REMOVAL OF THIOSULFATE FROM AQUEOUS SOLUTION VIA AIR ADVANCED OXIDATION PROCESS

ABUDZAR BIN MD RASHID

CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
JULY 2009

Removal of Thiosulfate from Aqueous Solution via Air Advanced Oxidation Process

by

Abudzar bin Md Rashid

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

JULY 2009

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Removal of Thiosulfate from Aqueous Solution via Air Advanced Oxidation Process

by

Abudzar bin Md Rashid

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

Dr. Farooq bin Ahmad
(Project Supervisor)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

July 2009

CERTIFICATION OF ORIGINALITY

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

ABUDZAR BIN MD RASHID

ACKNOWLEDGEMENT

The author wishes to take the opportunity to express his utmost gratitude to the individual that have taken the time and effort to assist the author in completing the project either directly or indirectly. Without the cooperation of these individuals, no doubt the author would have faced some minor complications through out the course.

First and foremost the author's greatest gratitude goes to the author's supervisor, Dr. Farooq bin Ahmad. Thanks for all the never-ending support and trust given to the author in order to carry out this project. Further gratitude goes to the co-supervisor, Mr. Naveed bin Ahmad, for providing the author with all the initial information required to begin the project. Without his guidance and patience, the author would not be succeeded to complete the project.

To all the technician in Chemical Engineering, Civil Engineering and Mechanical Engineering Department, thank you for assisting the author in completing his project.

Last but not least, to all individuals that has helped the author in any way, but whose name is not mentioned here, the author thank you all for the wonderful hands.

ABSTRACT

Wastewater stream from industrial plants, including petroleum refineries, chemical plants, pulp and paper plants, mining operations, electroplating operations and food processing plants, may contain offensive substances such as cyanide, sulfides, sulfites, thiosulfate and disulfides that tend to increase the chemical oxygen demand (COD) of the wastewater streams. Thiosulfate is an oxyanion of sulfur produced by reaction of sulfite ions with elemental sulfur in high temperature water. As some countries have a limitation for thiosulfate concentration, especially in the wastewater stream, the removal of thiosulfate is one of the major concerns by most of industries. This research and experimental project will be focusing in removal thiosulfate by using Air Advanced Oxidation Process (AOP). In this particular project, air is use as the medium because it is an unlimited source and oxidation process is naturally happen in the atmosphere. The experiment will be conduct in chemical laboratory. Some parameters such as thiosulfate and oxygen concentration, air flowrate, pH and temperature will be manipulate, monitor, record and finally the data will be trend for analyze process. These factors are believed to be the important factors in the real environment of removing thiosulfate. The expected result of the experiment is the thiosulfate concentration drop and sulfate formation. The analysis of the result will be done using UV Visible Spectrophotometer to determine the effectiveness of the study. At the end of the project, the kinetic model for the process would be developed.

TABLE OF CONTENT

CHAPTER 1: INTRODUCTION

CHAPTER 2:LITERATURE REVIEW

CHAPTER 3: METHODOLOGY

CHAPTER 4: RESULTS AND DISCUSSION

LIST OF FIGURES

LIST OF TABLES

LIST OF GRAPH

CHAPTER 1: INTRODUCTION

1.1) BACKGROUND OF STUDY

Thiosulfate is mainly produced by the spent caustic wastewater from the oxidation of sulfide present in offshore natural gas production. During the processing of the natural gas obtained from offshore gas production installations, the sulfur present in the natural gas is oxidized through a caustic oxidation process, and the wastewater generated contains predominantly thiosulfate at a concentration as high as 3000 mg/L. This wastewater causes severe pollution problems if discharged without treatment.

The traditional method of treating thiosulfate containing wastes is by oxidation to sulfate which can be accomplished either chemically using oxidizing agents and oxidation catalysts or biologically using aerobic processes.

Many methods have been proposed for the oxidation of thiosulfate based on a few factors such as the side effect to the environment, cost and energy used. There are several researcher who had done study on thiosulfate oxidation:

1.1.1) 1988- Julie Mason and Don P. Kelly. '*Thiosulfate Oxidation by Obligately Heterotrophic Bacteria*'

1.1.2) 1996- P.Khanna, B. Rajkumar, N. Jothikumar. '*Microbial Recovery of Sulfur from Thiosulfate-Bearing Wastewater with Phototrophic and Sulfur-Reducing Bacteria*'

1.1.3) 1998- Donald C. Schreiber and Spyros G.Pavlostathis. '*Biological Oxidation of Thiosulfate in Mixed Heterotrophic/Autotrophic Cultures*'

1.1.4) 2008- J.M. Gonzales, A. Roca, M. Cruells, F. Fatino. '*The oxidation of thiosulfates with copper sulfate-Application to an industrial fixing bath*'

1.2) PROBLEM STATEMENT

Thiosulfate is a contaminant compound usually found in aqueous solution. As some countries have a limitation for thiosulfate concentration, especially in the wastewater stream, the removal of thiosulfate is one of the major concerns by most of industries.

A number of microorganisms residing in the streams can use the thiosulfate ion as an energy source, whereby thiosulfate is oxidized and oxygen consumed. Therefore Thiosulfate contributes to the biochemical oxygen demand (BOD) of the stream. Also during the oxidation process sulfuric acid is produced, resulting in a loauthorring of the pH which can influence the chemistry of receiving stream and potentially impact the resident biotic community. Besides, the concentration of Thiosulfate that normally being discharged is above its allowable limit placed by EPA which is 100 ppm. It can causes severe pollution problems if discharge without proper treatment.

Air advanced oxidation is one of the few techniques to remove thiosulfate from an aqueous solution. Hoauthorver, this technique has its pro and cons and only little numbers of research and studies being done regarding this matter.

1.3) OBJECTIVES

1.3.1) To develop a technique of thiosulfate oxidation using air advanced oxidation process.

1.3.2) To conduct studies and laboratory experiments to determine the parameters which affect the thiosulfate advanced oxidation.

1.3.3) To develop kinetics model based on the laboratory data analysis.

1.3.4) To have an environmental-friendly technique for removal thiosulfate that will be lead to the better and greener environment.

1.3) SCOPE OF STUDY

The research will cover the process of removal thiosulfate using Air Advanced Oxidation Process. The effect of thiosulfate concentration (400 ppm to 1200 ppm), air flow rate (4 L/min – 10 L/min) and concentration of partial pressure of oxygen (21% – 60%) will be put on the laboratory experimental test.

Due to the lack of time, this study is not aimed to provide all the necessary information of the oxidation process using other method such as using H_2O_2 as the oxidation agent. The study also does not cover the effect of other advanced oxidation process combination which is with ultraviolet (UV) or other catalyst.

1.4) FLOW OF STUDY

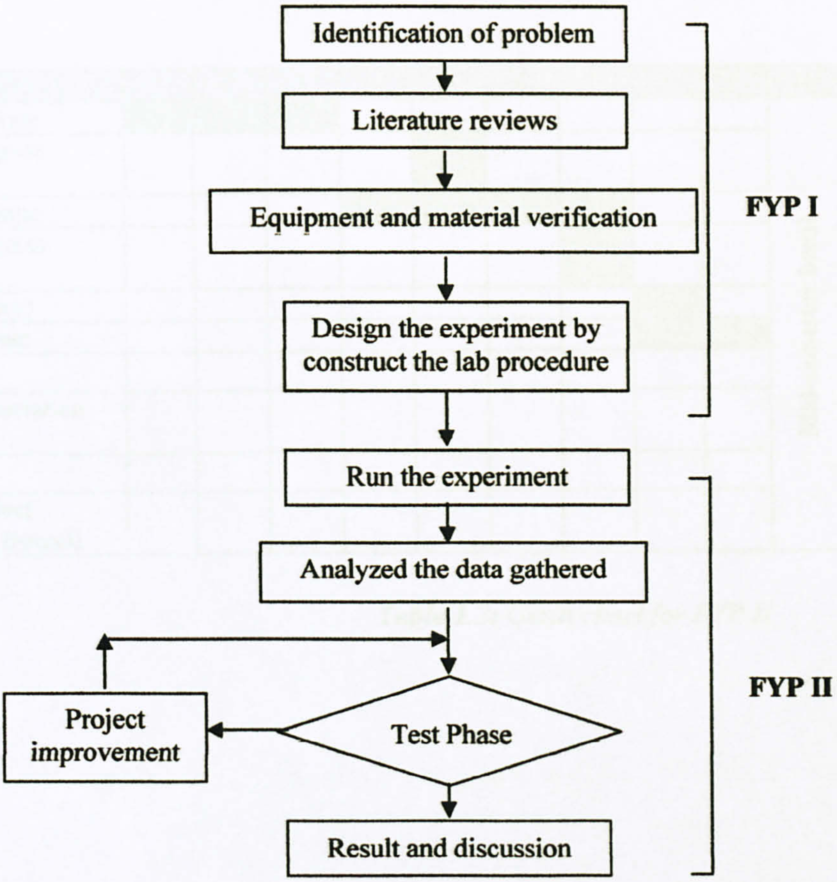


Figure 1.1: Flow of study

1.5) GANTT CHART

No	Detail/Authorek	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of project topic	🟩	🟩								Mid-semester break				
2	Preliminary research work			🟩	🟩	🟩									
3	Submission of preliminary report						🟩								
4	Calibration of ion-chromatograph				🟩	🟩	🟩	🟩							
5	Submission of progress report								🟩						
6	Seminar								🟩	🟩					
7	UV visible spectrophotometer familiarization									🟩		🟩			
8	Research and project work continues							🟩	🟩	🟩		🟩	🟩		
9	Submission of interim report													🟩	
10	Oral presentation														🟩

Table 1.1: Gantt chart for FYP I

No	Detail/Authorek	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continue	🟩	🟩	🟩							Mid-semester break				
2	Submission of Progress Report 1					🟩									
3	Project Work Continue				🟩	🟩	🟩	🟩							
4	Submission of Progress Report 2							🟩							
5	Seminar (compulsory)								🟩						
6	Project work continue								🟩	🟩					
7	Poster Exhibition											🟩			
8	Submission of Dissertation (soft bound)												🟩		
9	Oral Presentation													🟩	
10	Submission of Project Dissertation (Hard Bound)														🟩

Table 1.2: Gantt chart for FYP II

CHAPTER 2: LITERATURE REVIEW

2.1) THIOSULFATE

Basically, thiosulfate can be defined as the sulfate which one of the oxygen molecule is replaced by a sulfur molecule. Thiosulfate is an oxyanion of sulfur produced by reaction of sulfite ions with elemental sulfur in high temperature water. It is also occur naturally in hot springs and geysers. Thiosulfate also can be produced by certain biochemical processes. Thiosulfate is not found in large quantities in nature. Solutions of thiosulfate break down into sulfur, sulfites, and sulfates when exposed to acids, light, metal ions, and bacteria. It is useful in smelting silver ore, in producing leather goods. Thiosulfate can be use to set dyes in textiles industries and dissolving of silver salt from photographic film.

Most of thiosulfate's usefulness stems from its ability to convert certain insoluble metal compounds into soluble complexes, and its ability to act as a mild reducing agent. It is routinely used as a titrant to determine concentrations of oxidants such as hypochlorite in bleach and dissolved oxygen in water. It instantly dechlorinates water, and is used to stop bleaching action in the paper-making industry. Thiosulfate forms water-soluble complexes with many metals, making it useful in photo processing (where it dissolves excess silver bromide on the surface of exposed film, preventing excessive darkening). Thiosulfate is also useful in the extraction of silver from silver ore, in leather manufacture, and as a mordant in the textile industry (Merck & Co., 1968).

Thiosulfate can affect health and the environment. Thiosulfate is an antidote for cyanide poisoning. It reacts with cyanide to produce sulfite and thiocyanate ions:

$$CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$$

This reaction is catalyzed by an enzyme produced by cell mitochondria to neutralize small quantities of ingested cyanide (which occurs naturally in cassava root, lima beans, and almonds). Thiosulfate is an intermediate in several biochemical pathways, including the synthesis of L-cysteine (an amino acid). Thiosulfate is manufactured by some cells by oxidation of elemental sulfur and by degradation of L-cysteine. Thiosulfate is breakdown rapidly in the environment due to the action of air and certain bacteria, eventually producing sulfides and sulfates (S. W. Dahwak, 1993).

There are many process and chemical reaction that can remove or deform the thiosulfate, especially by converting it to another less-hazard component. One of them is by halogen reaction with thiosulfate:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

$$S_2O_3^{2-} + 4Br_2 + 5\,H_2O \rightarrow 2S_4^{2-} + 10H^+ + 8Br^-$$

Another reaction is betauthoren thiosulfate and acid:

$$S_2O_3^{2-} + 2H^+ \rightarrow SO_2^{2-} + S + H_2O$$

Next is reaction betauthoren thiosulfate and metal ion:

$$S_2O_3^{2-} + Cu^{2+} + H_2O \rightarrow SO_4^{2-} + CuS + 2\,H_3O^+$$

And last but not least, reaction of thiosulfate and bacteria:

2.1.1) Thiobacillus thioxidans

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2\,H^+$$

2.1.2) GSB

$$2S_2O_3 + CO_2 + H_2O \rightarrow CH_2O + 2SO_4 + 2S$$

Advanced Oxidation Processes including UV radiation, ozone, and/or hydrogen peroxide are used to destroy organic contaminants as water flows into a treatment tank. If ozone is used as the oxidizer, an ozone destruction unit is used to treat collected off gases from the treatment tank and downstream units where ozone gas may collect, or escape.

2.3) ATMOSPHERE AIR

In this study, atmosphere air will be use as the reagent to be reacting with thiosulfate solution. The reasons for using atmosphere air are this medium is available at no cost and it has no limitation in amount. Atmosphere air is also proposed as the oxidation agent in this study because of its properties that are not harmful to environment and less energy used to produce.

CHAPTER 3: METHODOLOGY

3.1) LITERATURE REVIEW AND RESEARCH

This step involved the determination and specification of the objectives and scope of the study, in addition to developing a detailed understanding of the process operation. Research on the topic and collects information from various sources such as internet, journal and book helps better understanding on thiosulfate removal and advanced oxidation process.

3.2) LABORATORY EXPERIMENT

The experiment will be conduct in chemical laboratory. Some parameters such as thiosulfate and oxygen concentration, air flowrate, pH and temperature will be manipulate, monitor, record and finally the data will be trend for analyze process. The expected result of the experiment is the thiosulfate concentration drop and sulfate formation.

3.2.1) Experiments involve

There are three experiments that will be conduct in chemical laboratory. The first experiment will be the effect of thiosulfate's concentration to the sulfate formation, thiosulfate's concentration drop, pH and temperature in the thiosulfate reaction with atmosphere air. The second experiment will be the effect of air flowrate to the sulfate formation, thiosulfate's concentration drop, pH and temperature in the thiosulfate reaction with atmosphere air. Final experiment will be the effect of oxygen concentration to the sulfate formation, thiosulfate's concentration drop, pH and temperature in the thiosulfate reaction with atmosphere.

3.2.1.1) Experiment 1 (effect of thiosulfate concentration)

Manipulated parameter: S_2O_3 concentration (ppm)

Constant parameters: Air flowrate (6 L/min), Oxygen concentration (21%)

3.2.1.2) Experiment 2 (effect of oxygen concentration)

Manipulated parameter: Oxygen concentration (%)

Constant parameters:S_2O_3 concentration (600ppm), Air flowrate (6 L/min)

3.2.1.3) Experiment 3 (effect of air flowrate)

Manipulated parameter: Air flowrate (L/min)

Constant parameters:S_2O_3 concentration (600ppm),O_2 concentration (21%)

3.2.2) Chemicals used

3.2.2.1) Sodium thiosulfate

This chemical is the main solution in this laboratory experimental. This solution will be put on the reaction with the atmosphere air. The solution will be manipulated in the range of 400 ppm to 1200 ppm.

3.2.2.2) Sulfate reagent (SulfaVer4)

This chemical is use to get the data from UV-vis spectrophotometer equipment. With addition of sulfate reagent (SulfaVer4), the UV-vis spectrophotometer will compare the concentration of aqueous solution (plus sulfate reagent) with the blank solution (without sulfate reagent).

3.2.2.3) Distilled water

This chemical is use to make the thiosulfate solution with required concentration. Distilled water also use to dilute the thiosulfate solution before it can be put on test on the UV-vis spectrophotometer.

3.2.3) Equipments used

3.2.3.1) Glass reactor

This equipment is use as mixing container for thiosulfate and air reaction. The suggested size for this experimental work is 1.5 liter beaker.

3.2.3.2) UV-visible spectrophotometer

The spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the color, or more specifically, the wavelength of light. The instrument used in ultraviolet-visible spectroscopy is called a UV- visible spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o are called the *transmittance*, and are usually expressed as a percentage (%T).

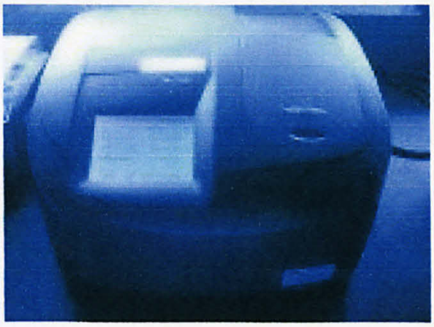


***Figure 3.1:** UV-vis spectrophotometer*

3.2.3.3) Dissolved oxygen (DO) probe

This probe is use to measure the amount of DO in the aqueous solution.

3.2.3.4) pH probe

This probe is use to measure the pH of the aqueous solution.

Figure 3.2: *DO and pH probes*

3.2.3.5) Thermometer

This probe is use to measure the temperature of the aqueous solution.

3.2.3.6) Flowmeter (2-10 L/min)

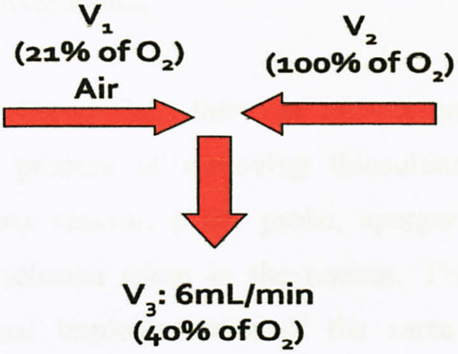
This probe is use to control and manipulate the air and oxygen flowrate.

3.2.3.6) Sparger

This equipment is use to distribute the air injection uniformly.

3.2.3.7) Glass Tubing T-Shaped Connectors

This equipment is use to distribute the air from laboratory air line and oxygen from oxygen tank in desired quantity. To meet the objective for this part, glass tubing t-shaped connector is being used. Theoretically, each of the tube represents V_1, V_2 and V_3.



From the schematic diagram above, a few calculations on material balance equation can be acquire to get the amount of unknown parameters as example below.

V1 + V2 = V3 = 6 ....(1)

V1 (0.21) + V2 (1) = V3 (0.4) ....(2)

V1, V2 =?

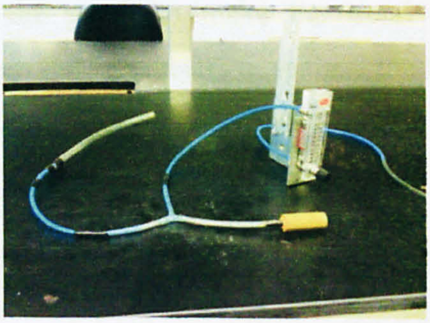


Figure 3.3: Glass Tubing T-Shaped Connectors

3.2.4) Experiments procedures

Three sodium thiosulfate experiments will be carrying out in a batch reactor. Oxidation of sodium thiosulfate will be done by bubbling air through the feed solution. Samples are withdrawn from time to time and analyzed by UV visible spectrophotometer instead of chromatographic technique and old titration technique. The effects of concentration of sodium thiosulfate and air flow rate will be investigated.

Referring figure 3.4, there is shown an experimental setup to demonstrate the process of removing thiosulfate ions from a solution, comprising a glass reactor, a pH probe, sparger for mixing the air and thiosulfate ions solution taken in the reactor. This experiment is used to emulate the actual implementation of the same process on wastewater, whereby oxidation of sodium thiosulfate in wastewater to generally harmless sodium sulfate occurs. It is to be noted the pH probe is to monitor the pH of the solution. The probe are merely measuring instruments and do not have any role whatsoever in the reaction betauthoren advanced oxidation of thiosulfate ions and air in solution. A glass reactor is chosen to hold the liquid that is being tested, besides having a transparent body so that the activities in the glass reactor can be vieauthord and analyzed.

The samples from the experiments will be taken from time to time and analyzed using UV-vis Spectrophotometer. The results are then tabled properly before plotting into the graph to make the trend and clear view of the correlations betauthoren the parameters tested and the thiosulfate concentration drop.

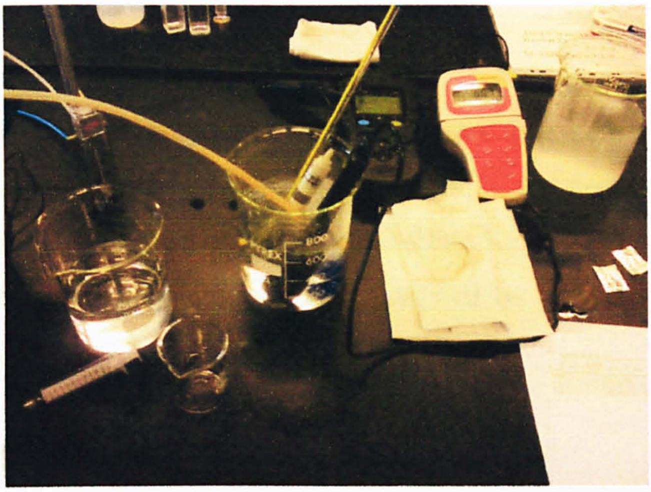


Figure 3.4: Experiment setup

Another apparatus that is submerged into the liquid in the glass reactor is a sparger, which comprises an opening at one end and at least one perforation to the other parts of the sparger to allow air that is being inserted to the said opening to flow to the perforated openings. In this setup, the perforated openings are submerged in the liquid, allowing atmospheric air to be inserted to the opening, which is not submerged in the liquid and to flow to the perforated openings, creating air bubbles in the liquid. This method will dissolve the atmospheric air into said liquid.

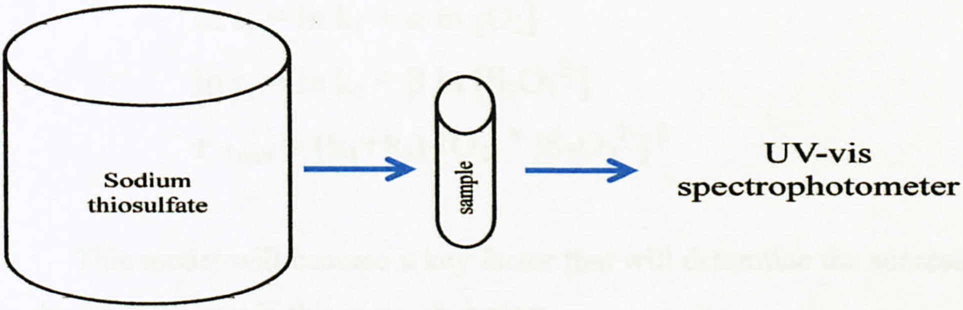


Figure 3.5: Flow of experiment

3.3) DATA COLLECTION AND ANALYSIS

Experimental result and data will be collected and tabled properly. The concern parameters are thiosulfate ions solution's temperature (in degree Celcius,^{0}C), dissolve oxygen (mg/L), pH and sulfate formation (ppm). For these three experiments, graph of all results and data will be plotted folloauthord by trending process.

3.4) KINETIC MODEL DEVELOPMENT

The last step in developing this process of thiosulfate removal technique is the identification of the kinetic model. This step typically involves the investigation of how authorll the developed models are able to track process conditions and their ability to remove the thiosulfate. The rate law of this oxidation process as written below:

$$\mathrm{Rate}_1 \propto [O_2]^{\alpha}$$

$$\mathrm{Rate}_2 \propto [S_2O_3^{2-}]^{\beta}$$

$$r_1 = k_1 [O_2]^{\alpha}$$

$$r_2 = k_2 [S_2O_3^{2-}]^{\beta}$$

$$\ln r_1 = \ln k_1 + \alpha \ln [O_2]$$

$$\ln r_2 = \ln k_2 + \beta \ln [S_2O_3^{2-}]$$

$$\mathbf{r_{Total} = (k_1+k_2)\,[O_2]^{\alpha}\,[S_2O_3^{2-}]^{\beta}}$$

This model will become a key factor that will determine the successful of the chosen technique in this research project.

CHAPTER 4: RESULTS AND DISCUSSION

4.1) Experiment 1 (effect of thiosulfate's concentration)

Below is the tables show the result of experiment 1. The hypothesis shows that increase of thiosulfate concentration will increase the formation of sulfate. Which mean there is more thiosulfate been removed from the aqueous solution by air advanced oxidation.

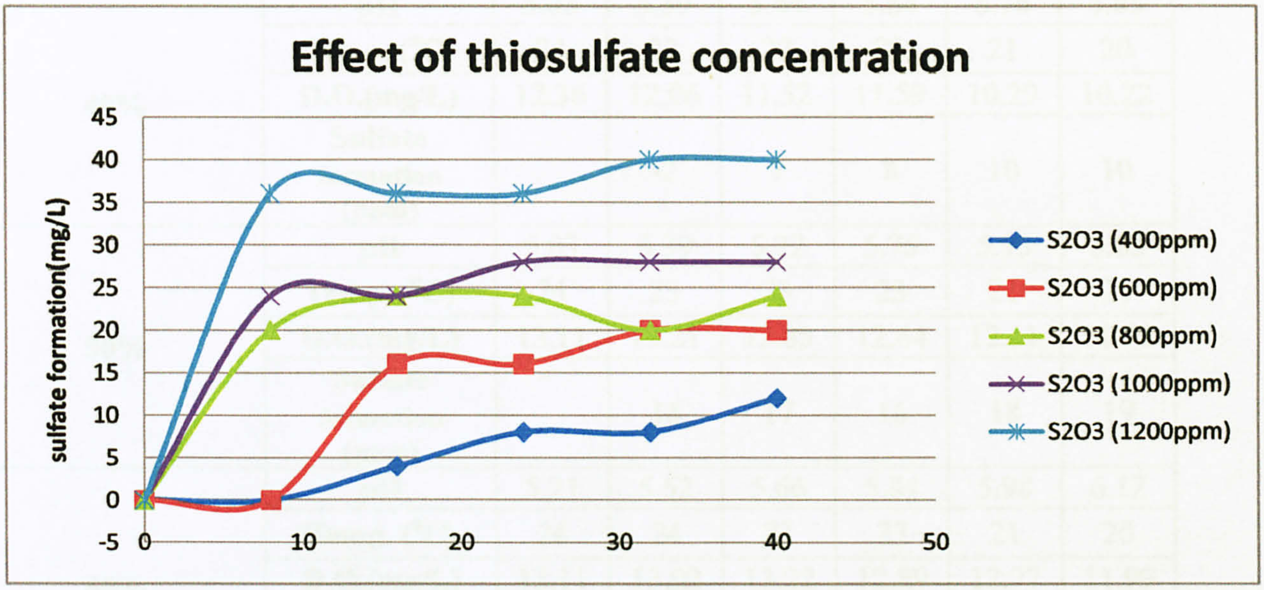
S_2O_3 concentration	Time(min)	0	8	16	24	32	40
400ppm	**pH**	5.75	4.65	4.57	4.53	4.48	4.47
	Temp. (°C)	25	24	24	23	23	22
	D.O.(mg/L)	7.3	7.06	7.23	7.19	7.25	7.11
	Sulfate formation (ppm)		-5	1	2	2	3
600ppm	**pH**	5.02	4.46	4.39	4.37	4.42	4.39
	Temp. (°C)	24	23	22	21	21	20
	D.O.(mg/L)	9.78	8.28	8.4	8.63	8.48	8.49
	Sulfate formation (ppm)		-4	4	4	5	5
800ppm	**pH**	5.42	5.51	5.51	5.62	5.64	5.78
	Temp. (°C)	28	27	25	25	24	24
	D.O.(mg/L)	10.05	10.36	10.75	10.89	11.08	11.27
	Sulfate formation (ppm)		5	6	6	5	6
1000ppm	**pH**	5.32	5.61	5.51	5.49	5.46	5.31
	Temp. (°C)	28	27	26	25	24	23
	D.O.(mg/L)	9.95	10.35	10.67	10.76	10.98	11.15
	Sulfate formation (ppm)		6	6	7	7	7
1200ppm	**pH**	5.05	5.61	5.51	5.59	5.57	5.7
	Temp. (°C)	28	27	26	24	24	23
	D.O.(mg/L)	9.95	10.35	10.67	10.76	10.98	11.15
	Sulfate formation (ppm)		9	9	9	10	10

***Table 4.1**: Result of effect on thiosulfate concentration*

After getting this result, the number of the sulfate formation is must to alter using the dilute factor of four (4). Dilute factor is when the sampling, the thiosulfate solution is diluted by the distilled water four time by its concentration. And by that, another table shows the actual concentration in ppm of sulfate formation.

	S_2O_3 (400ppm)	S_2O_3 (600ppm)	S_2O_3 (800ppm)	S_2O_3 (1000ppm)	S_2O_3 (1200ppm)
Time(min)	Sulfate formation (ppm)	Sulfate formation (ppm)	Sulfate formation (ppm)	Sulfate formation (ppm)	Sulfate formation (ppm)
8	0	0	0	0	0
16	0	0	20	24	36
24	4	16	24	24	36
32	8	16	24	28	36
40	8	20	20	28	40

Table 4.2: Result of effect on thiosulfate concentration (after calibration)



Graph 4.1: Graph of sulfate formation vs. time for manipulated thiosulfate concentration

From the above graph, author can conclude that higher thiosulfate concentration will result in higher sulfate formation or/and higher thiosulfate concentration drop. This is due to the increasing of the number of thiosulfate molecules which had been oxidize to become sulfate molecules. This observation tells that thiosulfate concentration is one of the main component in the rate law of this advanced oxidation process.

4.2) Experiment 2 (effect of oxygen concentration)

Below is the tables show the result of experiment 2. The hypothesis shows that increase of oxygen concentration will increase the formation of sulfate. Which mean there is more thiosulfate been removed from the aqueous solution by air advanced oxidation.

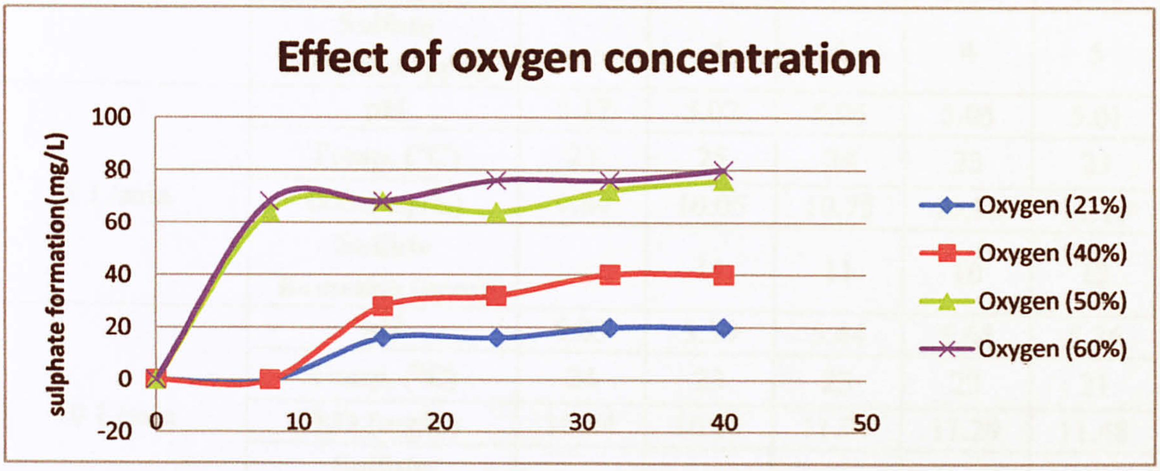
Oxygen concentration	Time(min)	0	8	16	24	32	40
21%	pH	5.02	4.46	4.39	4.37	4.42	4.39
	Temp. (°C)	24	23	22	21	21	20
	D.O.(mg/L)	9.78	8.28	8.4	8.63	8.48	8.49
	Sulfate formation (ppm)		-4	4	4	5	5
40%	pH	5.03	5.39	5.44	5.64	5.76	5.85
	Temp. (°C)	24	23	22	22	21	20
	D.O.(mg/L)	12.36	12.06	11.52	11.59	10.29	10.22
	Sulfate formation (ppm)		-2	7	8	10	10
50%	pH	5.03	5.39	5.22	5.75	5.95	5.85
	Temp. (°C)	24	23	23	23	21	20
	D.O.(mg/L)	13.11	13.21	12.85	12.64	12.11	11.75
	Sulfate formation (ppm)		16	17	16	18	19
60%	pH	5.21	5.52	5.66	5.84	5.98	6.12
	Temp. (°C)	24	24	23	23	21	20
	D.O.(mg/L)	13.11	13.02	13.22	12.89	12.77	11.99
	Sulfate formation (ppm)		17	17	19	19	20

Table 4.3: Result of effect on oxygen concentration

After getting this result, the number of the sulfate formation is must to alter using the dilute factor of four (4). Dilute factor is when the sampling, the thiosulfate solution is diluted by the distilled water four time by its concentration. And by that, another table shows the actual concentration in ppm of sulfate formation.

	Oxygen (21%)	Oxygen (40%)	Oxygen (50%)	Oxygen (60%)
Time(min)	Sulfate formation (ppm)	Sulfate formation (ppm)	Sulfate formation (ppm)	Sulfate formation (ppm)
8	0	0	44	44
16	16	22	44	44
24	16	22	40	55
32	20	20	22	22
40	20	20	48	48

Table 4.4: *Result of effect on oxygen concentration (after calibration)*



Graph 4.2: *Graph of sulfate formation vs. time for manipulated oxygen concentration*

From the above graph, author can conclude that hihger oxygen concentration will result in higher sulfate formation or/and higher thiosulfate concentration drop. This is due the concentration of oxygen increases, it provide more molecule to react with thiosulfate in advanced oxidation process that form sulfate. This observation tells that oxygen concentration is one of the main component in the rate law of this advanced oxidation process.

4.3) Experiment 3 (effect of air flowrate)

Below is the tables show the result of experiment 3. The hypothesis shows that increase of air flowrate will increase the formation of sulfate. Which mean there is more thiosulfate been removed from the aqueous solution by air advanced oxidation.

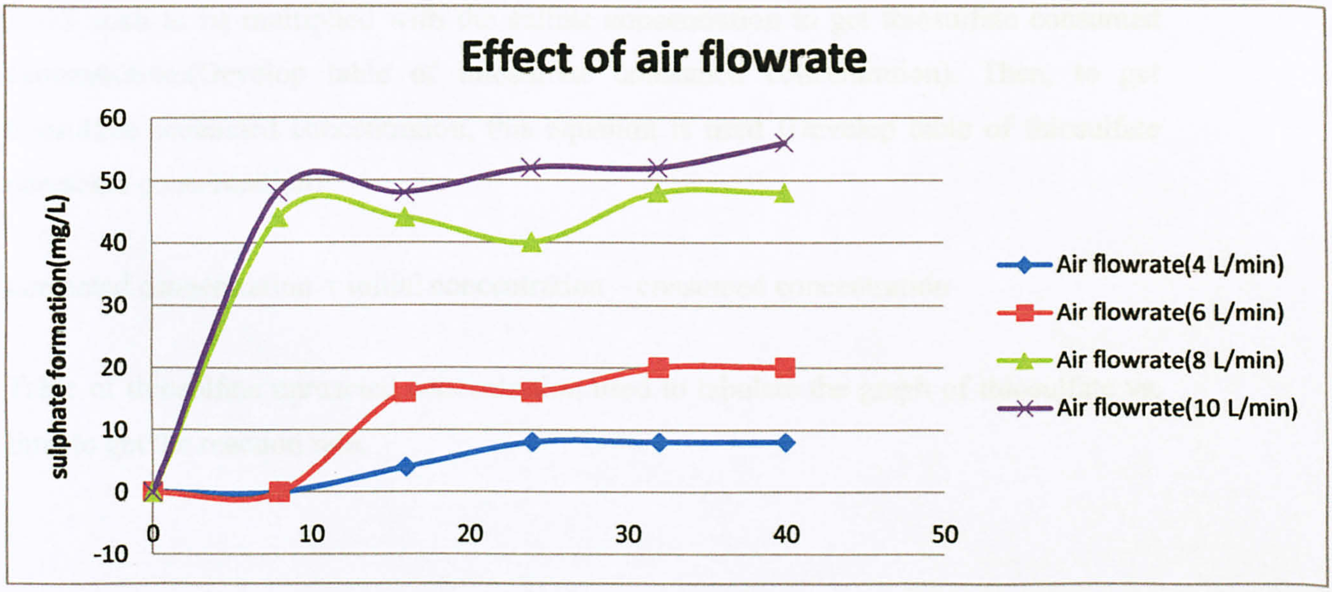
Air flowrate	**Time(min)**	**0**	**8**	**16**	**24**	**32**	**40**
4 L/min	**pH**	5.73	4.55	4.57	4.53	4.5	4.47
	Temp. (°C)	25	24	24	23	22	22
	D.O.(mg/L)	7.29	7.15	7.23	7.19	7.15	7.12
	Sulfate formation (ppm)		-5	1	2	2	2
6 L/min	**pH**	5.02	4.46	4.39	4.37	4.42	4.39
	Temp. (°C)	24	23	22	21	21	20
	D.O.(mg/L)	9.78	8.28	8.4	8.63	8.48	8.49
	Sulfate formation (ppm)		-4	4	4	5	5
8 L/min	**pH**	5.17	5.07	5.05	5.05	5.01	4.97
	Temp. (°C)	23	25	24	23	23	22
	D.O.(mg/L)	9.84	10.05	10.75	10.98	11.19	11.35
	Sulfate formation (ppm)		11	11	10	12	12
10 L/min	**pH**	5.03	5.39	5.44	5.64	5.76	5.85
	Temp. (°C)	24	23	23	23	21	20
	D.O.(mg/L)	10.04	10.85	11.07	11.29	11.48	11.62
	Sulfate formation (ppm)		12	12	13	13	14

Table 4.5: Result of effect on air flowrate

After getting this result, the number of the sulfate formation is must to alter using the dilute factor of four (4). Dilute factor is when the sampling, the thiosulfate solution is diluted by the distilled water four time by its concentration. And by that, another table shows the actual concentration in ppm of sulfate formation.

	Air flowrate (4 L/min)	Air flowrate (6 L/min)	Air flowrate (8 L/min)	Air flowrate (10 L/min)
Time(min)	Sulfate formation (ppm)	Sulfate formation (ppm)	Sulfate formation (ppm)	Sulfate formation (ppm)
8	0	0	0	0
16	0	0	44	48
24	4	16	44	48
32	8	16	40	52
40	8	20	48	52

***Table 4.6:** Result of effect on air flowrate (after calibration)*



***Graph 4.3:** Graph of sulfate formation vs. time for manipulated air flowrate*

From the above graph, author can conclude that higher air flowrate will result in higher sulfate formation or/and higher thiosulfate concentration drop. This is because of oxygen molecules that contain in the air system which provide more molecules to react with thiosulfate in advanced oxidation process that form sulfate.

4.4) Rate law

Stoichiometry for reaction betauthoren thiosulfate and air is:

$$S_2O_3^{\ 2-} + 2O_2 + H_2O \leftrightarrow 2SO_4^{\ 2-} + 2H^+$$

The stoichiometry shows that 1 $mol\ of\ S_2O_3^{\ 2-}$ is needed to produce 2 $mol\ of\ SO_4^{\ 2-}$.

So $1g\ of\ SO_4^{\ 2-} = \frac{112}{(96)}$

$= 1.1667$ (for 1 mol)

For 2 mol of $SO_4^{\ 2-} = 1.1667 \times 2$

$= 2.333$

2.333 need to be multiplied with the sulfate concentration to get thiosulfate consumed concentration.(Develop table of thiosulfate consumed concentration). Then, to get thiosulfate unreacted concentration, this equation is used (Develop table of thiosulfate unreacted concentration):

unreacted concentration = initial concentration – consumed concentration

Table of thiosulfate unreacted concentration used to tabulate the graph of thiosulfate vs. time to get the reaction rate.

This is the derivation of rate law:

$$r_1 \propto [O_2]^{\alpha} \text{..........(1)}$$

$$r_2 \propto [S_2O_3^{2-}]^{\beta} \text{.......(2)}$$

$$r_1 = k_1[O_2]^{\alpha}$$

$$r_2 = k_2[S_2O_3^{2-}]^{\beta}$$

$$\ln r_1 = \ln k_1 + \alpha \ln[O_2] \text{........(3)}$$

$$\ln r_2 = \ln k_2 + \beta \ln[S_2O_3^{2-}] \text{..........(4)}$$

Combine equation (3) with (4):

$$r_T = (k_1+k_2)\,[O_2]^{\alpha}\,[S_2O_3^{2-}]^{\beta}$$

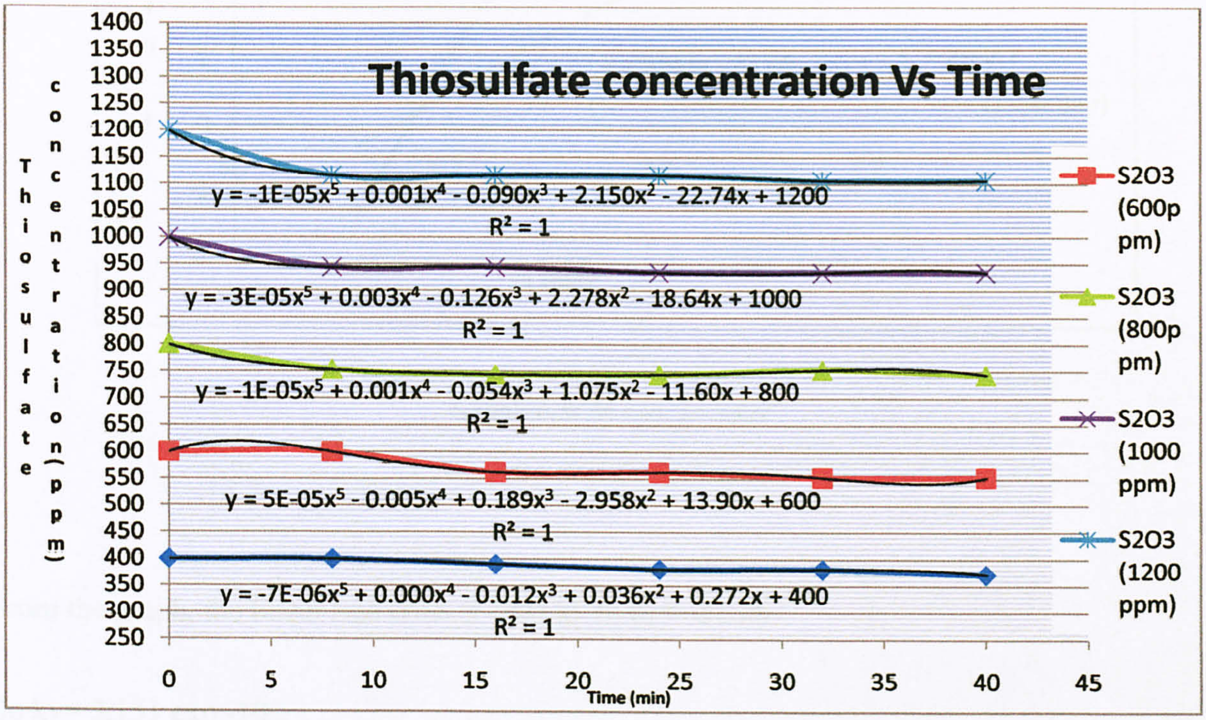
4.4.1 Experiment 1 (effect of thiosulfate's concentration)

	S_2O_3 (400ppm)	S_2O_3 (600ppm)	S_2O_3 (800ppm)	S_2O_3 (1000ppm)	S_2O_3 (1200ppm)
Time(min)	Thiosulfate consumed (mg/L)	Thiosulfate consumed (mg/L)	Thiosulfate consumed (mg/L)	Thiosulfate consumed (mg/L)	Thiosulfate consumed (mg/L)
0	0.0000	0.0000	0.0000	0.0000	0.0000
8	0.0000	0.0000	46.6600	55.9920	83.9880
16	9.3320	37.3280	55.9920	55.9920	83.9880
24	18.6640	37.3280	55.9920	65.3240	83.9880
32	18.6640	46.6600	46.6600	65.3240	93.3200
40	27.9960	46.6600	55.9920	65.3240	93.3200

Table 4.7: *Thiosulfate consumed concentration (Exp 1)*

	S_2O_3 (400ppm)	S_2O_3 (600ppm)	S_2O_3 (800ppm)	S_2O_3 (1000ppm)	S_2O_3 (1200ppm)
Time(min)	Thiosulfate unreacted(mg/L)	Thiosulfate unreacted(mg/L)	Thiosulfate unreacted(mg/L)	Thiosulfate unreacted(mg/L)	Thiosulfate unreacted(mg/L)
0	400.00	600.00	800.00	1000.00	1200.00
8	400.00	600.00	753.34	944.01	1116.01
16	390.67	562.67	744.01	944.01	1116.01
24	381.34	562.67	744.01	934.68	1116.01
32	381.34	553.34	753.34	934.68	1106.68
40	372.00	553.34	744.01	934.68	1106.68

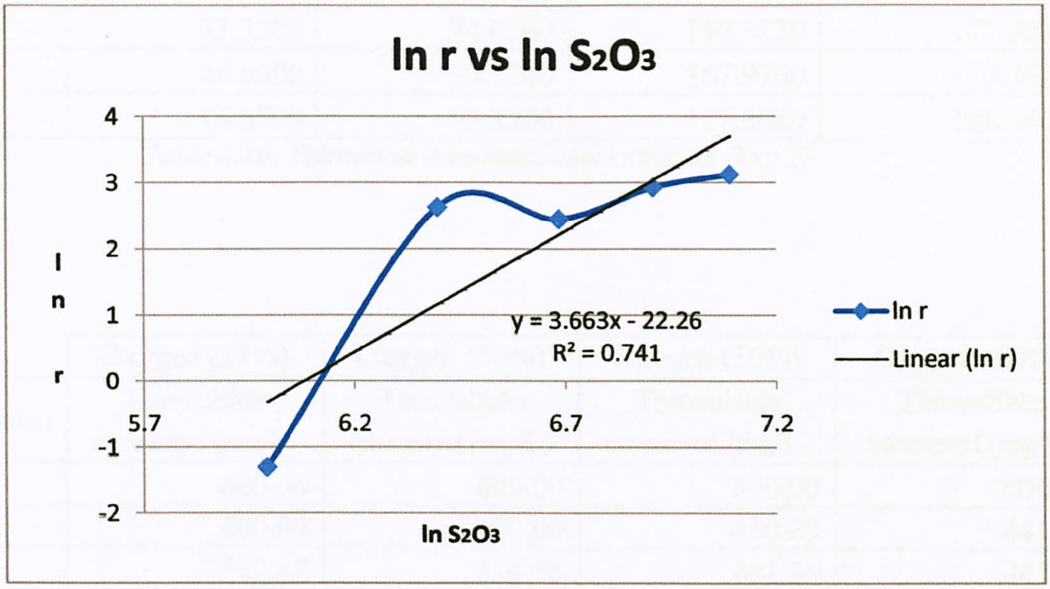
***Table 4.8:** Unreacted thiosulfate concentration (Exp 1)*



***Graph 4.4:** Unreacted thiosulfate concentration vs. Time (Exp 1)*

Thiosulfate concentration (mg/L)	S2O3	S2O3	S2O3	S2O3	S2O3
	400	600	800	1000	1200
Rate, r	0.272	13.9	11.6	18.64	22.74
ln S2O3	5.991464547	6.396929655	6.684611728	6.907755279	7.090076836
ln r	-1.301953213	2.63188884	2.451005098	2.925309809	3.124125488

***Table 4.9:** Data for kinetic modeling S_2O_3*



***Graph 4.5:** ln r vs. ln $S_2O_3^{2-}$*

From the graph, the linear line cross Y-axis at $\ln k_2 = -22.26$

So $k_2 = 2.151$ exp -10

While the slope is $\beta = 3.663$

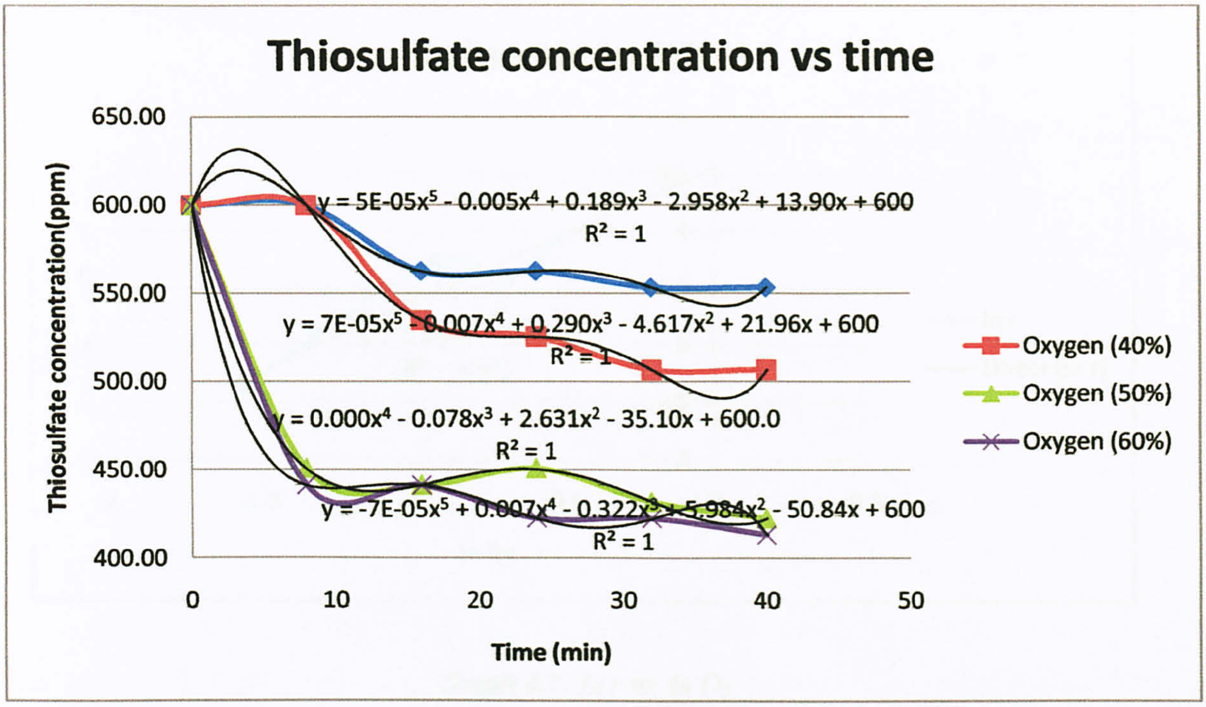
4.4.2 Experiment 2 (effect of oxygen concentration)

	Oxygen (21%)	Oxygen (40%)	Oxygen (50%)	Oxygen (60%)
Time(min)	Thiosulfate consumed (mg/L)	Thiosulfate consumed (mg/L)	Thiosulfate consumed (mg/L)	Thiosulfate consumed (mg/L)
0	0.0000	0.0000	0.0000	0.0000
8	0.0000	0.0000	149.3120	158.6440
16	37.3280	65.3240	158.6440	158.6440
24	37.3280	74.6560	149.3120	177.3080
32	46.6600	93.3200	167.9760	177.3080
40	46.6600	93.3200	177.3080	186.6400

Table 4.10: *Thiosulfate consumed concentration (Exp 2)*

	Oxygen (21%)	Oxygen (40%)	Oxygen (50%)	Oxygen (60%)
Time(min)	Thiosulfate unreacted (mg/L)	Thiosulfate unreacted (mg/L)	Thiosulfate unreacted (mg/L)	Thiosulfate unreacted (mg/L)
0	600.00	600.00	600.00	600.00
8	600.00	600.00	450.69	441.36
16	562.67	534.68	441.36	441.36
24	562.67	525.34	450.69	422.69
32	553.34	506.68	432.02	422.69
40	553.34	506.68	422.69	413.36

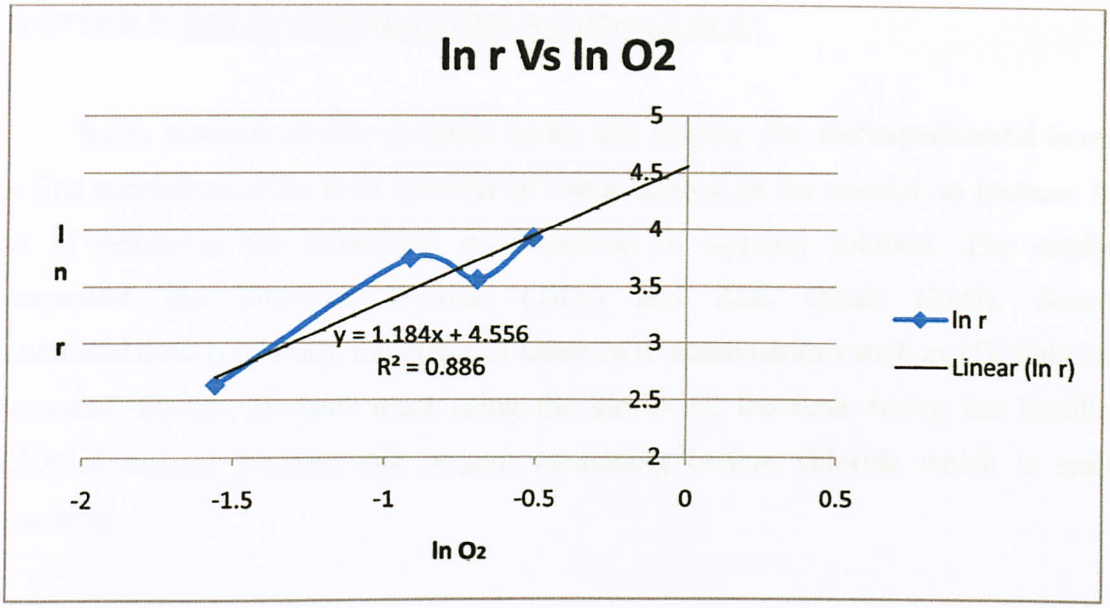
Table 4.11: *Unreacted thiosulfate concentration (Exp 2)*



Graph 4.6: *Unreacted thiosulfate concentration vs. Time (Exp 2)*

Oxygen concentration (%)	O_2	O_2	O_2	O_2
	0.21	0.4	0.5	0.6
Rate, r	-13.9	-42.38	35.1	50.84
ln O_2	-1.560647748	-0.916290732	-0.693147181	-0.510825624
ln r	2.63188884	3.746676553	3.55820113	3.928683446

Table 4.12: *Data for kinetic modeling* O_2



Graph 4.7: ln r vs. ln O_2

From the graph, the linear line cross Y-axis at ln $k_1 = 4.556$

So $k_1 = 95.201$

While the slope is $\alpha = 1.184$

The data collected from experiment 1 and 2 are used for kinetic modeling to find the rate value for formation of sulfate. Formation of sulfate is equal to thiosulfate removed. The value for α and β are 1.184 and 3.663.

$$r_T = (k_1+k_2)\,[O_2]^{\alpha}\,[S_2O_3^{2-}]^{\beta}$$

$$r_T = (95.201)\,[O_2]^{1.184}\,[S_2O_3^{2-}]^{3.663}$$

CHAPTER 5: RECOMMENDATION & CONCLUSION

Some recommendation is stated under this chapter. For the experimental issues, the first recommendation is to consider of using catalyst in the reaction to increase the rate of removing the thiosulfate concentration in aqueous solution. The catalyst recommend are Titanium Dioxide (TiO_2) and Zinc Oxide (ZnO). Second recommendation is to study the effect of other AOP combinations such as UV light and ultrasound. Finally, students must using the gloves all the time during the handling sulfaVer4 reagent because this reagent containing barium chloride which is really hazardous.

As for the conclusion, this project is to study on the parameters affecting the oxidation of thiosulfate using atmosphere air. Result for the three experiments show that by increasing all the parameters' value (thiosulfate concentration, oxygen concentration and air flowrate), more sulfate molecule will form and more thiosulfate molecule will be removed.

Rate law equations show that α and β have the positive values as the rate of thiosulfate oxidation is directly proportional with thiosulfate and oxygen concentration. The rate depends on both thiosulfate and oxygen concentration but is more dependent on thiosulfate concentration since β value is bigger compared to α

AOP increases the rate of thiosulfate oxidizes which will lead to the better removal of thiosulfate from the aqueous solution. This method was proven to be effective for thiosulfate removal.

REFERENCES

1) Thomas Oppenlander, *Photochemical Purification of Water and Air, Advanced Oxidation Processes(AOPs),Principles, Reaction Mechanisms, Reactor Concepts* (2003)

2) P.Khanna, B. Rajkumar, N. Jothikumar, *Microbial Recovery of Sulfur from Thiosulfate-Bearing Wastewater with Phototrophic and Sulfur-Reducing Bacteria* *(*1996*)*

3) FredSenese,<http://antoine.frostburg.edu/chem/senese/101/compounds/faq/thiosulfate.shtml> (1998)

4) J.M. Gonzales, A. Roca, M. Cruells, F. Fatino, *The oxidation of thiosulfates with copper sulfate. Application to an industrial fixing bath (*2008*)*

5) Donald C. Schreiber and Spyros G. Pavlostathis, *Biological Oxidation of Thiosulfate in Mixed Heterotrophic/Autotrophic Cultures.* (1998)

6) Hayao Sakamoto, Junichirou Taniyama and Kagoshima Yonehara, *Analytical Sciences, Determination of Ultra-Trace Amounts of Total Mercury by Gold Amalgamation-Cold Vapor AAS in Geothermal Water Samples by Using Ozone as Pretreatment Agent*. (1997)

7) S. W. Dahwak, *Thiosulfate Chem. Ed.*(1993).

8) Alisdair Boraston, *Beer's Law (*2008*)*

9) Rendina, George, *Experimental Methods in Modern Biochemistry* (1976)

REMOVAL OF THIOSULFATE FROM AQUEOUS SOLUTION VIA AIR ADVANCED OXIDATION PROCESS

ABUDZAR BIN MD RASHID

CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
JULY 2009

ABUDZAR BIN MD RASHID B. ENG. (HONS) CHEMICAL ENGINEERING JULY 2009