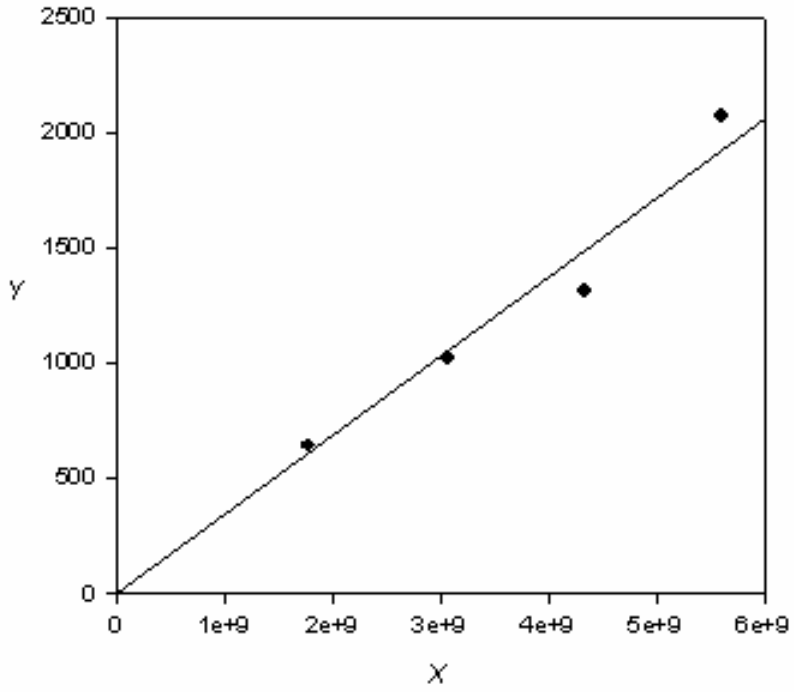


Figure 4.24 Plot of *Y* vs *X*, Eq 4.15

4.2 Biological Oxidation as Post-treatment

4.2.1 Biological Oxidation

The degradation experiment of alkanolamines by Fenton oxidation shows that not more than about 65% of COD could be removed even with a high concentration of Fenton's reagent and manipulating different modes of addition of Fenton's reagent. In reality, Fenton treatment is suitable for fractional degradation of organic compounds followed by biological oxidation. This partially degraded compound is simpler and of low toxicity fragments compared to the pure compound. Hence, it could be easy to degrade by microorganism. Many researchers reported this technique. Alaton and Teksoy (2005) studied the effectiveness of Fenton's reagent to pre treat acid dye-bath effluents of a textile industry before conventional biological treatment. Solozhenko et al. (1995) could successfully degrade the contaminants in wastewater from dyeing and finishing industries. Biodegradation of a pharmaceutical wastewater was greatly improved by Fenton's treatment as reported by Tekin et al. (2006) since of breakdown of the organics into smaller fragments makes it amenable to normal biological oxidation.

Accordingly, a biological experiment was set up to study the biodegradability of partially degraded amine. In the discussion below, all parameters which were studied in the biological oxidation study are explained.

Partially degraded amine after about 40% COD elimination was tested for biological oxidation using activated sludge collected from the wastewater treatment plant at Universiti Teknologi Petronas (Malaysia). Biodegradation studies were conducted in an aerobic batch bioreactor according to the materials and methods specifications in the Zahn-Wellens/EMPA Test of the US Environmental Protection Agency (EPA) method OPPTS 835.3200. Test compounds were added in separate reactors to achieve an initial COD of approximately 1000 mg/L and seed bacterial sludge from an activated sludge was added to the reactors to achieve initial biomass

concentration of approximately 1000 mg/L MLVSS. The biological oxidation of partially degraded amine, untreated amine and of the reference compound were done in parallel. The COD removal versus time is plotted to show the degradation profile of each test compound compared to the reference. Figure 4.25 shows that the COD removal of partially degraded amine, either MEA or DEA, amounts to more than 85% within 12 hours. MEA needs 24 hours and DEA needs more that 50 hours to reach 90% elimination. At the same time, the reference compound was 70% degraded within 2 weeks. The degradation rate of untreated 'pure' amine was slower. It was because of longer acclimatization time.

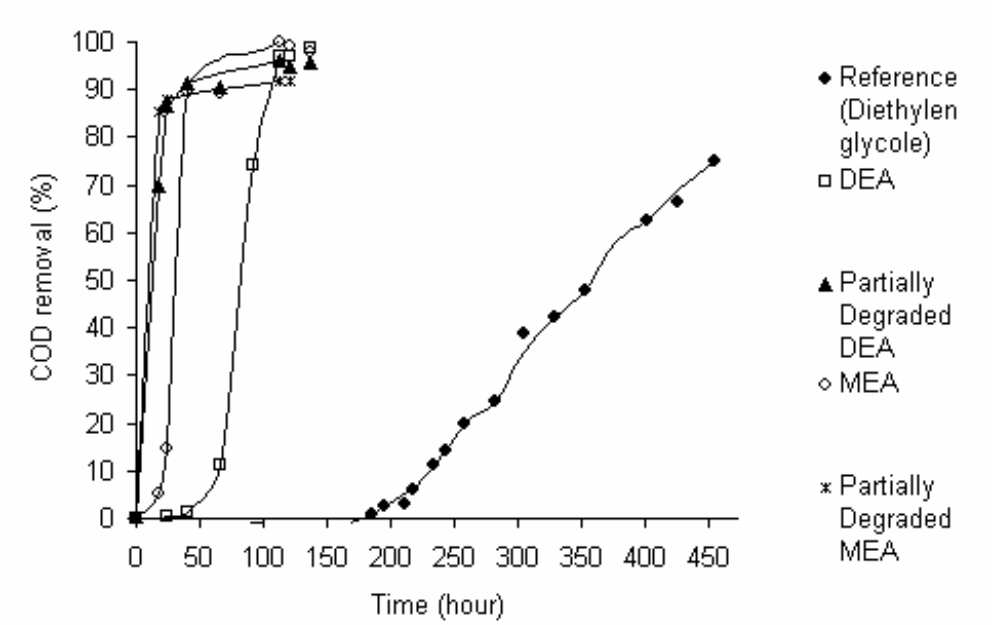


Figure 4.25 Biodegradability of partially degraded amine (MEA and DEA) and pretreatment amine (MEA and DEA) compare with reference. Initial COD is 1000 mg/L and initial biomass concentration is 1000 mg/L MLVSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

A separate experiment was conducted to study the degradation parameters of partially degraded amine. Initial COD was about 1000 mg/L and initial biomass concentration was about 100 mg/L MLSS. The change of biomass and substrate concentration with respect to time for both untreated amine and partially degraded amine are plotted in Figure 4.26 for MEA and Figure 4.27 for DEA.

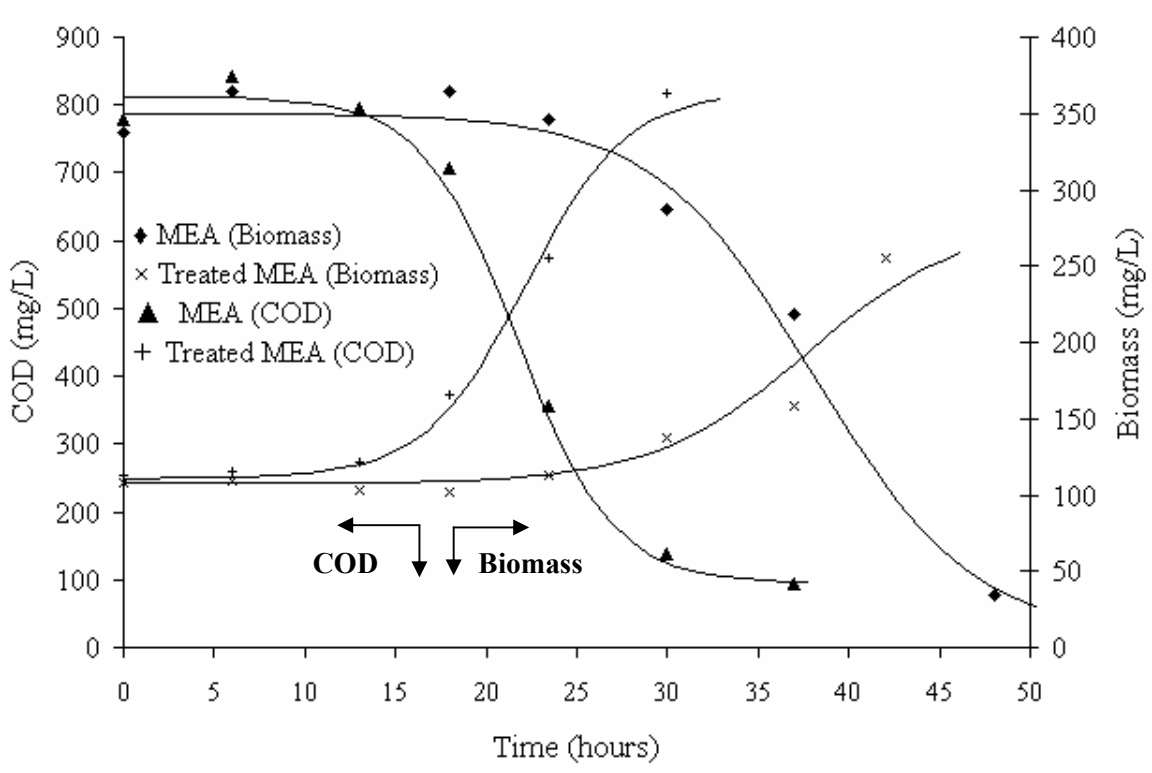


Figure 4.26 COD degradation and MLSS profile in the biological oxidation of partially degraded MEA and pure MEA. Initial COD is 1000 mg/L and initial biomass concentration is 100 mg/L MLSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

Based on visual examination of the plots it is clear that biomass acclimatization was much faster in partially degraded amine compared to untreated alkanolamines. It was indicated by the duration of the lag phase which was reduced by about 50% from 24 hours to about 12 hours for MEA and reduced from 35 hours to 20 hours for DEA. The duration for maximum COD removal was also reduced from 50 hours in untreated MEA to about 33 hours in partially degraded MEA. However, the ultimate COD removal (substrate utilisation) does not seem to have been affected by Fenton's oxidation. Nonetheless, the biomass yield appears to be much increased in partially degraded MEA.

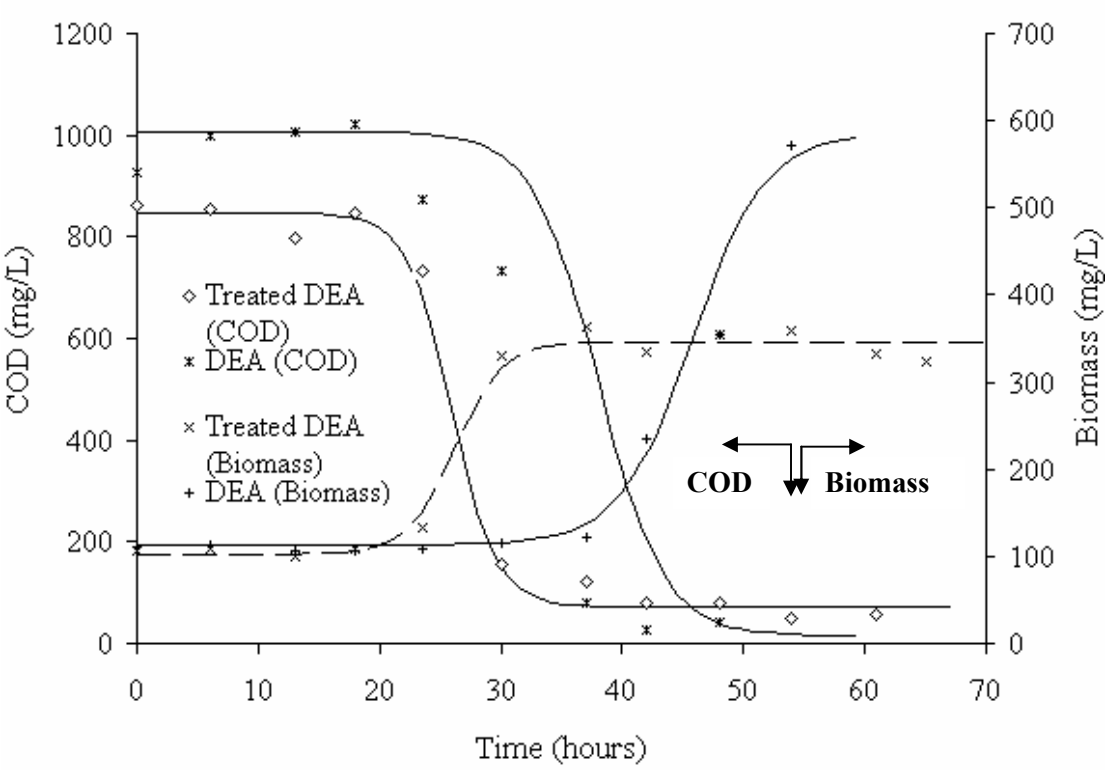


Figure 4.27 COD degradation and MLSS profile in the biological oxidation of partially degraded DEA and pure DEA. Initial COD is 1000 mg/L and initial biomass concentration is 100 mg/L MLSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

Since MEA contains the elements C, H, O and N, oxidation of alkanolamines by hydroxyl radical HO• is expected to transform the organic nitrogen into NH_4^+, NO_2^- and NO_3^-. Klare et al (2000) presented a possible mechanism of amine degradation by hydroxyl radical which identified NH_3 as a product in partially degraded alakanolamine. Figure 4.28 and 4.29 shows the profile of dissolved ammonia as biodegradation proceeds. About 300 mg/L of NH_3 is present in the partially degraded MEA/DEA initially compared to negligible amounts in the untreated MEA/DEA. As biological oxidation proceeds, the concentration of ammonia increases in both untreated and pretreated MEA/DEA with higher final dissolved ammonia content in the pretreated MEA/DEA compared to untreated MEA)/DEA. These results show that ammonia is produced in substantial amounts both during Fenton's oxidation and during aerobic biological oxidation.

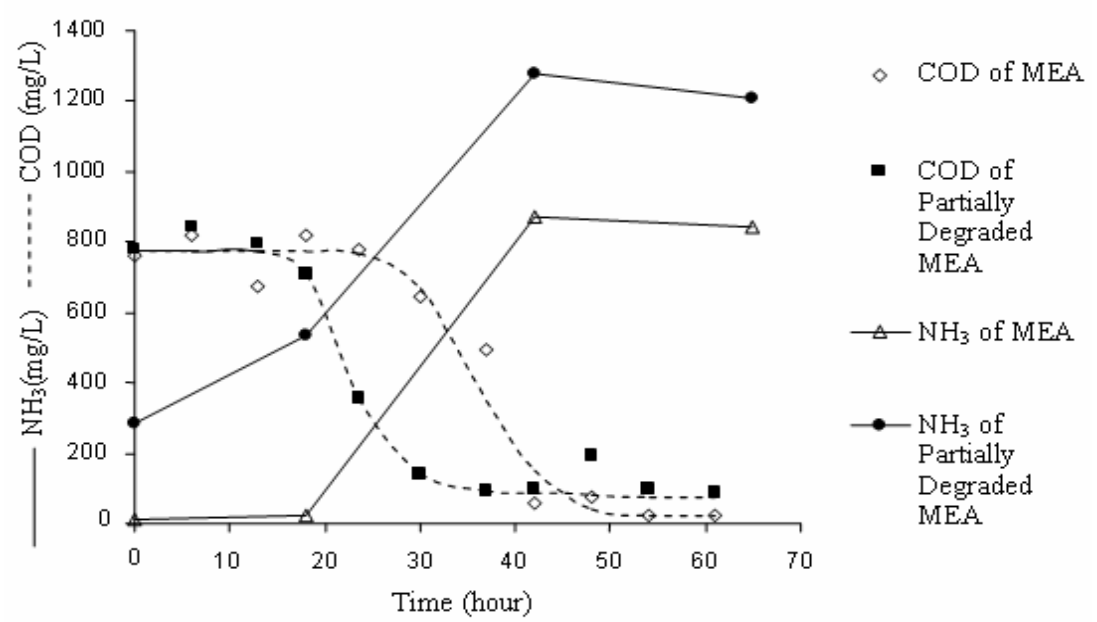


Figure 4.28 COD degradation and NH_3 profile in the biological oxidation of partially degraded MEA and pure MEA. Initial COD is 1000 mg/L and initial biomass concentration is 100 mg/L MLSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

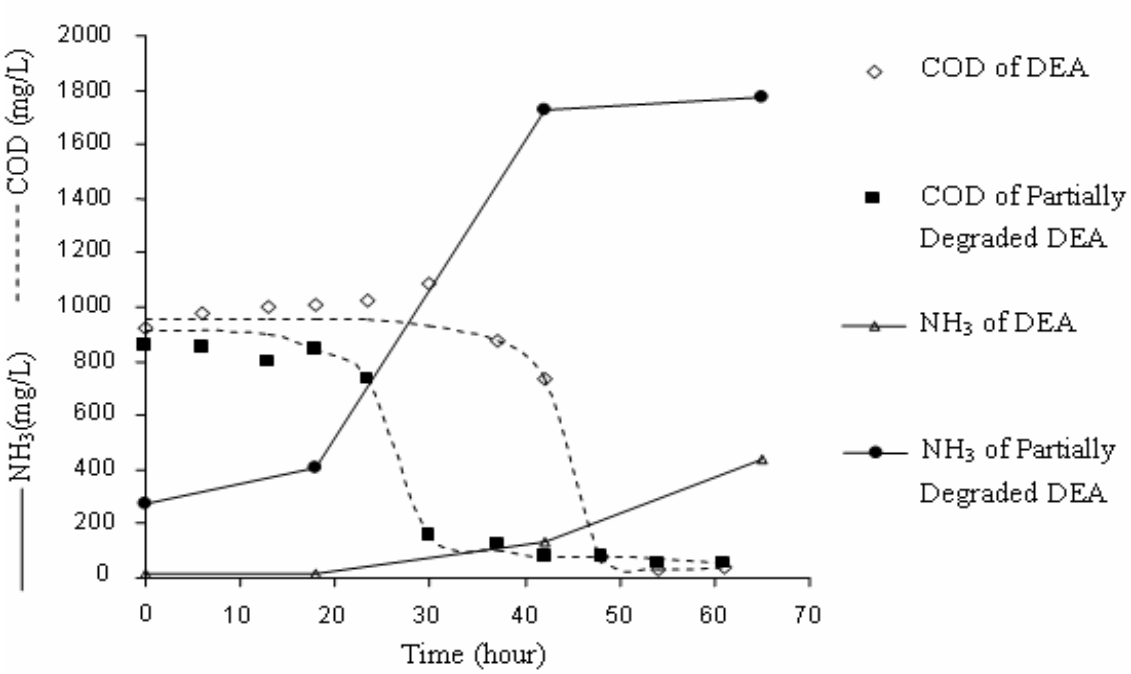


Figure 4.29 COD degradation and NH_3 profile in the biological oxidation of partially degraded DEA and pure DEA. Initial COD is 1000 mg/L and initial biomass concentration is 100 mg/L MLSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

4.2.2 Kinetics of Biological Oxidation

The biomass growth rate and substrate utilization rate are generally described according to equations (4.19) and (4.20) that form the basic of the Monod model of biological degradation of organics in an aqueous medium.

$$\frac{dX}{dt} = \mu X \tag{4.19}$$

$$\frac{dS}{dt} = kX \tag{4.20}$$

where X, S, μ and k represent the biomass concentration (MLSS, mg/l), substrate concentration (COD, mg/l), specific growth rate (h^{-1}) and specific substrate utilisation rate (h^{-1}) respectively. The use of dry solids (MLSS) instead of volatile solids (VSS) for biomass estimation can be justified in this case because any increase in solids concentration during the experiment can only be attributed to biomass growth, since inorganic solids precipitation is unlikely and there are no material input after the experiment has begun.

The Monod model describes the relationship between the specific rates and the substrate concentration and is represented by equations (4.21) and (4.22) below:

$$\mu = \mu_{\max} \frac{S}{K_S + S} \tag{4.21}$$

$$k = k_{\max} \frac{S}{K_S + S} \tag{4.22}$$

where μ_{max} is the maximum specific growth rate (h^{-1}), K_S is the half saturation coefficient (mg/l COD) and k_{max} is the maximum substrate utilization rate (h^{-1}). To obtain the kinetic coefficients, biomass (X) and concentration (S) vs. time data were fitted to a sigmoid equation of the form indicated below in equation (4.23), which adequately describes the lag, acceleration, exponential, declining and stationary phases of biomass growth. A similar form of this equation (with half-life used instead of the exponential term) has been employed in a previous study to model activated sludge bacterial growth (Cabrero et al., 1998). The best fit was obtained using the Solver tool in Microsoft ® Office Excel 2003 by minimizing the residual sum-of-squares.

$$y = \frac{a}{b + e^{-kt}} + c \tag{4.23}$$

From equation (4.19), the specific growth rate could be calculated by dividing the slope of equation (4.23) with the biomass concentration at each designated time. Then, the linear regression was used to fit the linearized form of equation (4.21) by plotting $1/\mu$ vs. $1/S$ to obtain the values of μ_{max} and K_S. The biomass yield, $Y_{X/S}$ is calculated by dividing the total biomass growth by the substrate consumed. Finally, the maximum substrate utilisation rate k_{max} was estimated using equation (4.24) (Orhon and Artan, 1994).

$$k_{max} = \frac{\mu_{max}}{Y_{X/S}} \tag{4.24}$$

The exercise was done for the partially degraded amines (both MEA and DEA) as well as for the 'pure' amines for comparison. The plots of $1/\mu$ vs $1/S$ are shown in Figure 4.30, 4.31, 4.32 and 4.33 respectively and the evaluated kinetic parameters are presented in Table 4.1.

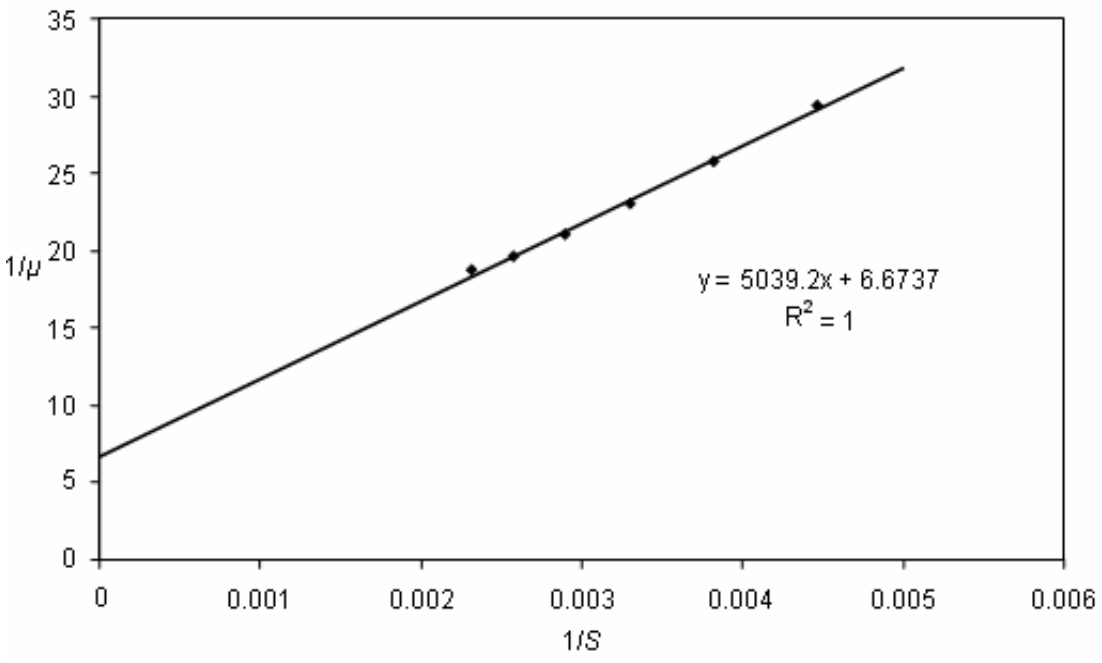


Figure 4.30 Plots of $1/\mu$ vs. $1/S$ on MEA degradation

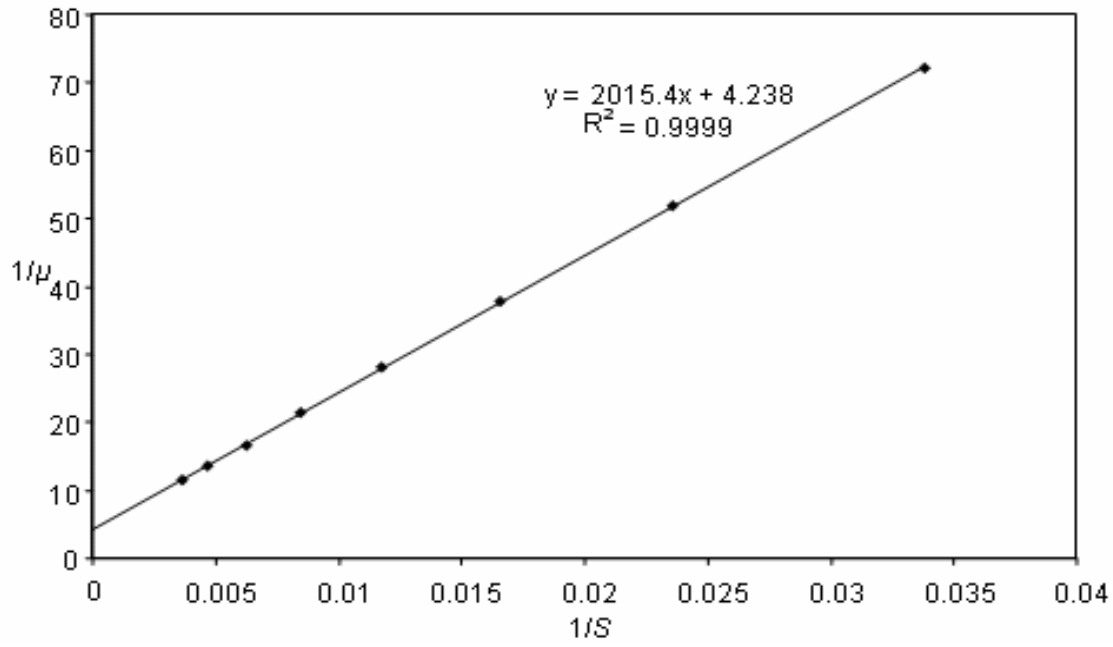


Figure 4.31 Plots of $1/\mu$ vs. $1/S$ on partially degraded MEA degradation

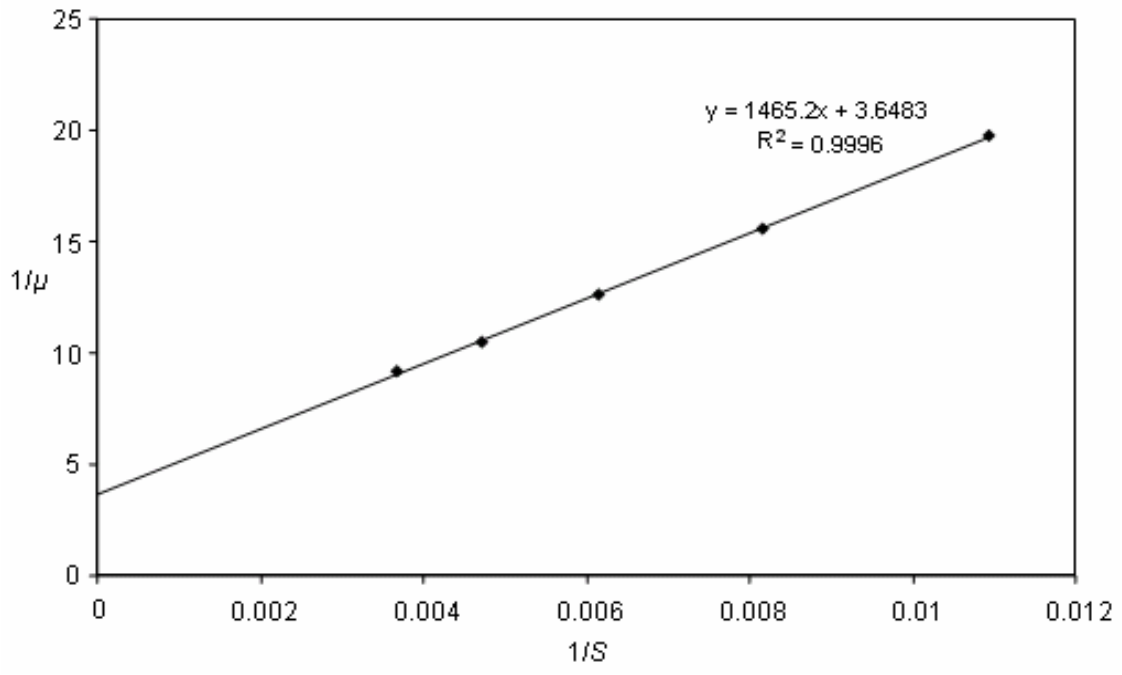


Figure 4.32 Pplots of 1/μ vs. 1/S on DEA degradation

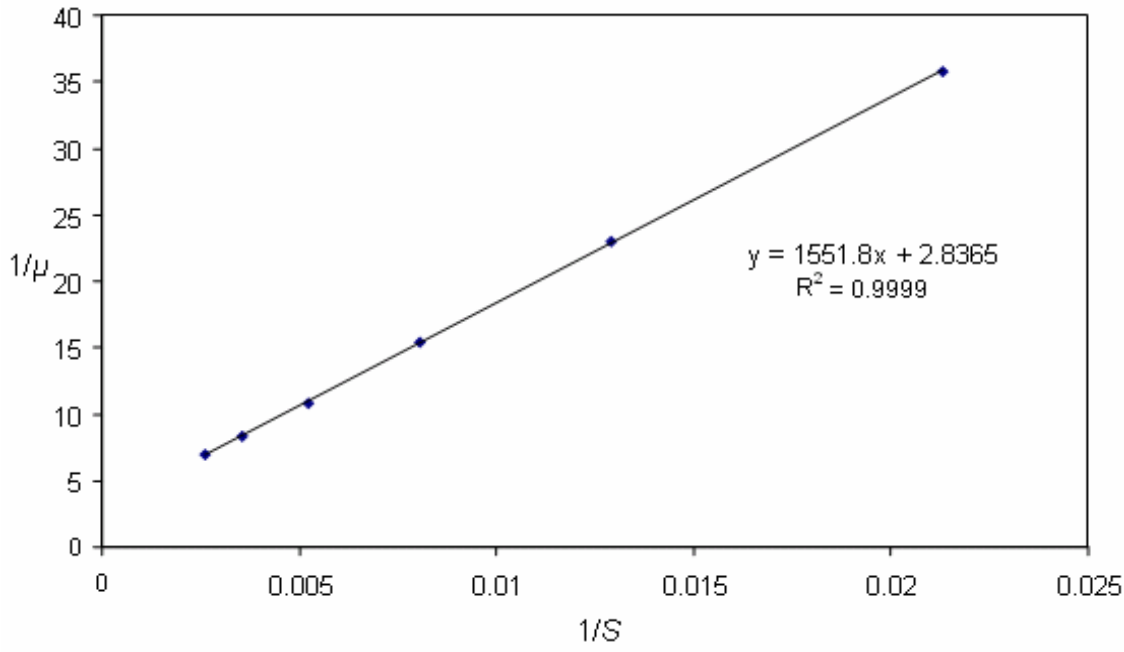


Figure 4.33 Plots of 1/μ vs. 1/S on partially degraded DEA degradation

The biodegradability improvement is further confirmed by estimation of kinetic constants, which were calculated as described previously. Table 4.1 shows the estimated kinetic constants for both untreated alkanolamines and partially degraded alkanolamines. The results show improvement in almost all the kinetic constants including maximum specific biomass growth rate, biomass yield and maximum specific substrate utilisation rate for partially degraded MEA compared to untreated MEA. Only the half-saturation coefficient, which is a measure of the biomass affinity to the substrate, does not show improvement. Mean while, result for DEA a bit different. Maximum specific biomass rate, half saturation, and maximum specific substrate utilization for partially degraded DEA is improved compared to untreated DEA, but the biomass yield did not show improvement.

Table 4.1 Estimated biological kinetic coefficients for untreated alkanolamines and partially degraded alkanolamines.

	μ_{max} (h^{-1})	K_S (mg/l COD)	$Y_{X/S}$	k_{max} (h^{-1})
Untreated MEA	0.14	691	0.223	0.63
Partially degraded MEA	0.24	475.6	0.353	0.67
Untreated DEA	0.27	401.6	0.476	0.58
Partially degraded DEA	0.35	547.1	0.315	1.12

The result of this study agrees with Tekin et al (2006) and Gotvajn and Zogorc-Koncan (2005) who reported that after Fenton's oxidation, the organic compound would break into smaller fragments resulting in improved biodegradability.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

The following conclusions can be drawn from the experimental work degradation of alkanolamines by Fenton's reagent and biological post-treatment.

1. Fenton's reagent is able to rapidly remove the COD of alkanolamines to a certain level after which the COD reduction become very slow. The percentage COD removal increases as the initial alkanolamines concentration increases provided the dosing ratios for Fenton's reagent are maintained. At the maximum initial alkanolamines concentration used in this study, Fenton's oxidation was able to reduce the COD by 54.5% for MEA and 43.17% for DEA.

2. Beside initial alkanolamine concentration, pH and Fenton's reagent dosage were found to be critical parameters in the Fenton's oxidation. The optimum pH was 3 and Fenton's reagent concentration was 175 ml H_2O_2 30% (by weight) to 8 g $FeSO_4;7H_2O$ with 16000 ppm initial alkanolamines concentration.

3. Glycine was identified as a reaction intermediate in Fenton's oxidation using HPLC and FTIR. It was also shown in this study that dissolved ammonia was

formed in significant quantities both during Fenton's oxidation and during biological oxidation. Other degradation products could not be identified.

4. A theoretical model for mineralization was developed and the kinetic constants were evaluated.

5. Biological oxidation followed the Monod kinetics. The rate constants for the Monod's model were obtained from aerobic batch mixed culture study from the biomass and substrate data numerically. The results showed that the kinetic parameters as well as acclimatization time were improved after Fenton's oxidation. Thus, Fenton's oxidation was able to not only reduce the COD but also improve the biodegradability of alkanolamines. Fenton's oxidation has a strong potential to be an effective pre-treatment method before conventional biological treatment for the abatement of wastewater polluted with alkanolamines.

5.2 Recommendation

1. The main limitation of the alkanolamines degradation by Fenton's process is the less COD removal. Combinations of many advanced oxidation processes such UV/H_2O_2 or Photo-Fenton's may help increase the COD removal. Hence, the complete removal of alkanolamine abatement in the wastewater is simpler.

2. Ferric oxide in the form of a sludge is the big problem in the Fenton's processes. The solid remains in the form of finely divided suspension that settle very slow. Settling of hydrated ferric oxide itself may be taken up as a research problem. Application of a magnetic field may prove useful to enhance the rate of sedimentation.

3. For commercial application, the Fenton reactor generally acts as a CSTR. However, a plug flow type of reactor may work better. Since continuous addition of the Fenton reagent proved to be more effective than batch addition, a tubular plug flow reactor with multiple dosing points along the reactor tube may simulate continuous reagent addition. This study may be done in a property designed setup.

4. Other amines, particularly proprietary solvents like sulfinol, which is a mixture of solvents, are used for removal of acidic gases and are found in the wastewater for gas treatment plants. The application of the Fenton reagent for degradation of these materials will be interesting and useful.

5. The rate model for Fenton's mineralization developed in this work is found to be applicable to MEA alone. A more versatile rate model is required to be developed.

REFERENCES

Alanton, I. A. and Teksoy, S., Acid dyebath effluent pretreatment using Fenton's reagent: process optimization, reaction kinetics and effects on acute toxicity, *Dyes Pigments*, **73**, (2007) 31-39.

Ali Safarzadeh-Amiri, Bolton, J.R. and Cater, S.R., Ferrioxalate-Mediated Photodegradation of Organic Pollutant in Contaminated water, *Wat. Res*. **Vol. 31**, No. 4, (1997) pp. 787-798.

Alshamsi, F. A., Albadwawi, A.S**.,** Alnuaimi, M.M., Rauf, M.A. and Ashraf, S.S., Comparative Efficiencies of the Degradation of Crystal Violet using UV/hydrogen peroxide and Fenton's reagent**,** *Dyes Pigments*, ***xx***, (2006) 1-5.

Alnuaimi, M.A., Rauf, M.A. and Ashraf, S. Salman, Comparative decoloration of Neutal Red by defferent oxidative processes, *Dyes and Pigments* **72** (2007) 367-371

Arnold, K., and Stewart, M., **,** Surface Production Operation, Volume 2: Design of gas handling systems. *Gulf Publishing Company. Book Division. Houston*. ,(1989) ISBN 087-201-175-5.

Bilad MR, Treatment of Wastewater Containing Amine using Sequencing Batch Reactor (SBR) and Sequencing Batch Membrane Bioreactor (SBMBR), *Master Thesis*, Universiti Teknologi Petronas, (2007).

Brillas, E., Mur, E.**,** Sauleda, R., Sànchez, L., Peral, J., Domènech, X. and Casado, J., Aniline mineralization by AOP's: anodic axidation, photocatalysis, electro-Fenton and photoelectron-Fenton processes, *Appl. Catalysis B: Environ*., **16**, (1998) 31-42.

British Petroleum (BP), BP Statistical Review of World Energy, (2008).

Burbano, A.A., Dionysiou D.D., Suidan M.T. and Richardson T.L., Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent, *Water Res*., **39,** (2005) 107-118.

Buxton, G. V., Greenstock C. L., Helman W. P. and Ross A. B., Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (HO• , •O^-) in aqueous solution, *J. Phys. Chem. Ref. Data*, **17** (1988) 513-886.

Buzzi, R.A., Chemical Hazards at Water and Wastewater Treatment Plants, Lewis Publisher, (1992) Chelsea, USA.

Cabrero, A. et al., Effects of copper and zinc on the activated sludge bacteria growth kinetics, *Wat. Res*., **Vol. 32 (5)**, (1998) 1355-1362.

Casero, I. et al.**,** Chemical degradation of aromatic amines by Fenton's reagent, *Water Res*, **31**, **No 8**, (1997) 1985-1995.

Coates, J., Interpretation of Infrared Spectra, A Practical Approach, Encyclopedia of Analytical Chemistry, *R.A. Meyers* (Ed) (2000) pp. 10815 – 10837.

De, A. K., Dutta, B. K. and Bhattacharjee, S., Reaction kinetics for the degradation of phenol and chlorinated phenols using Fenton's reagent, *Environ. Progr*., **25**, **No 1**, (2006) 64-71.

De Laat, J.and Gallard, H., Catalytic Decomposition of Hydrogen peroxide by Fe^{3+} in Homogeneous aqueous solution: Mechanism and Kinetic modeling, *Environment Science. Technology*, **33,** (1999) 2726-2732.

Eckenfelder, W.W and Musterman Jack, L**,** Activated Sludge Treatment of Industrial Wastewater, Technomic Publishing Company, (1995), Inc, Pennsylvania 17604, USA.

Gulkaya, I., Surucu, G.A. and Dilek, F.B., Importance of H_2O_2/Fe2+ ratio in Fenton's treatment of a carpet dyeing wastewater, *J. Hzard. Mater*., **B136**, (2006) 763-769.

Gotvajn, Z. G. and Zogorc-Koncan, J., Combination of Fenton and Biological Oxidation for Treatment of Heavily Polluted Fermentation Waste Broth, *Acta Chim. Slov.*, **52**, (2005) 131-137.

Hickey, W. J., Arnold, S. M. and Harris, R. F., Degradation of atrazine by Fenton's reagent: conditions of optimization and product quantification, **29**, (1995) 2083-2089.

Jones, C.W.**,** Application of Hydrogen Peroxide and Derivatives, RSC Clean Technology Monographs, (1999), Formerly of Solvay Interox R & D, Widnes, UK

Kang, N., Lee, D.S. and Yoon, J., Kinetic modeling of Fenton oxidation of phenol and monochlorophenols, *Chemosphere*, 47 (2002) 915-924.

Klare, M., Sceen, J., Vogelsang, K., Jacobs, H., and Broekaert, J.A.C., Degradation of short-chain alkyl- and alkanolamine by TiO2- and Pt/TiO2-assisted photocatalysis, *Chemosphere,* **41,** (2000) 353-362

Kohl, A. I.& Nielsen, R., Gas Purification. 5th ed, (1997) Gulf Publising Company, Houston, Texas.

Koprivanac and H Kusic, AOP as an Effective Tool for the minimization of Hazarduce Organic Pollutants in Colored Wastewater; Chemical and Photochemical Processes, *Hazardous Material and Wastewater*, ISBN 1-60021-257-3, Nova Science Publiser, Inc, (2007) 149-199.

Laws of Malaysia; (act 127), (1999)**,** Environmental Quality Act 1974 & Subsidiary Legislations International Law Book Services.

Lenntech, Water treatment & air purification holding B.V. Rotterdamseweg 402 M, 2629 HH Delft, (2008) The Netherlands

Lou, J. C. and Lee, S. S., Chemical oxidation of BTX using Fenton's reagent, *Hazard. Waste Hazard. Mater*., ***12*****, No 2**, (1995)185-193.

Lodha B and Chaudhari, Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions, *Journal of Hazardous Material.,* **148** (2007) 459-466.

Mantzavinos D, Advanced Oxidation Processes for Treatment of Industrial Effluent: Fundamental & Case Studies of Process Integration, Workshop on Advanced Oxidation Processes for Industrial Wastewater Treatment, 4-5 October, 2007, Aula Magna, Aulario III, Universidad Rey Juan Carlos, Campus de Mostoles, Nadrid, Spain..

Mendham J, R C Denney, J D Barnes, and MJK Thomas, Vogel's Textbook off Quantitative Chemical Analysis, 6th edition, (2000) Prectice Hall, UK.

Metcalf and Eddy, *Wastewater engineering*, 3rd edition, (1991),McGraw-Hill, New York, USA.

Nesheiwat, F. K. and Swanson, A. G., Clean contaminated sites using Fenton's reagent, *Chem. Eng. Progr*., (2000) 61-66.

Neyens, E. and Baeyens, J., A review of classic Fenton's peroxidation as an advanced oxidation technique, *Journal of Hazardous Materials*, **B98**, (2003) 33-50

Orhon D. and Artan N., Modelling of Activated Sludge Systems, *Technomic, Basel, Switzerland,* (1994) 111-122.

Oturan, M. A., et al**.,** Production of hydroxyl radicals by electrochemically assisted Fenton's reagent, *J. Electranalyt. Chem*., **507**, (2001) 96-102.

Qiang Z, Chang J, and Huang C, Electrochemical regeneration of Fe^{2+} in Fenton oxidation processes, *Water Research* **37**, (2003) 1308-1319.

Ray, A.B., Selvakumar, A., and Tafuri, A.N., Treatment of Methyl-Butyl Ether (MTBE)-Contaminated Waters with Fenton's Reagent, Urban Watershed Management Branch, United States Environmental Protection Agency, 2890 Woodbridge Avenue, Edison, NJ 08837, (2003) EPA/600/JA-03/117.

Russell D. L., Practical Wastewater Treatment, Global Environmental Operations, Inc. Lilburn, (2006) Gorgia.

Silverstein R.M., Webster, F.X. and Kiemle, D.J., Spectrometric Identification of Organic Compounds, 7^{th} edition , Jonh Wiley and Sons, Inc, (2005) page 72 – 126.

Stephenson R. L. and Blackburn J.B. Jr., The Industrial Wastewater Systems Handbook, Lewis Publishers, CRC Press LLC, (1998) US

Solozhenko, E. G., Soboleva, N.M. and Goncharuk, V.V.**,** Decolorization of azodye solutions by Fenton's oxidation, *Water Res.,* **29, No 9**, (1995) 2206-2210.

Talinli, J. and Anderson, G.K., Interference of Hydrogen Peroxide on the Standard COD Test, *Wat. Res*. **Vol. 26, No. I**, (1992) pp. 107-110.

Tekin, H., Bilkay, O., Ataberk, S.S., Balta, T.H., Ceribasi, I.H., Sanin, F.D., Dilek, F.B. and Yetis, U., Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater, *J. Hazard. Mater*, **B136**, (2006) 258-165.

US EPA Method, Fate, Transport and Transformation Test Guidelines, (1998) OPPTS 835.3200, Zahn-Wellens/EMPA Test.

Walling, C.**,** Fenton reagent revisited, Accounts Che. Res., **8, No 5**, (1975) 125-131.

Xu M., Wang Q., and Hao Y., Removal of organic carbon from wastepaper pulp effluent by lab-scale solar photo-Fenton process, *Journal of Hazardous Material* , **148**, (2007) 103-109.

PUBLICATION

1. Sominidevi, Nurul H. S. Mulok, S. Harimurti, K. Ragavan and Binay K Dutta., "Degradation of Monoethanolamine in Aqueous Solution by Fenton's Reagent ", WEC, Penang, 2007.

2. Sabtanti Harimurti., "Effectiveness of Fenton's Reagent on Diethanolamine Degradation, National Postgraduate Conference I (NPC I), Perak 2008.

3. Sabtanti Harimurti, Idzam F M Arief, Raihan Mahirah Ramli, Putri N Faizura Megat Khamaruddin, Binay K Dutta," Biodegradability of Monoethanolamine after Fenton's Treatment", ICENV, Penang 2008.

4. Sabtanti Harimurti and Binay K Dutta, "Degradation of Alkanolamines by Fenton's Reagent wit Biological Oxidation Post-Treatment, National Postgraduate Conference II (NPC II), Perak 2009

APPENDIXES

Raw Data of Figure 4.1 Effect of initial concentration on MEA degradation. {(800 ppm MEA: 0.4 g $FeSO_4$;$7H_2O$, 9.3ml H_2O_2 30%; 5000 ppm MEA: 2.5 g $FeSO_4$;$7H_2O$, 54.8 ml H_2O_2 30%; 10000 ppm MEA: 5 g $FeSO_4$;$7H_2O$, 106.67 ml H_2O_2 30%; and 16000 ppm MEA: 8 g $FeSO_4$;$7H_2O$, 175 ml H_2O_2 30%) at pH 3.

Time(min)	**Initial Concentration**			
	800 ppm mg/L COD	**5000 ppm mg/L COD**	**10000 ppm mg/L COD**	**16000 ppm mg/L COD**
0	1128.75	6093.9	11261.23	13634.72
2	988.75	5514.4	8808.4	8296
4	1005	5368	8613.2	8198.4
6	1007.5	5319.2	8906	7588.4
8	990	5758.4	8003.2	6417.2
10	1002.5	5709.6	8393.6	6612.4
15	993.75	5294.8	8247.2	6148.8
25	980	5612	8418	5929.2
30	968.75	5099.6	8149.6	6197.6

Raw Data of Figure 4.2 Effect of initial concentration of DEA degradation. {(800 ppm DEA: 0.4 g $FeSO_4$;$7H_2O$, 9.3ml H_2O_2 30%; 5000 ppm DEA: 2.5 g $FeSO_4$;$7H_2O$, 54.8 ml H_2O_2 30%; 10000 ppm DEA: 5 g $FeSO_4$;$7H_2O$, 106.67 ml H_2O_2 30%; and 16000 ppm DEA: 8 g $FeSO_4$;$7H_2O$, 175 ml H_2O_2 30%) at pH 3.

	Initial Concentration			
Time(min)	**800 ppm**	**5000 ppm**	**10000 ppm**	**16000 ppm**
	mg/L COD	**mg/L COD**	**mg/L COD**	**mg/L COD**
0	1329	8175.323	15014.05	21117.22
2	1065	5510	11802	15320
4	1119	5280	11578	14920
6	1092	5480	11382	13360
8	1062	4960	10822	13200
10	1119	5180	10514	14080
15	1122	5330	10276	14360
30	1059	5090	9562	12000

Raw Data of Figure 4.3 Effect of Hydrogen peroxide concentration on MEA degradation {16000 ppm MEA, 8 g $FeSO_4;7H_2O$ at pH 3 at four different H_2O_2 concentration }.

Time(min)	**Hydrogen Peroxide (H_2O_2) 30% (ml)**			
	58.33 mg/L COD	**116.66 mg/L COD**	**175 mg/L COD**	**233.33 mg/L COD**
0	16786.22	14847.35	13634.72	13763.63
2	12297.6	9850	8296	9200
4	11468	8950	8198.4	9075
6	11443.6	9275	7588.4	8400
8	11297.2	10150	6417.2	9175
10	11199.6	13875	6612.4	7875
15	10906.8	8475	6148.8	8575
25	11053.2	8850	5929.2	7875
30	10516.4	8325	6197.6	8600

Raw Data of Figure 4.4 Effect of Hydrogen peroxide concentration on DEA degradation {16000 ppm DEA, 8 g $FeSO_4;7H_2O$ at pH 3 at four different H_2O_2 concentration }.

Time(min)	**Hydrogen Peroxide (H_2O_2) 30% (ml)**			
	58.33 mg/L COD	**116.66 mg/L COD**	**175 mg/L COD**	**233.33 mg/L COD**
0	21504.49	21305.13	21117.22	21713.33
2	17200	15600	15320	16250
4	16800	15975	14920	15575
6	15875	16150	13360	15425
8	15975	16100	13200	15025
10	16225	14850	14080	14175
15	16250	15150	14360	13975
30	15800	13350	12000	12550

Raw Data of Figure 4.5 Effect of pH on MEA degradation {(16000 ppm MEA: 8 g $FeSO_4;7H_2O$, 175 ml H_2O_2 30% at different pH: 2 - 5)}

Time(min)	pH 2 mg/L COD	pH 3 mg/L COD	pH 4 mg/L COD	pH 5 mg/L COD
0	16533.8	13634.72	14511.25	14449.5
2	13225	8296	9225	12125
4	13575	8198.4	9100	12125
6	13350	7588.4	9150	11825
8	12975	6417.2	9000	12025
10	13075	6612.4	8900	11375
15	12950	6148.8	8850	11075
25	12800	5929.2	8750	11500
30	13375	6197.6	8825	10525

Raw Data of Figure 4.6 Effect of pH on DEA degradation {(16000 ppm DEA: 8 g $FeSO_4;7H_2O$, 175 ml H_2O_2 30% at different pH: 1-4)}

Time(min)	pH 2 mg/L COD	pH 3 mg/L COD	pH 4 mg/L COD	pH 5 mg/L COD
0	21245.58	21134.62	21117.22	21435.35
1	15225	15200	15320	17625
2	15275	15200	14920	17350
4	15675	14825	13360	17525
6	15125	13875	13200	17250
8	14350	13925	14080	16950
15	15325	13125	14360	16500
30	14925	12125	12000	16125

Raw Data of Figure 4.7 Effect of $FeSO_4;7H_2O$ on MEA degradation{(16000 ppm DEA: 175 ml H_2O_2 30% at pH 3) at different amount of $FeSO_4;7H_2O$: 4g, 8g, 12g and 16g, respectively)}

Time(min)	**$FeSO_4;7H_2O$**			
	4 (g)	**8 (g)**	**12 (g)**	**16 (g)**
	mg/L COD	**mg/L COD**	**mg/L COD**	**mg/L COD**
0	15435.2	13634.72	13796.25	13605.35
2	14425	8296	12000	10600
4	13775	8198.4	11050	11225
6	14300	7588.4	9925	11000
8	13675	6417.2	9750	10825
10	14575	6612.4	9325	10900
15	14275	6148.8	8850	10375
25	13625	5929.2	8875	10400
30	13575	6197.6	8875	10650

Raw Data of Figure 4.8 Effect of $FeSO_4;7H_2O$ on DEA degradation{(16000 ppm DEA: 175 ml H_2O_2 30% at pH 3) at different amount of $FeSO_4;7H_2O$: 4g, 8g, 12g and 16g, respectively)}

	$FeSO_4;7H_2O$			
Time(min)	**4 (g)**	**8 (g)**	**12 (g)**	**16 (g)**
	mg/L COD	**mg/L COD**	**mg/L COD**	**mg/L COD**
0	21744.05	21117.22	21338.97	21090.43
2	17425	15320	16225	15250
4	16975	14920	15300	15625
6	16575	13360	15500	14725
8	16100	13200	14925	14175
10	15850	14080	14475	13550
15	15750	14360	14000	13325
30	14275	12000	13325	12325

Raw Data of Figure 4.9 COD and H_2O_2 profile on equivalent concentration of DEA and Fenton's reagent with one time addition of Fenton's reagent (5000 COD (700 ml) + 44.7 ml H_2O_2 30% + 121.6 g $FeSO_4;7H_2O$ pH 3).

Time(min)	COD (mg/L)	H_2O_2 (M)
0	4565.217	0.546842
5	1748.792	0.009791
10	1763.285	0.012239
20	1734.3	0.011015
30	1826.087	0.009791
45	1647.343	0.012239
60	1801.932	0.012239

Raw Data of Figure 4.10 Partially Degraded DEA with New Fenton Reagent (6050 mg/L COD)+ 26.5 ml H_2O_2 30 % + 1 gram $FeSO_4;7H_2O$ pH 3)

Time (min)	COD (mg/L)
0	5700
2	5160
4	4900
6	4920
8	4920
15	4750
30	4730

Raw Data of Figure 4.11 Degradation of Glycine compare to MEA {(5000 ppm Glycine + 54.8 ml H_20_2 30% + 2,5 g $FeSO_4,7H_20$ pH 3) and (5000 ppm MEA + 54.8 ml H_20_2 30% + 2,5 g $FeSO_4,7H_20$ pH 3)

Time (min)	Glycine (mg/L COD)	MEA (mg/L COD)
0	4174.8	6366.15
2	3577.5	5250
4	3652.5	5302.5
6	3607.5	5130
8	3577.5	5062.5
10	3607.5	5070
15	3540	5160
25	3660	5047.5
30	3510	4965

Raw Data of Figure 4.12 COD and H_2O_2 profile on equivalent concentration of DEA and Fenton's reagent with continuous addition of $FeSO_4;7H_2O$ (5000 COD (700 ml) + 44.667 ml H_2O_2 30% + 121.633 g $FeSO_4;7H_2O$ pH 3).

Time(min)	COD (mg/L)	H_2O_2 (M)
0	4571.527	
1	4668.279	0.009302
5	4334.485	0.016155
10	4261.921	0.02203
20	3865.238	0.046508
30	2926.745	0.058747
45	2172.08	0.074249
60	1538.355	0.048956

Raw Data of Figure 4.13 COD and H_2O_2 profile when H_2O_2 and $FeSO_4;7H_2O$ continuous for 30 minute (16000 ppm DEA; 175 ml H_2O_2 30% ; 16 g $FeSO_4;7H_2O$ pH 3)

Time(min)	COD (mg/L)	H_2O_2 (M)
0	22898.19	
1	18917.46	0.08375
2	17877.45	0.13667
4	17106.4	0.24
6	15922.94	0.32
8	15851.22	0.4225
15	13717.4	0.655
30	9395.969	0.78

Raw Data of Figure 4.14 COD and H_2O_2 profile when H_2O_2 one time addition in the beginning and $FeSO_4;7H_2O$ continuous for 30 minute (16000 ppm DEA; 175 ml H_2O_2 30% ; 16 g $FeSO_4;7H_2O$ pH 3)

Time(min)	COD (mg/L)	H_2O_2 (M)
0	20272.89	2.167
1	13672.41	1.997384
2	15032.4	1.896506
4	12747.62	1.805716
6	12928.95	1.785541
8	12783.89	1.462731
15	10027.65	1.00878
30	7253.27	0.52961

Raw Data of Figure 4.15 Effect of different addition mode of Fenton's reagent (16000 ppm DEA; 175 ml H_2O_2 30%; 16 g $FeSO_4;7H_2O$ pH 3)

Time(min)	COD (mg/L)		
	Onetime	**Continuous**	**Semi-continuous**
0	21117.22	22898.19	20272.89
1	15320	18917.46	13672.41
2	14920	17877.45	15032.4
4	13360	17106.4	12747.62
6	13200	15922.94	12928.95
8	14080	15851.22	12783.89
15	14360	13717.4	10027.65
30	12000	9395.969	7253.27

Raw Data of Figure 4.16 Different addition model of Fenton's Reagent (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3) run 30 minute on COD profile

Time (min)	Continuous addition (COD mg/L)	One time addition (COD mg/L)
0	6108.863081	6366.15
1	4800.427873	5250
2	5403.667482	5302.5
4	4876.894866	5130
6	4817.420538	5062.5
8	5021.332518	5070
10	3967.787286	5160
15	4044.254279	5047.5
30	3279.584352	4965

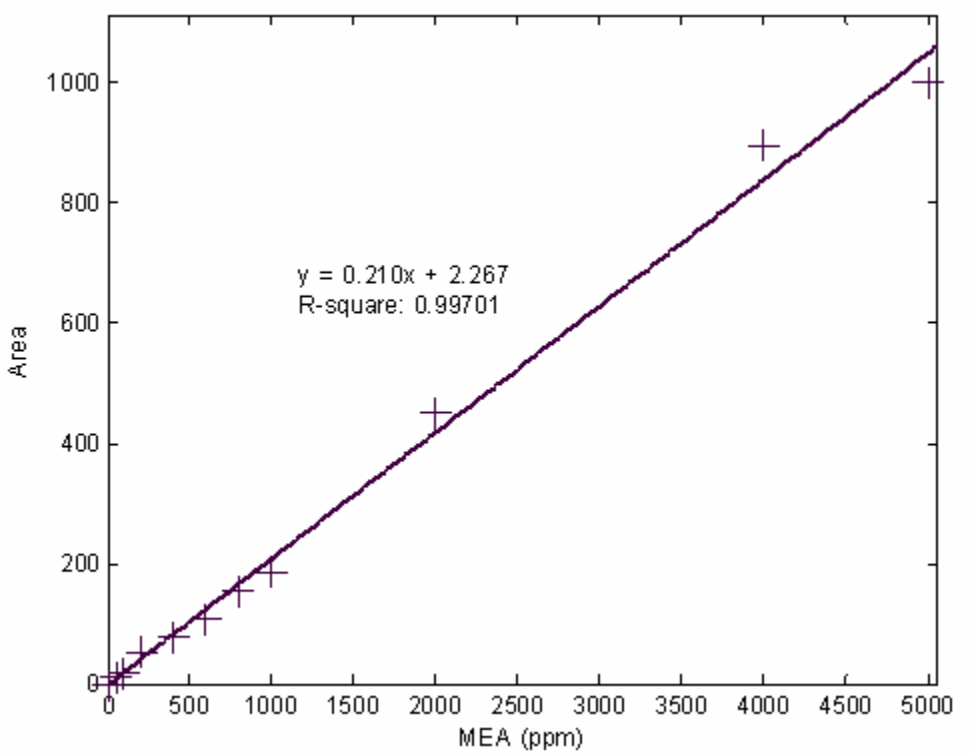
Raw Data of Figure 4.17 Continuous addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3)

Time (min)	MEA (mg/L)	COD (mg/L)	H_2O_2 (M)
0	4700	6108.863081	
1	3827.291	4800.427873	0.025667
2	3676.364	5403.667482	0.042583
4	3553.379	4876.894866	0.0665
6	3354.105	4817.420538	0.098583
8	3237.056	5021.332518	0.12425
10	3030.54	3967.787286	0.149625
15	2976.864	4044.254279	0.214375
30	1717.058	3279.584352	0.343

Raw Data of MEA Calibration Curve

MEA (ppm)	Area
0	0
50	10.40205
100	18.36301
200	51.16589
400	78.61724
600	107.84474
800	154.27692
1000	184.67085
2000	449.70560
4000	894.58624
5000	998.92334

Plot of Calibration Curve (MEA vs. Area)

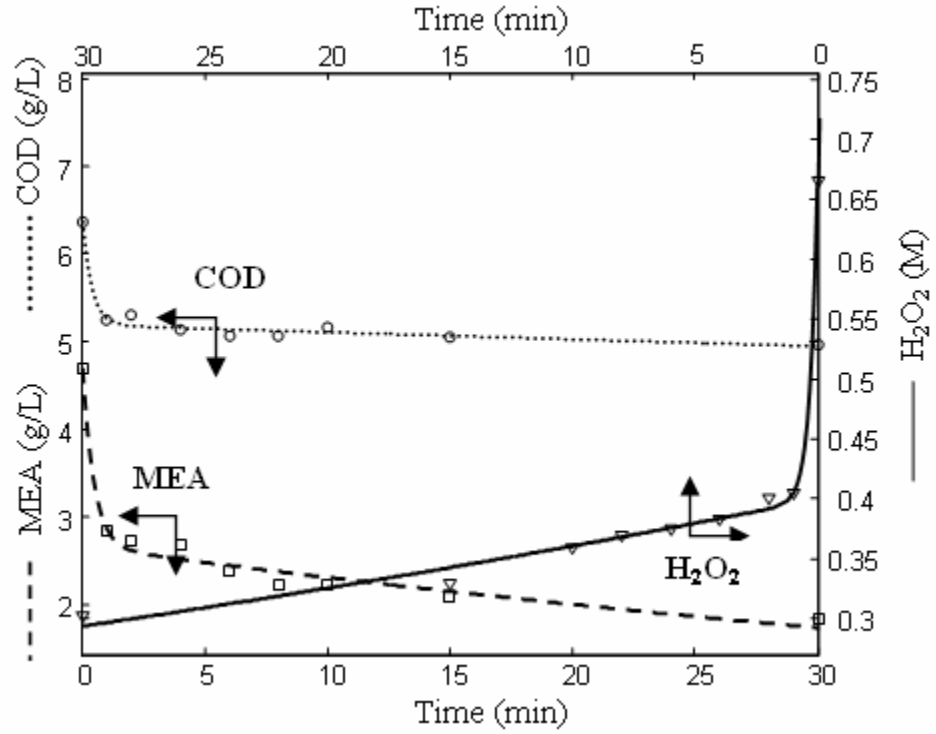


Where: x = MEA (ppm) and y = Area

Raw Data One time addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3).

Time (min)	MEA (mg/L)	COD (mg/L)	H_2O_2 (M)
0	4692.211	6366.15	**0.664419**
1	2846.705	5250	0.40425
2	2735.893	5302.5	0.40075
4	2685.728	5130	0.38325
6	2401.176	5062.5	0.3745
8	2231.249	5070	0.36925
10	2231.963	5160	0.35875
15	2086.973	5047.5	0.329
30	1846.567	4965	0.301875

Plot of One time addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm MEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3).



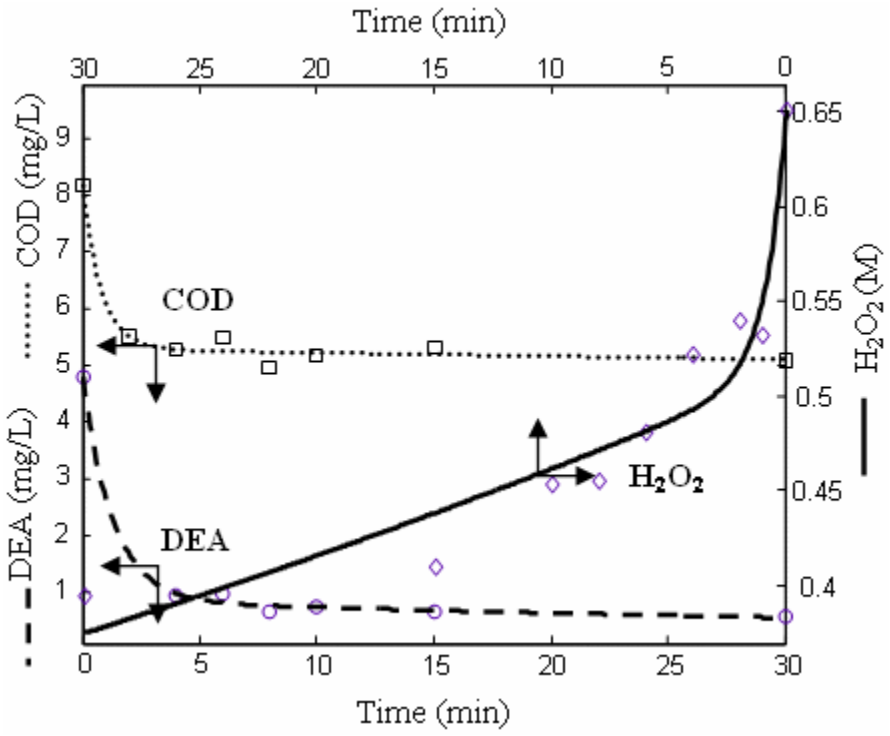
Raw Data of Figure 4.18 Continuous addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm DEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3)

Time (min)	DEA (mg/L)	COD (mg/L)	H_2O_2 (M)
0	4665.871	8110.58	
1	4038.574	7491.9	0.024835
2	3753.363	7339.35	0.048459
4	2938.499	6635.93	0.088437
6	2384.354	6424.05	0.10395
8	1885.713	5830.8	0.154193
10	1555.547	5483.33	0.192308
15	1103.806	5339.25	0.274601
30	392.1756	4178.18	0.44352

Raw Data One time addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm DEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3).

Time (min)	DEA (mg/L)	COD (mg/L)	H_2O_2 (M)
0	4789.628	8175.323	0.664
1	733.9522	5300	0.5448747
2	896.8189	5510	0.5527163
4	931.4338	5280	0.5345941
6	973.9082	5480	0.4934714
8	645.6136	4960	0.4677698
10	727.9947	5180	0.4660564
15	635.5005	5330	0.4232203
30	566.2534	5090	0.4077993

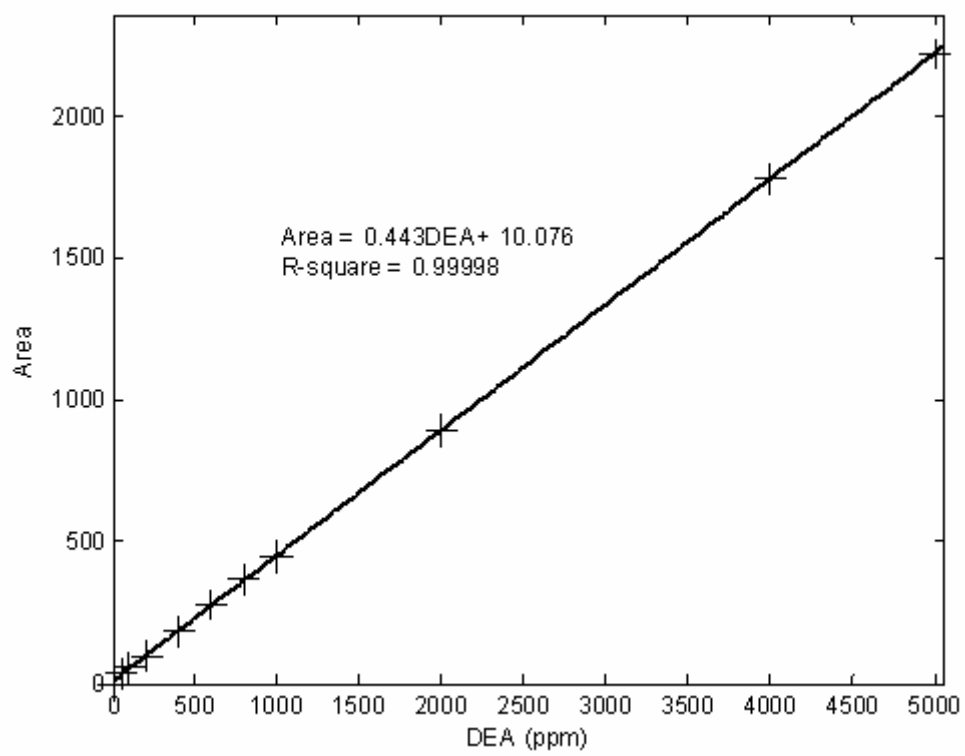
Plot of One time addition of H_2O_2 and $FeSO_4;7H_2O$ (5000 ppm DEA + 54.8 ml H_2O_2 30% + 2.5 g $FeSO_4;7H_2O$ at pH 3).



Raw Data of DEA Calibration Curve

DEA (ppm)	Area
0	0
50	36.37734
100	58.37358
200	100.44745
400	188.27611
600	279.96454
800	367.0938
1000	447.93091
2000	893.80267
4000	1787.10339
5000	2225.46484

Plot of Calibration Curve (DEA vs. Area)

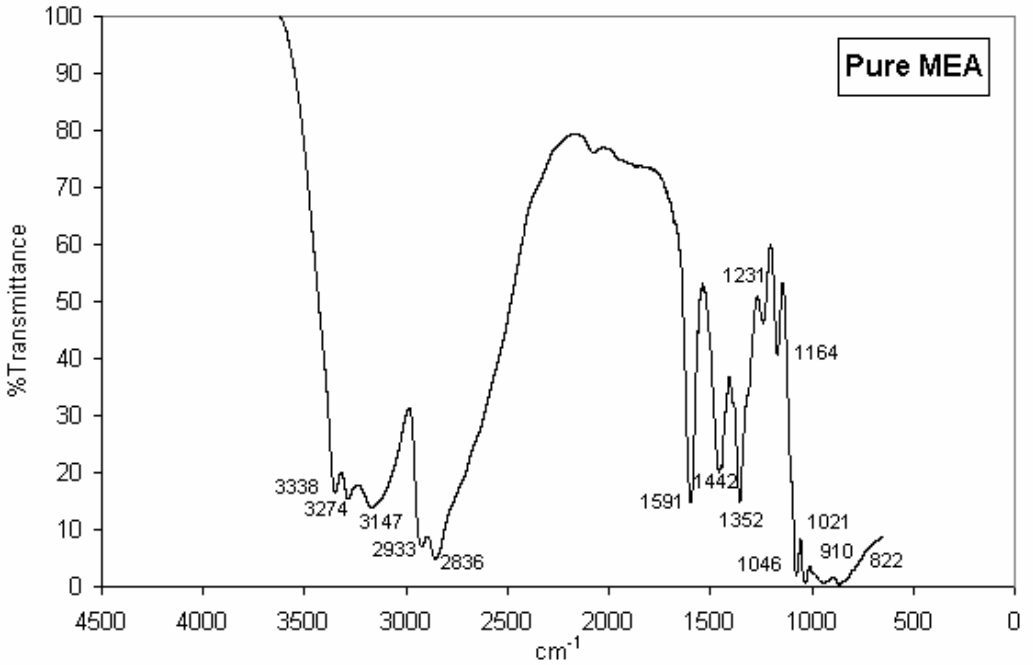


Where: x = DEA (ppm) and y = Area

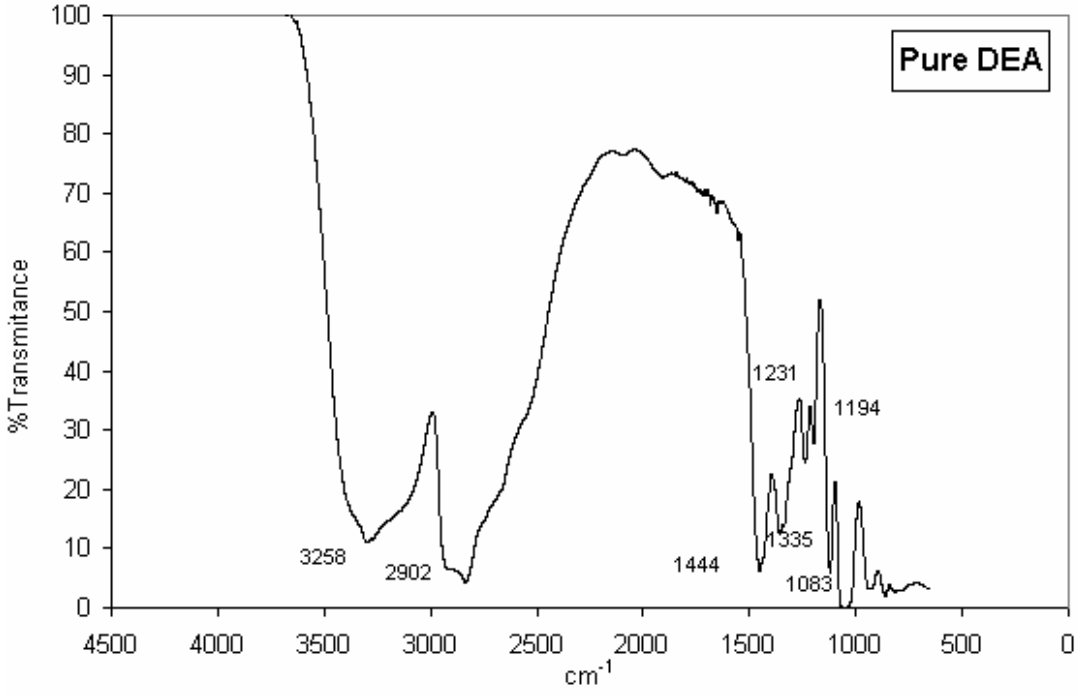
Raw Data of figure 4.19 COD and TOC profile by Fenton's reagent on DEA degradation {10000 ppm and 16000 ppm DEA initial concentration}.

Time	10000 ppm		16000 ppm	
(min)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)
0	15014.05	4377.604	21117.22	6157.895
2	11802	4151	15320	5600
4	11578	4186	14920	5120
6	11382	4067	13360	5340
8	10822	4207	13200	5380
10	10514	3941	14080	5500
15	10276	3941	14360	5420
30	9562	3948	12000	5140

Infrared Spectra of "pure" MEA



Infrared Spectra of "pure" DEA



Raw Data of Figure 4.25 Biodegradability of partially degraded amine (MEA and DEA) and pretreatment amine (MEA and DEA) compare with reference. Initial COD is 1000 mg/L and initial biomass concentration is 1000 mg/L MLVSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

Time	COD Removal (%)				
(hour)	MEA	P. D. MEA	DEA	P. D. DEA	Reference
0	0	0	0	0	0
17	5.194805	85.29241	-1.71398	69.75089	-3.0269058
24	14.52184	87.95599	0.642742	86.52771	-3.7556054
40.5	89.61039		1.124799	91.40824	-4.0358744
65.5	89.0791		11.35512	90.4423	-6.4461883
92			74.23674		-1.0650224
113	99.88194	91.89346	96.83985	96.03457	-3.0269058
121.5	98.99646	91.95136	96.94697	94.96695	-1.793722
138	97.87485		98.60739	95.62786	-2.4103139
145.5					-1.6816143
161.5					-1.5695067
169					-0.7847534
186					1.00896861
195					2.46636771
211					2.80269058

218	5.88565022
234.5	11.1534276
243.5	14.2085359
258.5	19.6659483
282.5	24.5392312
306	38.9905713
330	42.1109902
353.5	48.0176211
378	62.7805145
402	62.2932745
426	66.3355408
455	74.9721913

Raw Data of Figure 4.26 COD degradation and MLSS profile in the biological oxidation of partially degraded MEA and pure MEA. Initial COD is 1000 mg/L and initial biomass concentration is 100 mg/L MLSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

Time	**MEA**		**P. D. MEA**	
(hour)	**COD (mg/L)**	**Biomass (mg/L)**	**COD (mg/L)**	**Biomass (mg/L)**
0	759	107.3799	779	112.3663
6	821	108.8909	842	115.5394
13	674	103.3001	796	121.1303
18	821	102.0913	707	166.159
23.5	778	113.2729	355	255.3098
30	645	137.1472	138	362.5929
37	491	158.6038	95	309.7069
42	60	255.3098	101	303.6627
48	77	217.534	190	300.6407
54	23	226.6002	97	291.5745
61	24	223.5781	85	243.2215
65		213.0009		246.2436

Raw Data of Figure 4.27 COD degradation and MLSS profile in the biological oxidation of partially degraded DEA and pure DEA. Initial COD is 1000 mg/L and initial biomass concentration is 100 mg/L MLSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

Time	**DEA**		**P. D. DEA**	
(hour)	**COD (mg/L)**	**Biomass (mg/L)**	**COD (mg/L)**	**Biomass (mg/L)**
0	759	109.9486	779	105.8688
6	821	112.3663	842	108.2865
13	674	106.9266	796	99.97582
18	821	106.4733	707	109.6464
23.5	778	109.1931	355	132.6141
30	645	115.5394	138	330.8613
37	491	122.7924	95	364.104
42	60	234.1553	101	333.8833
48	77	353.5267	190	353.5267
54	23	571.1151	97	359.5709
61	24	338.4164	85	332.3723
65		329.3503		323.3061

Raw Data of Figure 4.28 COD degradation and NH_3 profile in the biological oxidation of partially degraded MEA and pure MEA. Initial COD is 1000 mg/L and initial biomass concentration is 100 mg/L MLSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

Time	**MEA**		**P. D. MEA**	
(hour)	**COD (mg/L)**	**NH_3 (mg/L)**	**COD (mg/L)**	**NH_3(mg/L)**
0	759	12.45	779	287
6	821		842	
13	674		796	
18	821	22.95	707	532.5
23.5	778		355	
30	645		138	
37	491		95	
42	60	872	101	1280
48	77		190	
54	23		97	
61	24		85	
65		842		1210

Raw Data of Figure 4.29 COD degradation and MLSS profile in the biological oxidation of partially degraded DEA and pure DEA. Initial COD is 1000 mg/L and initial biomass concentration is 100 mg/L MLSS (EPA method (OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998).

Time	**DEA**		**P. D. DEA**	
(hour)	**COD (mg/L)**	**NH_3 (mg/L)**	**COD (mg/L)**	**NH_3(mg/L)**
0	925	12.85	861	273
6	975		854	
13	999		798	
18	1008	19.35	846	403
23.5	1020		733	
30	1089		154	
37	875		123	
42	733	131.5	80	1730
48	78		78	
54	28		51	
61	41		56	
65		436.5		1770

Raw Data Figure 4.30 plots of $1/\mu$ vs. $1/S$ on MEA degradation

t	$1/\mu$	$1/S$
37	18.73957	0.002313
38	19.61551	0.002573
39	21.03019	0.002898
40	23.06026	0.003306
41	25.8157	0.003818
42	29.4458	0.004461

Raw Data Figure 4.31 plots of $1/\mu$ vs. $1/S$ on partially degraded MEA degradation

t	1/μ	1/S
23	11.49256	0.003659
24	13.54945	0.004707
25	16.69757	0.006238
26	21.34887	0.008478
27	28.112	0.011754
28	37.87195	0.016545
29	51.90585	0.02355
30	72.05014	0.033795

Raw Data Figure 4.32 plots of $1/\mu$ vs. $1/S$ on DEA degradation

t	1/μ	1/S
46	9.145414	0.003681
47	10.53163	0.004719
48	12.59102	0.006161
49	15.55197	0.008161
50	19.74285	0.010939

Raw Data Figure 4.33 plots of $1/\mu$ vs. $1/S$ on partially degraded DEA degradation

t	1/μ	1/S
26	6.996369	0.002617
27	8.291279	0.003573
28	10.84517	0.005217
29	15.34265	0.008047
30	22.98935	0.012917
31	35.83511	0.021296