EFFICIENCY OF DIISOPROPANOLAMINE (DIPA) DEGRADATION WITH DIFFERENT VISIBLE LIGHT INTENSITIES UNDER PHOTO-FENTON OXIDATION

by

RITCHIE LIM LI ZHI

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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2013

CERTIFICATION OF ORIGINLITY

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.

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(RITCHIE LIM LI ZHI)

ABSTRACT

Advanced Oxidation Process (AOP) is commonly known as one of the chemical treatment designed specifically to remove unwanted materials or waste, either in the form of organic or inorganic materials. This technology is commonly being utilized in the waste water treatment industry by performing complex oxidation reactions in order to breakdown the biologically toxic materials. Basically, this project will be conducted based on a specific method of advanced oxidation process (AOP) namely Fenton's oxidation with the aid of photolysis on one of the rare amine wastes, Diisopropanolamine (DIPA) based on different light intensities as the experimental parameters.

The major motivation for the author to perform this study is to find out the effect of degradation efficiency of DIPA under different light radiation. The author has constructed a simple experiment setup for Photo-Fenton oxidation process with light radiation available where the reaction system will be placed directly under the light source. Standard solutions for each reagent were also prepared with proper procedures by the author. Prior to the experiments, the author has produced a calibration curve for concentration estimation of the processed samples. Degradation efficiency is mainly determined by Chemical Oxygen Demand (COD) by utilizing COD digester and Hach® DR 5000.

Experimental work started with optimization of hydrogen peroxide (H_2O_2) under both light sources, 1.0 M of hydrogen peroxide gave the highest COD removal in percentage instead of 0.01 M and 0.1 M in both cases. Then, optimization of DIPA concentration is carried out for both light intensities. 300 ppm of DIPA solution became the most optimum concentration for 500 Watt environment; whereas 500 ppm for 300 Watt light radiation. The most optimum systems were compared for the most efficient light intensity for DIPA degradation under Photo-Fenton oxidation. 300 Watt light source gives the highest COD removal percentage of 60.64% and said to be the higher efficiency light condition for such oxidation process.

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CHAPTER 1.0

PROJECT BACKGROUND

1.1 General Background Study

Waste products are commonly seen in most of the chemical process industries and special treatments are required on these produced wastes before discharging or releasing them to the environment or even decomposing them. Performing waste treatment is not only being responsible to the respective industries but also as a fulfilment of the environmental rules and regulations. For the past few decades, conventional methods of waste treatment have been used in order to pre-treat unwanted or harmful waste products. For example, electrolysis is used to separate different materials using electrical charges. Although these commercial methods are widely used in the industries, however most of the treatment processes only managed to achieve the basic level or in another words primary or secondary separation of unwanted wastes from the primary substance. Studies shown these waste treatment methods hardly managed to proceed further into microscopic level in removing undesired waste materials. In the year 1987, the technology of Advanced Oxidation Process (AOP) has been introduced to the industry by Glaze et al. (2003) which utilizes the principle of possible generation of hydroxyl radicals (•OH) in a sufficient quantity for better purification (Oppenländer, 2003). The major difference between AOP and conventional oxidation process is the generation of active hydroxyl radical group (•OH) which will lead to a chain reaction on the oxidation process instead of Redox reaction (reduction-oxidation process) which involves losing or gaining of valence electrons between two (2) or more elements. Since AOP portrays better capability in driving oxidation process than others, it is then being categorized as a tertiary treatment in waste product removal process in which most organic and inorganic contaminants can be eliminated successful (Oppenländer, 2003). Applications of AOP are mostly presented in Europe and United States (Oppenländer, 2003) compared to other developing contraries, this might due to the reason of higher operating cost which relatively reduces gross revenue. However, there are still some developing contraries like China (Oppenländer, 2003) interested in implementing AOP technology for enhanced waste treatment. Due to the fact that China is developing fast not only in manufacturing industry but energy production technologies as well. Along with the rapid development, local legislative authorities tend to stringent the rules and regulations especially in waste water discharge covered under environmental section. In addition, the increasing interest in reusing and recycling water resources also contribute to the development of AOP technologies in countries like China.

1.2 Problem Statement

Since 1980's, Advanced Oxidation Process (AOP) has been introduced to enhance the efficiency of amine waste and wastewater treatment. Even though the technology of AOP is available in treating amine waste, however a common problem is noticed which is that most of the existing studies are only restricted to basic Fenton's oxidation. Whereas Fenton oxidation process with the assistance of photolysis or known as Photo-Fenton process is rarely to be seen. Other than that, advanced oxidation treatments were normally covered limited range of amine waste such as Monoethanolamine (MEA) and Diethanolamine (DEA). No significant findings or researches were done based on the degradation efficiency of another type of secondary alkanolamine known as Diisopropanolamine (DIPA) by utilizing Photo-Fenton reaction. In addition, experimental parameter such as different intensities of light irradiation, especially using visible light was not being taken into serious considerations. On the opposite, common experimental parameters for example initial dosage of Fenton's reagent, pH condition of the system and temperature were conventionally being studied for the efficiency effect of amine degradation. Other problems have also surfaced which related to the optimization of experimental parameters; such as suitable dosage of hydrogen peroxide as oxidizing agent, initial DIPA sample waste concentration to be treated for different light intensities for the process of DIPA degradation using Photo-Fenton oxidation. These relevant problems will lead to more concrete research objectives for the project development.

1.3 Objectives of Study

A few ultimate objectives which have to be achieved at the end of this research study are as follow.

I. To optimize the most suitable parameter configurations for each light intensity to degrade Diisopropanolamine (DIPA) by utilizing Photo-Fenton oxidation process.

II. To evaluate and compare the degradation efficiency of Diisopropanolamine (DIPA) under different light intensities in Photo-Fenton oxidation process based on the optimized experimental parameter.

1.4 Scope of Project Work

Under this project study, the scope of work can be summarized as follow in order to construct a more concrete research boundary:

a) Type of amine waste : Secondary amine (Diisopropanolamine, DIPA)
b) Experiment Temperature range : Ambient temperature (≈ 25-27^{o}C)
c) Experiment Pressure : Atmospheric pressure (1 atm)
d) Initial Fenton's reagent dosage range : 0.1 Molar
e) Concentration of oxidizing reagent, H_2O_2 : 0.01 M, 0.1 M and 1.0 M
f) Concentration of DIPA model waste : 500ppm, 300ppm and 100ppm
g) Light irradiation power : 300 and 500 Watts
h) Solution pH value range : 3 (acidic condition)
i) Reaction duration : 60 minutes (with 15minutes sample test interval)

1.5 Feasibility of Project Study

This project work will be performed with the usage of Fenton's reagent as the catalyst which known as Iron (II) Sulphate Heptahydrate ($FeSO_4.7H_2O$) to carry out Fenton's oxidation process. Besides, the experiment has to be conducted based on several constant parameters such as reaction system temperature which is suggested to be at ambient temperature, between 25-27^oC as well as initial concentration of Fenton's reagent in order to amplify the significance of effects from the experimental parameters.

1.6 Relevancy of Project

Advanced Oxidation Process (AOP) is still uncommonly utilized in the industry due to high operating cost although the effectiveness is relatively higher than other controversial waste treatment methods. This research study can serves as a stepping stone for further studies on the parameter properties which will affect the quality of photolysis assisted Fenton's oxidation process. In return, this may help in expanding the usage of AOP on waste treatment processes including waste water treatment in the future.

CHAPTER 2.0

LITERATURE REVIEW

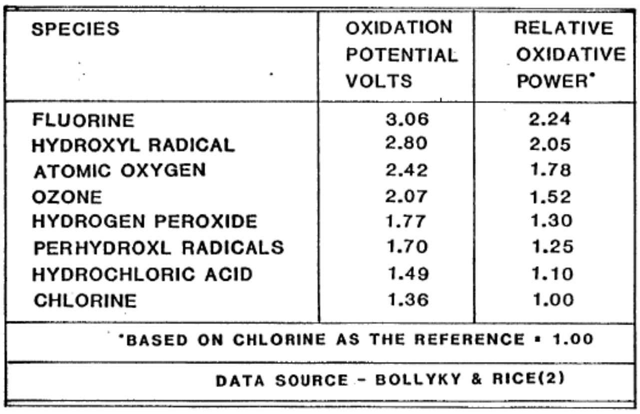
2.1 Advanced Oxidation Process (AOP)

Advance Oxidation Process (AOP) is another level of oxidation process comparable to other commercial oxidation reactions or waste treatment methods. This technology is being introduced by Glaze et al. (2003) by suggesting the possibility of producing highly reactive hydroxyl radicals (•OH) which will actively react with the surrounding substances causing a chain reaction. Propagation of hydroxyl radicals will lead to breakdowns of unwanted waste particles in the form of other less harmful waste products such as carbon dioxide (CO_2), water (H_2O) and other mineral salts. The process involved can be known as mineralization. Advanced Oxidation Process (AOP) is also called as an in-situ generation process, involving the generation of hydroxyl radicals (•OH) as mentioned above. This technology manages to accelerate and improves the non-selective oxidation which leads to the possibility of destructing a wider range of organic as well as inorganic contaminants in the solution (Kim, 2004). This particular achievement is barely feasible by biological waste treatment. Due to its relatively high oxidative capability and efficiency, AOP is then being categorized as one of the popular technique used in tertiary waste treatment (Oppenländer, 2003) which is another advanced step to remove stubborn or micro-sized contaminants that cannot be eliminated during the secondary waste treatment (Siemens, 2011). In order to perform advanced oxidation process (AOP), there are several chemical principles that need to be taken into consideration. These principles can be then segregated into three (3) parts (Oppenländer, 2003):

I. Formation of hydroxyl radicals (•OH) – Initiation
II. (•OH) attacks and break molecules into smaller fragments – Propagation
III. (•OH) recombine together and form water molecules (H_2O) – Termination

Ability of generating hydroxyl radicals (•OH) brings huge advantage to the Advanced Oxidation Process (AOP) due to its high oxidation power. High value of oxidation power makes these highly active radicals more powerful as an oxidizing reagent as well as non-selective chemical oxidant. A general comparison of the oxidation power among several oxidation species is shown on Table 2.1.1

Table 2.1.1 Relative Oxidation Power of Oxidizing Species
Source: Edward, 1987



SPECIES	OXIDATION POTENTIAL VOLTS	RELATIVE OXIDATIVE POWER*
FLUORINE	3.06	2.24
HYDROXYL RADICAL	2.80	2.05
ATOMIC OXYGEN	2.42	1.78
OZONE	2.07	1.52
HYDROGEN PEROXIDE	1.77	1.30
PERHYDROXL RADICALS	1.70	1.25
HYDROCHLORIC ACID	1.49	1.10
CHLORINE	1.36	1.00

*BASED ON CHLORINE AS THE REFERENCE = 1.00

DATA SOURCE – BOLLYKY & RICE(2)

As shown in the table, relative oxidation power of hydroxyl radical (•OH) is considered high in comparison with other common oxidizing species used in AOP such as Ozone (O_3) and hydrogen peroxide (H_2O_2).

In general, different types of Advanced Oxidation Processes (APOs) are used for waste treatment (H. Movahedyan & Assadi, 2009) such as follows:

2.1.1 Ozone (O_3)

Ozone (O_3) is applied as an oxidation reagent in the oxidation process for degrading the organic compound in alkaline condition (R. Andreozzi, 1999). Ozone (O_3) can be generated manually using ozone generator by taking air or oxygen (O_2) as feed component. In this process of AOP, ozone can react with targeted organics either directly or indirectly via decomposition and formation of hydroxyl radicals.

$$O_3 + H_2O + OH^- \rightarrow \bullet OH + O_2 + HO_2\bullet \quad (2.1)$$

2.1.2 Ozone (O_3) + Hydrogen Peroxide (H_2O_2)

Besides applying ozone alone in the process, it can be combined with other oxidant such as hydrogen peroxide (H_2O_2) in the ozone solution in order to enhance ozone decomposition and accelerate the formation of hydroxyl radicals (•OH) (R. Andreozzi, 1999). Furthermore, this acceleration process can even be enhanced by increasing the pH of the solution by making it more alkaline. In this case, hydroxide ion (OH^-) acting as the initiator:

$$OH^- + O_3 \rightarrow O_2 + HO_2^- \quad (2.2)$$

$$HO_2^- + O_3 \rightarrow HO_2\bullet + \bullet O_3^- \quad (2.3)$$

$$HO_2\bullet \leftrightarrow H^+ + \bullet O_2^- \quad (2.4)$$

$$\bullet O_2^- + O_3 \rightarrow O_2 + \bullet O_3^- \quad (2.5)$$

$$\bullet O_3^- + H^+ \rightarrow HO_3\bullet \quad (2.6)$$

$$HO_3\bullet \rightarrow \bullet OH + O_2 \quad (2.7)$$

$$\bullet OH + O_3 \rightarrow HO_2\bullet + O_2 \quad (2.8)$$

2.1.3 Photooxidation (with UV source)

Photooxidation is known as an oxidation process with the existence of light radiation. Due to the fact that conventional ozone or hydrogen peroxide oxidation does not completely oxidize the organic compound into carbon dioxide (CO_2) and water (H_2O) (Kim, 2004). Thus, in order to overcome this problem, ultraviolet radiation (UV) is being introduced. As the organic compound absorbs energy from the UV source, it becomes more reactive (exited state) towards chemical oxidants which in return fasten the process of oxidation.

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \quad (2.9)$$

$$H_2O_2 + hv \rightarrow 2\bullet OH \quad (2.10)$$

2.1.4 Photocatalysis (with TiO_2)

In extension to photooxidation process, it can be further enhanced by applying solid metal catalyst. The major function of UV radiation is to excite the metal catalyst in order to form electron-hole as well as free electrons on the surface of the catalyst (Kim, 2004). An opposite positive-negative charge is created as the electron-hole is formed, this will then promote the process of redox reaction which involves electrons transfer. In common, the preferable catalyst will be titanium dioxide (TiO_2) due to several benefits. Titanium dioxide is firstly economical to obtain, more importantly is its high stability below various conditions as well as its high potential in producing free radicals that accelerates the oxidation process. An example of photocatalysis is shown in the figure below.

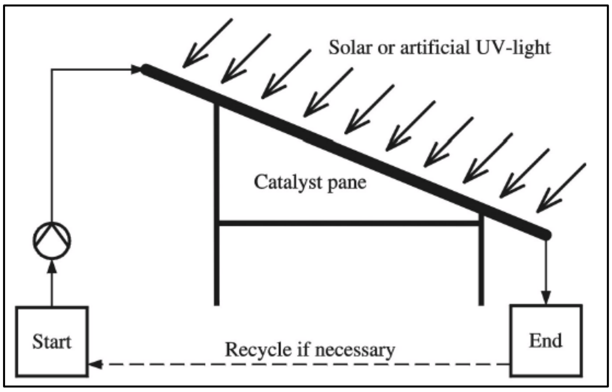


Figure 2.1.1 Thin Film Fixed Bed Reactor (TFFBR) for Photocatalysis
Source: A. Vogelpohl. and S.M. Kim, 2004

2.1.5 Electron Beam Irradiation (E-beam irradiation)

This technique works based on the principle of releasing high energy and free electrons in order to create excited state species and desired free radicals. These free radicals function as the same as those mentioned above which is to oxidize the organic and inorganic compounds, resulting in formation of by-products such as CO_2 and H_2O (C.L. Duarte, 2002). Generally, E-beam irradiation produces aqueous electrons (e^-_{aq}) and hydroxyl radical (•OH) in approximately equal concentration respectively. The aqueous electron (e^-_{aq}) undergoes single electron transfer with various organic compounds producing hydroxyl radicals. Moreover, the process can be exampled with the reaction as follow (Cooper et al., 1992):

$$e^-_{aq} + ROH \rightarrow R\bullet + \bullet OH \qquad (2.11)$$

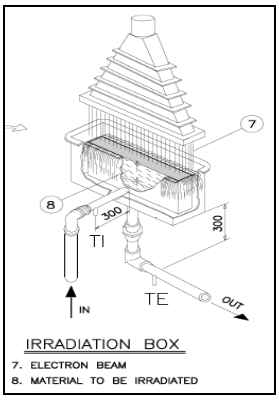


Figure 2.1.2 E-beam Irradiation Box
Source: Duarte et al., 2002

2.1.6 Sonolysis

Sonolysis utilizes ultrasonic irradiation by introducing ultrasonic sound energy with the range of frequency from 15kHz to 1MHz (Kim, 2004). By applying ultrasonic energy, electrohydraulic cavitation will then be induced for the oxidation process to take place. Water molecules will produce desired hydroxyl radicals which needed for the oxidation process as well as hydrogen atom by undergoing thermal dissociation (Capelo, Lavilla, & Bendicho, 2000).

$$H_2O \rightarrow \bullet OH + H \tag{2.12}$$

One of the benefits in introducing sonolysis is that it eliminates the necessity of chemical oxidants, high temperature and pressure conditions for degradation of organic compounds (J.L. Capelo, 2000).

2.2 Fenton's Reaction and Photo-Fenton Process

2.2.1 Fenton Reaction

Fenton's treatment was being founded by M.J.H. Fenton back in the year 1894 when this technology is proven where ferrous ion (Fe^{2+}) actually promotes oxidation process with the presence of hydrogen peroxide (H_2O_2) (Montserrant Pèrez, 2002). However, Fenton's reaction operates based on the exact same concept of oxidation which is to generate highly reactive hydroxyl radicals (•OH). The production of hydroxyl radicals can be summarized into a chemical equation as shown below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \qquad (2.13)$$

Hydroxyl radicals are generated once the H_2O_2 is being added into a ferrous salt solution containing Iron (II) ions (Fe^{2+}). A common salt solution will be used as the reagent namely Ferrous Sulphate ($FeSO_4$) due to its high abundance and it is a non-toxic element (Stasinakis, 2008). The production of hydroxyl radicals from Fenton reagent is said to be a relatively easier method since no specific reactants and special apparatus are needed in order to carry out this process (R. Andreozzi, 1999). In addition, hydrogen peroxide (H_2O_2) is chosen because it is easy to be handled and manage to breakdown contaminants into environmentally benign products (Jordi Bacardit, 2007). There are several conditions that needed extra attention while carrying out the process of Fenton's reaction in order to increase the effectiveness of the overall oxidation process. Studies show that the suitable pH condition for Fenton's reaction is in acidic condition with the range of pH 2-4. Acidic condition tends to accelerate the production of hydroxyl radicals (•OH) as well as the degradation rate of the organic or inorganic compounds. Apart from that, Fenton's reaction does not require specific environmental condition such as high pressure and high temperature (HPHT) for the oxidation process to take place. Thus, ambient temperature variance from 25^oC to 28^oC and the pressure of 1 atm is sufficient enough for Fenton's reaction to perform which indirectly became one of its advantages compared to other Advanced Oxidation Processes (AOPs).

Fenton's reagent is being widely used due to its effectiveness on degrading wide range of contaminants in waste treatment processes including aromatic hydrocarbons, amines, phenol, polycyclic aromatics, alcohol, mineral oils and etc. (Lou and Lee, 1995). Its effectiveness can also be proved by the ability to completely remove unwanted contaminants in a short period of time, approximately 10minutes. Figure below shows the illustration of a Fenton's process.

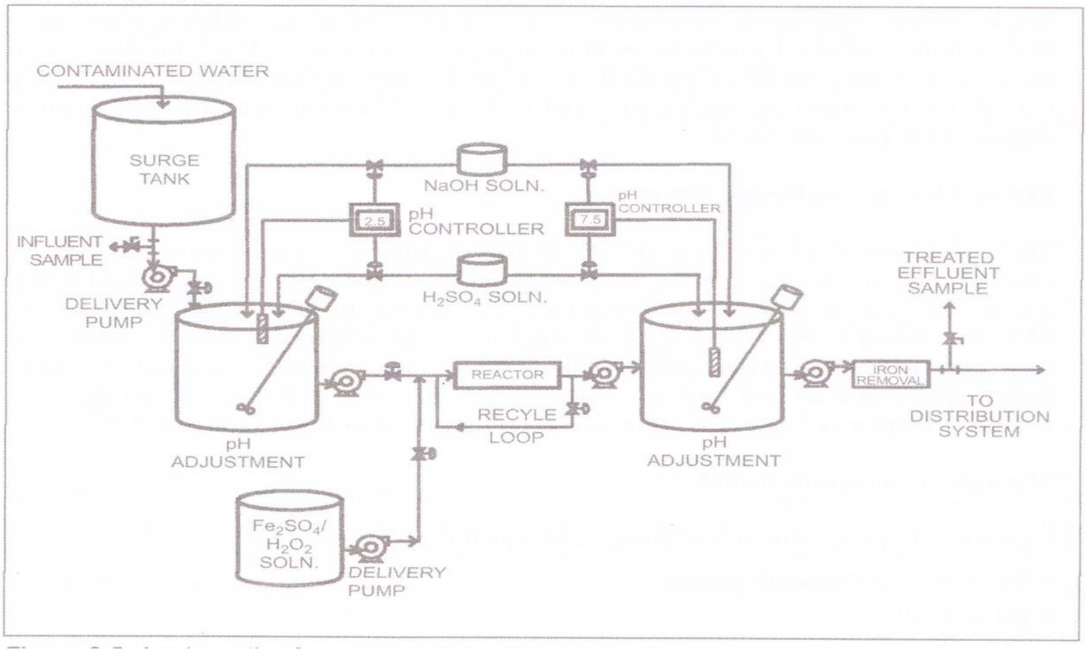


Figure 2.2.1 Schematic System of Fenton's Reaction

Source: Komex H2O Science, 1998

2.2.2 Photo-Fenton Reaction

Efficiency of Fenton oxidation in terms of COD removal percentage is strongly depends on several operating conditions. As the research carried out before, COD removal efficiency by oxidation increases when the system is under acidic condition with pH value range from 2-4. However, COD removal efficiency tends to decrease as the reaction pH increases from 4-7 or in alkaline conditions due to decomposition of hydrogen peroxide as the oxidizing agent (Hwang, 2000). In addition, based on the study of Fenton oxidation on non-biodegradable landfill leachate, research found out that the dosage of Fenton reagent plays an important role as well. COD removal efficiency is satisfactory until Fenton dosage exceeded 500 mg/L (Hwang, 2000). Besides than operating parameters, the initial condition of the sample waste does affect the outcome of the entire Fenton process. A research on Fenton oxidation of natural gas plant wastewater shows that pre-treated wastewater gives higher COD removal in terms of percentage compared to partially treated and untreated waste sample (Abdul Aziz Omar, 2010).

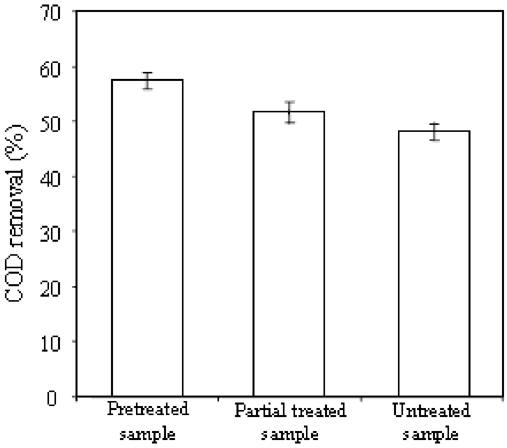


Figure 2.2.2 COD removal (%) on different treated samples
Source: A.A.Omar, R.M.Ramli and Puteri

Fenton's process not only can be a stand-alone process, but it can also be assisted with other process like photolysis. With the application of UV-Visible light irradiation, the process is then known as Photo assisted Fenton process or Photo-Fenton process. As the availability of UV-VIS irradiation, the rate of degradation for organic or inorganic contaminants are strongly accelerated by forming more hydroxyl radicals (•OH). In photo Fenton process, Iron (III) complexes (Fe^{3+}) can also be used other than iron (II) alone. The process steps of photo-Fenton reaction can be summarized in Figure 2.2.3.

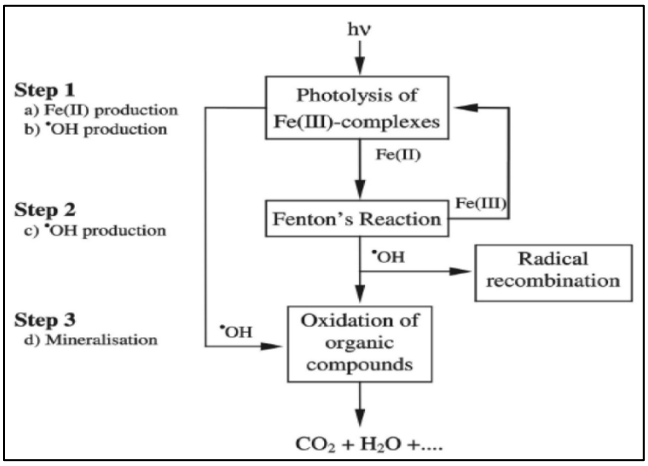


Figure 2.2.3 Reaction Path of Photo-Fenton Process
Source: A. Vogelpohl. and S.M. Kim, 2004

Fe(III) complexes will absorb UV energy from the irradiation of UV-VIS light source and go through photolysis by producing Fe(II) ions (Fe^{2+}) and hydroxyl radical (•OH) respectively.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH \quad (2.14)$$

Photolysis of the Fe(III) complexes will drive to the production or regeneration of Fe(II) reagent which used to further produce hydroxyl radicals for chain oxidation processes (Kim, 2004).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \quad (2.15)$$

Since the existence of Fe(III) ions have the tendency to form sludge by precipitation if Fe(III) is in excess, one of the solution to this problem is to recycle the Fe(III) due to the fact that Fenton reaction is being catalysed by Fe(III) as well in this case.

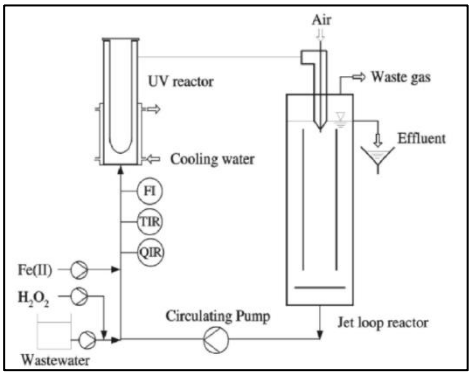


Figure 2.2.4 Example of Photo Fenton Pilot Plant

Source: A. Vogelpohl. and S.M. Kim, 2004

Photo-Fenton oxidation is believed as one of the cheaper advanced oxidation process to treat wastewater compared to other methods like ozone, ozone/UV and UV/H_2O_2 systems. Research has been carried out to study and compare the difference between energy cost in terms of usage and chemical cost for various AOP including Photo-Fenton oxidation. Table below shows the distribution of degradation time (hours) and costs for each process (Fallmann, 1997).

Table 2.2.1 Distribution of degradation time and costing
Source: Y.W. Kang and K.Y. Hwang

	Degradation time [h]	TOC eliminated [ppm]	Chemical costs [ATS/m^3]	Energy demand [kWh/m^3]	Energy costs [ATS/m^3]	Total costs [ATS/m^3]	Total costs [ATS/kg TOC]
Ozone	6	322 (59%)	1440	2400	3744	5184	16122
Ozone/UV	4	332 (61%)	960	2400	3744	4704	14149
UV/H_2O_2	6	71 (13%)	82	1200	1872	1954	27579
Photo-Fenton	2.5	327 (60%)	84	500	780	864	2642
Photo-Fenton (Sunlight)	ca. 4	327 (60%)	84	0	0	84	257

By utilizing Photo-Fenton oxidation, the degradation time managed to be cut down to 2.5 hours instead of the maximum degradation time which is 6 hours in total. In addition, the degradation efficiency is sufficiently high with approximately 60% in TOC removal in such short period of degradation time. Furthermore, the total costing which consists of chemical cost and energy cost for Photo-Fenton oxidation is lowered by few folds in comparison with other systems.

2.3 Amine Waste and Diisopropanolamine (DIPA)

In general, amine is known as a group of basic organic components derived from ammonia (NH_3). However, amine can be classified into different categories such as primary amine which one (1) of the hydrogen atoms is replaced by alkyl group (-R) or free radicals, secondary amine is where two (2) hydrogen atoms are replaced and tertiary amine is where all three (3) hydrogen atoms are substituted ("Diisopropanolamine," 2013). One of the common functions of amine is to act as reducing agent which can be easily oxidized by other oxidizing agent. It is also being widely used in the organic synthesis of polymerization catalyst ("Diisopropanolamine," 2013). Diisopropanolamine (DIPA) is known as one of the secondary alkanolamines available in the industry. Two (2) hydrogen atoms of the ammonia (NH_3) compound are replaced with $[(CH_3)_2CH]$ groups. Thus, DIPA portrays with a chemical formula of $[(CH_3)_2CH]_2NH$ as shown in the figure below.

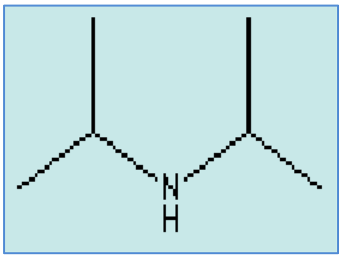


Figure 2.3.1 Chemical Formula of DIPA
Source: Guidechem, 1993

Physical and chemical properties of DIPA such as physical states as well as boiling, melting points are available in most of the technical data sheets. DIPA exists in the form of liquid state in ambient condition with a melting point of -61^{o}C and boiling point of 84^{o}C. In short, temperature condition should be maintained below its boiling point while performing any kind of experiment involving DIPA to avoid changes in its properties. Diisoproponalamine is a colourless solution which identical to normal drinking water, however it has an amine-like odour which makes the differentiation more obvious. DIPA functions similarly as commercial amine products which serve as a catalyst for polymerization process. Sometimes, DIPA is considered as undesired product due to its tendency of polymerizing other substances, especially monomers such as styrene. Health, Safety and Environment issues are important when dealing with DIPA. Although there is no significant effect of DIPA on humans' health in terms of toxicity and exposure, however DIPA is relatively hazardous to the aquatic life. Thus, DIPA is not being disposed to the environment; instead it is normally being recycled whenever possible due to its non-biodegradability property. In addition, another method of dealing with DIPA disposal can be done by dissolving it in combustible solvents and burn in an enclosed furnace. ("Diisopropanolamine," 2013)

2.4 Oxygen Demand Testing

Conventionally, there are many methods in determining the efficiency of waste treatment or the level of pollution for the subjected waste product. One of the most important parameter in determining pollution amount is via oxygen demand. Various measurements can be carried out in order to identify the level of contamination. For example, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and Total Organic Carbon (TOC) measurements are commonly used especially in waste treatment industries in order to determine the degradation efficiency of the waste elements. In definition, Chemical Oxygen Demand (COD) is the total amount of oxygen (O_2) is being consumed when the substances are being oxidized by an oxidizing agent, (Laws, 2000) . In order to carry out COD test, a strong chemical oxidant is being used in an acidic condition and heat is eventually applied for duration of 120 minutes by using a COD digester. This process will then promote oxidation reaction from happening to the organic carbon available in the pollutants and converting them into other waste products such as carbon dioxide (CO_2) and water (H_2O). The result of COD measurement can be obtained by titration process with a titrating reagent known as Ferrous Ammonium Sulphate (FAS) after the effluent mixture is brought back to room temperature. End point of the titration process is recorded for COD value calculation. COD value can be calculated by using the following formula:

$$\text{COD value} = \frac{(A-B)*N*8000}{Volume\ of\ Sample} \tag{2.16}$$

where A – exact volume of FAS reagent used for blank sample (mL)

B – exact volume of FAS reagent used for subject sample (mL)

N – Normality of FAS reagent

8000 – miliequivalent weight of oxygen (O_2) in unit of mL/L

and the formula used to calculate normality (N) of FAS reagent is :

$$N = \frac{volume\ of\ Dichromate*0.25}{volume\ of\ FAS\ used} \tag{2.17}$$

On the other hand, Biochemical Oxygen Demand (BOD) is defined as the rate of oxygen (O_2) consumed by the microorganisms in the polluted waste or the measure of oxygen amount required by aerobic bacteria in order to stabilize decomposable organic materials, (P. Aarne Vesilind, 2010). A standard BOD test is normally being carried out for duration of five (5) days under a condition without light radiation; it is also being defined as five-day BOD (BOD_5). Light radiation is avoided due to the reason of existing microorganisms available may produce extra amount of oxygen to the system when being exposed to light source which will literally affect the end result of the test. Usually, BOD test is being carried with the standard container which is the BOD bottle with a standard capacity of 300 mL.This kind of BOD bottle is also being widely utilized by Hach® Company for their invention of BODTrak™ for BOD measurements. (Company, 1998)

However, Total Organic Carbon (TOC) is another alternative for oxygen demand measurement which utilizes heat, ultra-violet light and a strong chemical oxidant in order to oxidize organic pollutants into by-products. (Boyles, 1997) This method of oxygen demand test is not as popular as the other two (2) methods mentioned above. This is due to the reason where TOC test does not differentiate between compounds having the same number of carbon atoms which will then lead to a different result. Since BOD and COD tests are measuring the amount of oxygen (O_2) required in a direct manner compared to TOC method. Besides, COD is said to be more sensitive towards processing oxidation capacity and represents the total parameters of all organic compounds that are readily oxidized. (Jordi Bacardit, 2007) Thus, this research project will be carried out mainly based on the measured values of BOD and COD in order to identify the degradation efficiency of amine waste.

2.5 Light intensity

By nature, light travels in every direction from the radiation source at a speed of 3.0×10^8 m/s. Thus, is can be assumed that light radiation is travelling across a surface of sphere with increasing radius as the light waves propagate. With is property, measurement of light intensity is said to be obeying the inverse square law of light. Light intensity is in a relation with the power (P) of light source as well as the distance travelled by the light which indicated by the radius (r) of the sphere. In general, light intensity can be expressed by the ratio between the power of light and the surface area of sphere with the formula of :

$$\text{Surface area of sphere, } S = 4\pi r^2 \qquad (2.18)$$

In summary, the light intensity calculation can be done by applying the formula below:

$$I = \frac{P}{4\pi r^2} \qquad (2.19)$$

where I – light intensity [Watt/m^2]

P – Power of light [Watt]

r – distance of light travelled [m^2]

Thus, the light intensity is expressed by the inverse proportionality of squared distance travelled by the light source. Propagation of light source based on the inverse-square law can be illustrated on Figure 2.5.1

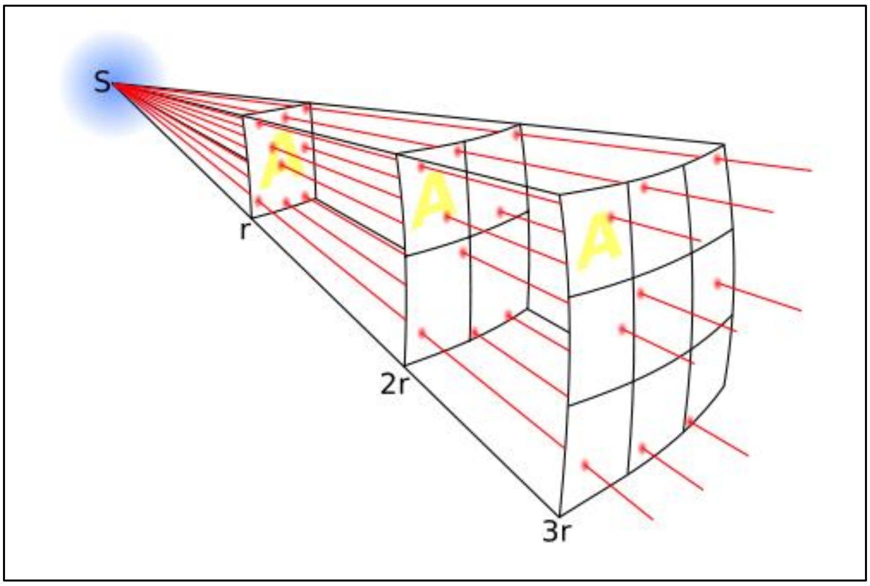


Figure 2.5.1 Inverse-square law light radiation
Source: Borb, 2009

Light intensity can be easily controlled using alternating either the power of the light source in Watts or changing the distance of light source from the reaction system in Photo-Fenton oxidation process. However, more advanced procedures can also be taken place in order to efficiently control the light intensity by embedding a photolysis system onto the Fenton process.

CHAPTER 3.0

METHODOLOGY

3.1 Research Methodology and Procedures

In order to successfully conduct this research, the methodologies which will be utilized throughout this project are exploration and discovery. Hence, several experimental tests need to be carried out in order to identify the outcome which suits the research objectives. Experimental results gathered at the laboratory work can be then compared with the outcomes from other similar researches. Besides, the experiment results can also be used for further investigation or studies on the relevant topics related to Advanced Oxidation Processes (AOPs) such as Photo-Fenton oxidation. The major experiment that will be performed is the Photo-Fenton oxidation of the model waste of Diisopropanolamine (DIPA) with the existence of light radiation at a control temperature condition. A specific experimental parameter is being taken into consideration which is light intensity. In the experimental work, light intensity will be adjusted by altering the light bulb with different output power namely 300 Watt and 500 Watt. Fixed period of time will be allocated for each test in order to identify the rate of degradation accurately. Apart from that, analysis procedures also play an important role in this research work. In order for the author to identify the degradation effect, determination of oxygen demand should be carried out. Chemical Oxygen Demand (COD) can be determined by using DR 5000 from Hach® Company by mixing the sample with COD reagent in COD TNTplus™ vials. Thus, the degradation rate is to be identified based on the difference in value for initial COD contents with those after oxidation process as well as the percentage of COD removal respectively. Lastly, all the end results will be recorded for further analysis as well as comparison with other research outcomes. Suitable interpretation will also be constructed based on the outcomes gained from the experimental work and finally be able to draw towards a conclusive statement for this research project.

3.2 Experimental Approaches

Basically, this research project involves four (4) general approaches starting from preparation of Diisopropanolamine (DIPA) model waste solution and other reagents including Fenton reagent ($FeSO_{4}.7H_2O$), hydrogen peroxide, sodium hydroxide and sulphuric acid solution. One of the reasons that hydrogen peroxide is chosen is due to its ability to generate hydroxyl radicals and it is more economical compared to other reagents. Then, it is followed by the Photo-Fenton's oxidation process in acidic environment to decompose the organic compound into other products such as carbon dioxide and water. For every 15 minutes of reaction interval, a sample will be collected from the reaction system for degradation test based on COD value. The collected sample is required to be titrated with sodium hydroxide (NaOH) in order to remove unwanted Ferrous ions (Fe^{2+}). Precipitated sample is then boiled for few minutes until no bubble is observed in order to remove excess oxygen content which may literally affect the COD reading. Lastly, the sample is filtrated before proceeding with COD digestion and measurement using Hach® DR 5000. In continuation, the experimental parameter will be altered for photo-Fenton reactions by substituting the oxidizing reagent's concentration and DIPA model waste concentration respectively to obtain an optimum reaction system. Following is to alter the light intensity by substituting the light bulb of the light source for comparison of degradation efficiency under different light intensities. Last but not least, the result data is then being analysed and made comparisons. A schematic flow of procedures can be summarized as show Figure 3.2.1

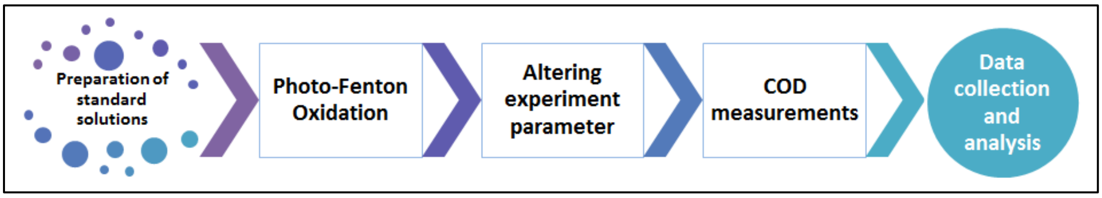


Figure 3.2.1 Schematic Flow Diagram of Experiment Procedures

3.2.1 Preparation of amine solution

For this research experiment, several concentrations of DIPA solution are required for calibration purposes as well as to identify the optimum DIPA concentration for better degradation rate. Thus, 1000 ppm is firstly prepared in general and then being diluted according to the respective desired concentrations.

Since the concentration of 1000 ppm is equivalent to 1000 mg/L, in order to prepare 1 litre of standard DIPA solution; 1000mg in mass of DIPA is required. In another words, 1.0 g of Diisopropanolamine is weighed using an electronic weighing machine and then dissolved in a beaker with distilled water. After all DIPA particles are completely dissolved, the solution is then being transferred into a 1.0 L capacity of volumetric flask for further diluted in order to achieve the desired concentration which is 1000 ppm. Lastly, the standard solution is then shaken well for uniform distribution in the flask. Moving on, the standard solution is being diluted further according to the calculated volume for different DIPA concentration. Table below illustrates the required amount of 1000 ppm DIPA solution in volume which needed to be diluted to the respective concentrations.

Table 3.2.1.1 Distribution of desired concentration with respective volume

Desired concentration, M2 (ppm)	Desired volume, V2 (mL)	Required vol. V1 (mL)	Dilution factor
1000	500	500	1.00
700	500	350	1.43
500	500	250	2.00
300	500	150	3.33
200	500	100	5.00
100	500	50	10.00
50	500	25	20.00
30	500	15	33.33
10	500	5	100.00

Calculation for the required volume of 1000ppm standard DIPA solution, V_1 is based on the formula below:

$$M_1V_1 = M_2V_2 \tag{3.1}$$

Where M_1 = molarity of amine before dilution
M_2 = molarity of amine standard solution after dilution
V_1 = volume of amine solution required for dilution
V_2 = final vol. of amine standard solution at desired concentration

3.2.2 Preparation of Fenton reagent solution ($FeSO_4.7H_2O$)

Iron (II) sulphate heptahydrate ($FeSO_4.7H_2O$) serves as the Fenton catalyst in this Photo-Fenton oxidation process which is responsible in creating hydroxyl radicals from the oxidizing agent, hydrogen peroxide in order to degrade the DIPA model waste with the assistance of light radiation. For all the reaction system, the concentration of Fenton reagent is selected at 0.1 Molar.

With the desired concentration, we are able to calculate the mass of $FeSO_4.7H_2O$ required for the preparation of Fenton reagent standard solution by utilizing its molecular weight. According to ChemSpider.com, the molecular weight of Iron (II) sulphate heptahydrate is 278.015 g/mol (ChemSpider, 2012). By having the idea of final volume of standard solution and the desired molarity, the number of moles of Fenton reagent can be calculated based on the formula below :

$$\text{Number of moles} = \text{concentration } (M_x) \text{ x volume } (V_x) \tag{3.2}$$
$$= M_xV_x$$

Final volume of standard solution = 1 litre
Desired concentration of standard solution = 0.1 Molar or mole/L

$$\text{No. of moles (mol)} = \frac{0.1\,mol}{1\,L}\ x\ 1\ liter = \mathbf{0.1\ mol}$$

Moving on, the amount of $FeSO_4.7H_2O$ solid particles which needed to be dissolved can be then calculated with the following formula :

$$\text{Mass of } FeSO_4.7H_2O \text{ (g)} = \text{number of moles (mol) x molecular weight (g/mol)} \tag{3.3}$$

$$\text{Mass of } FeSO_4.7H_2O \text{ (g)} = 0.1 \text{ mol} \times 278.015 \text{ g/mol}$$
$$= \underline{\mathbf{27.8015\ g}}$$

Thus, a total of 27.8015 g of $FeSO_4.7H_2O$ is weighed using electronic weighing machine and dissolved with distilled water in a 500 mL beaker before transferring into a 1 litre volumetric flask.

Besides, 1 litre standard solution of 0.5 Molar of sodium hydroxide (NaOH) can also be prepared according to the steps above. However, the amount of NaOH particles is calculated as **19.999 g** with its molecular weight of 39.997 g/mol.

3.2.3 Preparation of H_2O_2 and H_2SO_4

Standard solution of H_2O_2 and H_2SO_4 can be prepared from their highly concentrated solution respectively by utilizing Equation 3.1 above. However, the initial concentration of the concentrated solution before dilution can be calculated based on their concentration percentage. The calculations of the amount of concentrated solution can be summarized in the following table:

Table 3.2.3.1 Information of standard solution for sulphuric acid and hydrogen peroxide

Component	Density (g/L)	Molecular weight, MW	Total conc. at 100%	Concentrated Percentage (%)	Actual concentration, M1	Required vol. V1 (mL)	Desired concentration, M2	Final vol. V2 (mL)
Sulphuric acid	1840	98.079	18.760	97	18.198	**54.95**	1.00	1000.00
Hydrogen peroxide	1450	34.01	42.635	30	12.790	**78.18**	1.00	1000.00

$$\text{Total concentration at 100\%} = \frac{Density\ (g/L)}{MW\ (g/mol)} \qquad (3.4)$$

$$\text{Actual concentration, } M_1 = \text{Total concentration (100\%)} \times \text{Concentrated \%} \qquad (3.5)$$

$$V_1 = \frac{M2V2}{M1} \qquad (3.6)$$

Procedures of preparing standard solution can be summarized in Figure 3.2.1.1

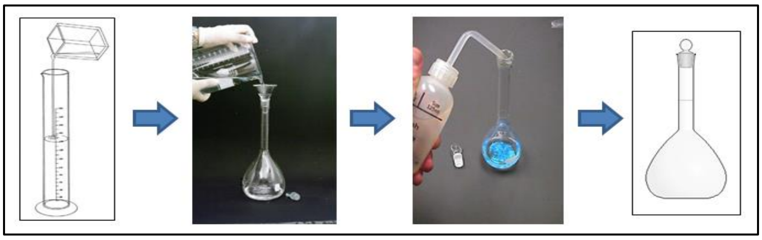


Figure 3.2.1.1 Preparation of standard solutions

The final standard solution of $FeSO_4.7H_2O$, DIPA, H_2O_2, NaOH and H_2SO_4 reagents are shown in Figure 3.2.1.2

Figure 3.2.1.2 Prepared standard solutions

3.2.4 Apparatus Setup for Photo-Fenton process

In general Photo-Fenton oxidation can be carried under the common setup as shown in the following schematic diagram.

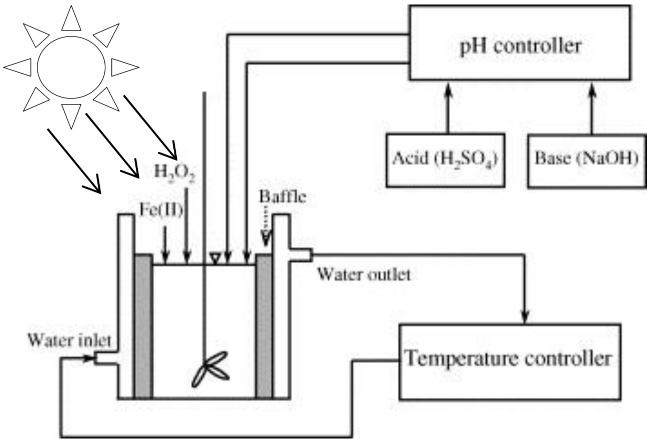


Figure 3.2.4.1 Schematic diagram of Photo-Fenton oxidation.
Source: H. Zhang et al., 2005

However, Photo-Fenton process can be carried out under experimental scale with a simple configuration as illustrated below.

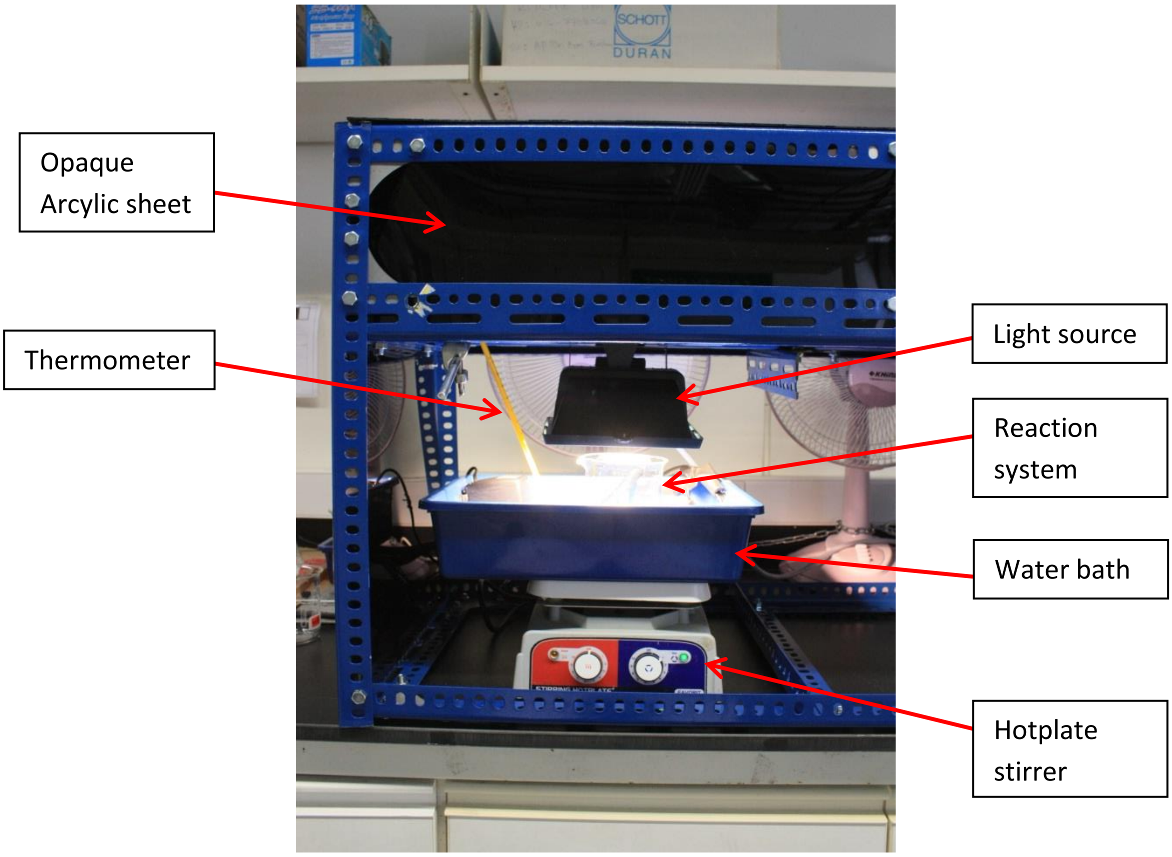


Figure 3.2.4.2 Experimental setup for Photo-Fenton process

Focus shifts onto the reaction system which is placed inside one of the water bath with cold circulating water in order to efficiently maintain the temperature of the reaction at certain level. Due to the limitation of space, a thermometer is restricted to be placed in the reaction system itself. Thus, an alternative is taken which is to place the thermometer in the water bath to monitor the water bath temperature in correlation with the reaction system temperature.

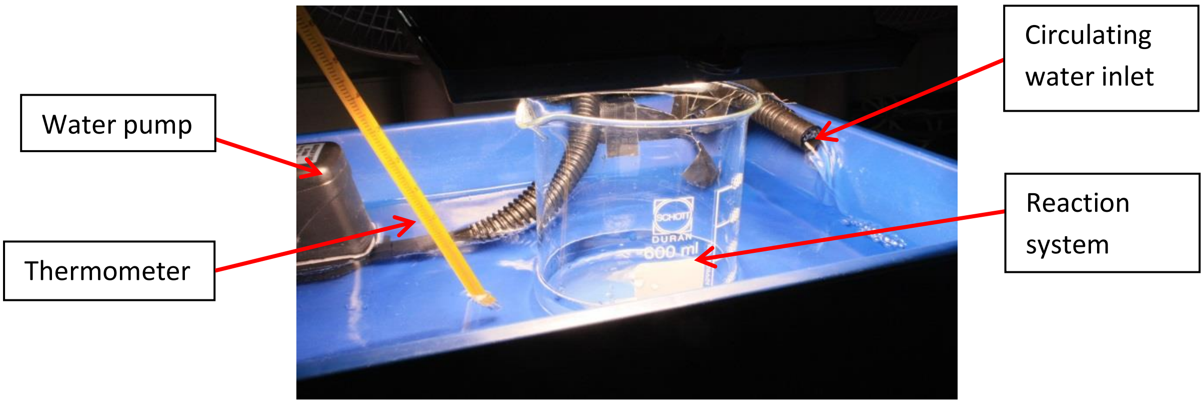


Figure 3.2.4.3 Reaction system in circulating water bath

Prior to the actual experiment, a series of temperature monitoring has been done to find out the temperature difference between the water bath and the reaction system. The difference varies between 7-9 ^{o}C and thus the water bath temperature should be maintained within 16-18 ^{o}C in order to ensure the reaction system temperature is controlled under ambient condition. Apart from the reaction system, there are also some other setups to enhance the overall experiment. For example, table fan as shown in the figure below is placed behind the reaction setup to improve air cooling effect due to the extreme amount of heat generated by the light source. Besides, there is another water bath equipped with water pump as shown below which used to recycle the cooling water from the major water bath.

Figure 3.2.4.4 Table fan and minor water bath

Table 3.2.4.1 summarizes the major equipment which will be used in the experimental work together with their respective functions.

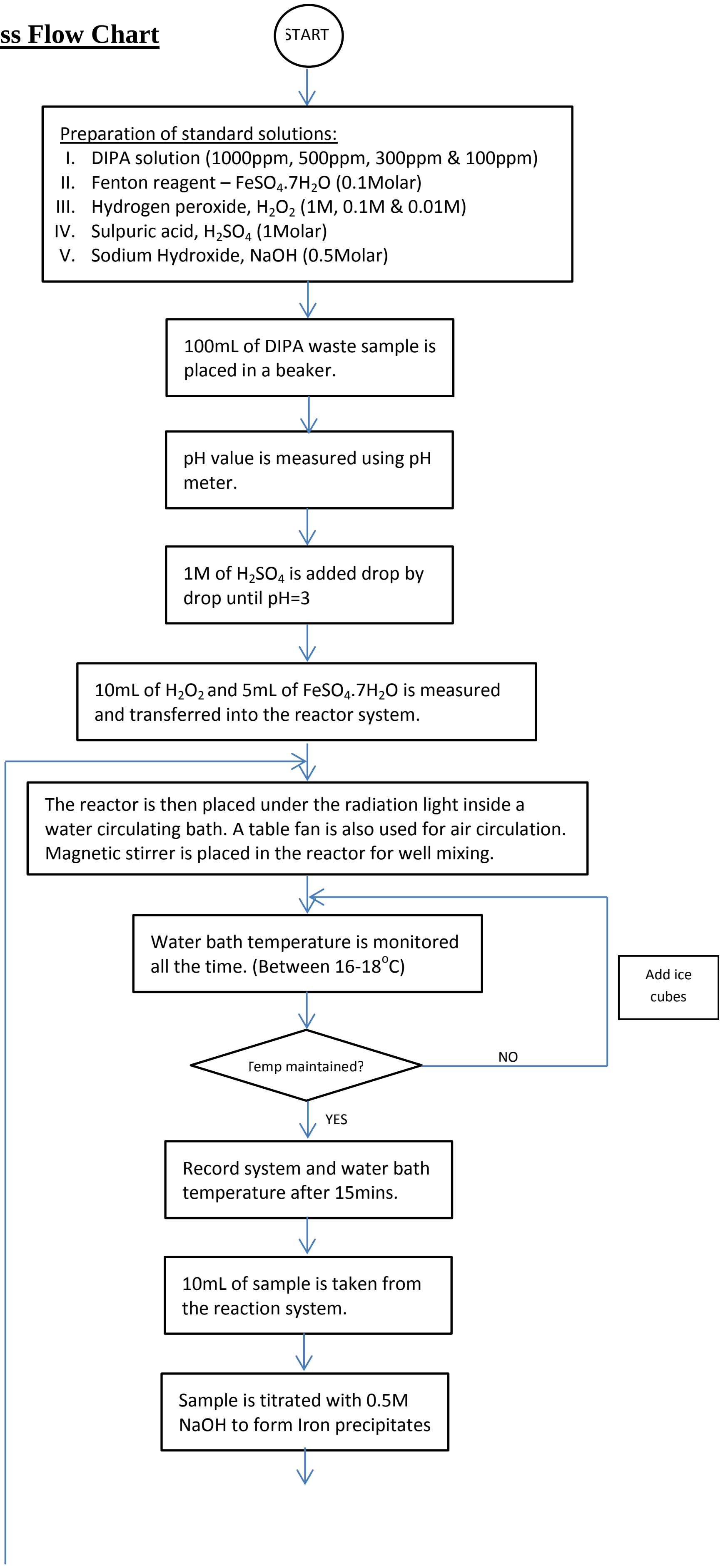
Table 3.2.4.1 Table of equipment with its respective function

Equipment	Function
Table fan	To cool down the air around light source
Stirrer system (Magnetic and hot plate stirrer)	To ensure uniform mixing of sample solution
Water bath	To maintain constant system temperature
Thermometers	To monitor the temperature of the system
Water pump	To circulate water as coolant to-and-from water bath
Opaque Arcylic sheet	To isolate ambient light radiation
Light source	To provide light radiation for Photo-Fenton process

Experimental Procedures

At the very beginning of the experiment, apparatus setup was prepared earlier and the circulation pump/water pump and table fan are activated to control the temperature of the water bath. Meanwhile, the temperature is to be observed for several minutes to ensure constant temperature condition of the system. Once temperature is stabilized, the amine solution is transferred into a beaker acting as the reactor. Few drops of 1 M H_2SO_4 is added into the amine solution until pH = 3.00. It is then followed by addition of 0.1M $FeSO_4.7H_2O$ reagent together with oxidizing agent (Hydrogen peroxide) into the reaction system and a magnetic stirrer is placed into the beaker as well. Moving forwards, the beaker is then placed in the water bath with the magnetic stirrer ON for uniform mixing of the solution. At the same time, light source is turned ON for the Photo-Fenton reaction to take place and the timer is also started for 15 minutes at the same time. Proceeding with the sample collection stage, one sample is retrieved at each 15 minutes interval from 60 minutes of overall reaction time for chemical oxygen demand tests. At the end of the experiment run, there will be a total of four samples being collected for Chemical Oxygen Demand (COD) testing.

Overall Process Flow Chart



Preparation of standard solutions:

I. DIPA solution (1000ppm, 500ppm, 300ppm & 100ppm)
II. Fenton reagent – $FeSO_4.7H_2O$ (0.1Molar)
III. Hydrogen peroxide, H_2O_2 (1M, 0.1M & 0.01M)
IV. Sulpuric acid, H_2SO_4 (1Molar)
V. Sodium Hydroxide, NaOH (0.5Molar)

100mL of DIPA waste sample is placed in a beaker.

pH value is measured using pH meter.

1M of H_2SO_4 is added drop by drop until pH=3

10mL of H_2O_2 and 5mL of $FeSO_4.7H_2O$ is measured and transferred into the reactor system.

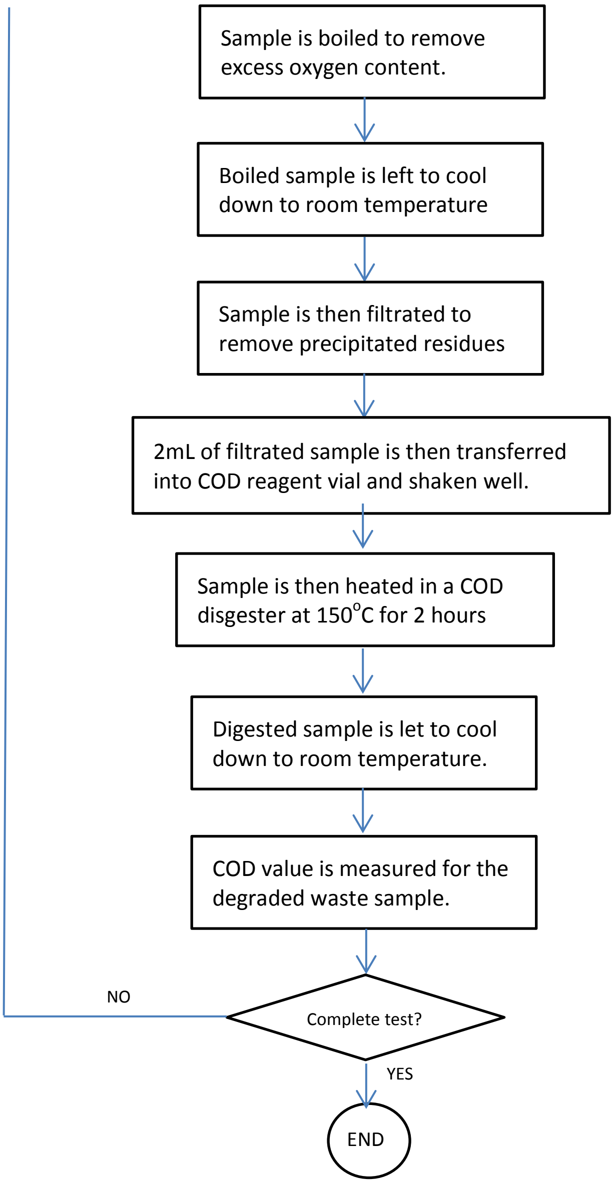
The reactor is then placed under the radiation light inside a water circulating bath. A table fan is also used for air circulation. Magnetic stirrer is placed in the reactor for well mixing.

Water bath temperature is monitored all the time. (Between 16-18^{o}C)

Record system and water bath temperature after 15mins.

10mL of sample is taken from the reaction system.

Sample is titrated with 0.5M NaOH to form Iron precipitates


Sample is boiled to remove excess oxygen content.
Boiled sample is left to cool down to room temperature
Sample is then filtrated to remove precipitated residues
2mL of filtrated sample is then transferred into COD reagent vial and shaken well.
Sample is then heated in a COD disgester at 150°C for 2 hours
Digested sample is let to cool down to room temperature.
COD value is measured for the degraded waste sample.
NO
Complete test?
YES
END

3.2.5 Chemical Oxygen Demand (COD) measurements

In order to obtain accurate COD value for DIPA degradation process, several important steps should not be neglected. These crucial procedures can be summarized as the followings after the sample is retrieved from the reaction system. Once the sample is obtained, it is being titrated against 0.5M of NaOH for the precipitation of unwanted Iron (II) ions (Fe^{2+}) as shown in Figure 3.2.5.1

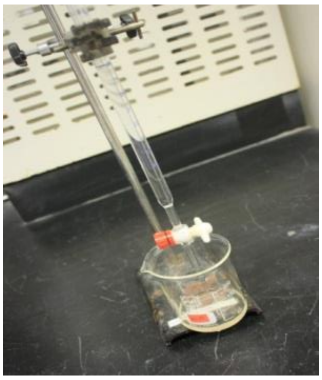


Figure 3.2.5.1 Titration of sample against NaOH

After the titration process, the samples are being transferred into separate containers and left for precipitation until all the residues settle down at the bottom of the container as shown in Figure 3.2.5.2.

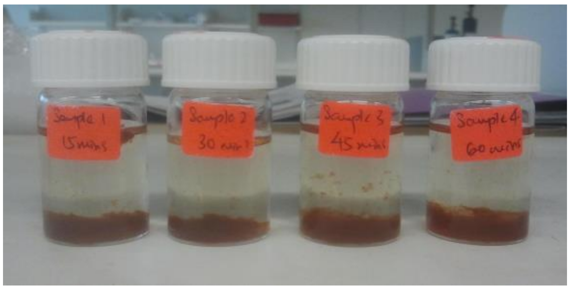


Figure 3.2.5.2 Precipitation of residues

Next, the samples are boiled using hot plate until no air bubble is observed. The purpose of this action is to remove the excess amount of oxygen.

Figure 3.2.5.3 Heating process of the samples

Moving on next, the samples are left to cool down to room temperature and proceed with filtration to separate the precipitates from clear sample solutions.

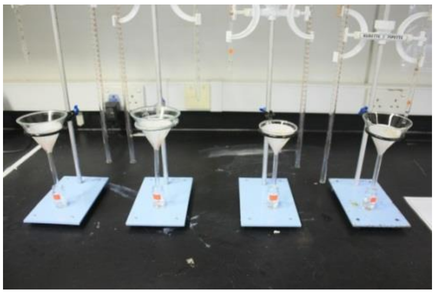


Figure 3.2.5.4 Filtration of samples

Marching towards the COD analysis, 2mL of each clear sample is firstly obtained and transferred into a COD TNTplus^{TM} vial containing COD reagent (HR) and shaken gently.

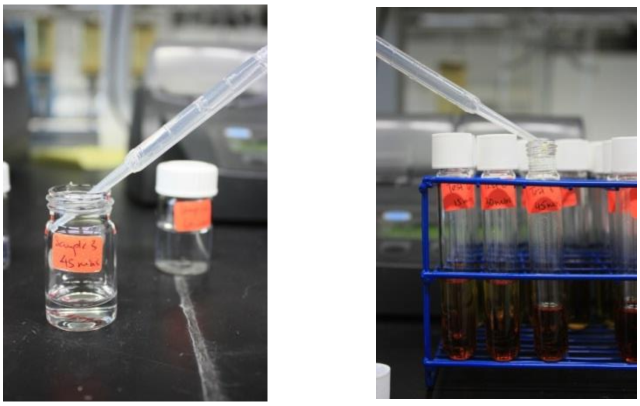


Figure 3.2.5.5 Transfer of sample solution into COD vials

Samples are meant to be digested before the measurement of COD value. Thus, COD digester DRB 200 is preheated to 150°C and the vials are placed in the digester for COD digestion process under duration of 120 minutes.

Figure 3.2.5.6 Digestion of COD samples in HACH DRB 200 digester

Lastly, COD samples are let to cool down to room temperature after digestion. Lastly, the COD value is measured by Hach® DR 5000 spectrophotometer.

Figure 3.2.5.7 COD value measurement

CHAPTER 4.0

RESULTS AND DISCUSSION

4.1 DIPA sample calibration curve

Prior to all the experimental work, the original 1000ppm of Diisopropanolamine (DIPA) is being diluted into various concentrations and these sample solutions are taken for Chemical Oxygen Demand (COD) testing using Hach® DR 5000 available in the laboratory. The purpose of performing this action at the beginning is to obtain a calibration plot based on different DIPA concentration with its respective COD value (mg/L). Later in the result analysis process, this calibration curve will be then used to calculate the actual concentration of the sample after Photo-Fenton treatment based on its absorbance (Abs). With the availability of calculated concentration, the reaction kinetics can then be studied in order to figure out the type of reaction system. Each COD value with respect to their diluted concentration is being summarized in Table 4.1.1 below.

Table 4.1.1 Distribution of DIPA concentration and its COD measurements

DIPA Concentration (ppm)	COD (mg/L)	Absorbance (Abs)	Transmittance (%)	Dilution factor
1000	2054	0.905	12.4	0.00
700	1614	0.711	19.4	1.43
500	1118	0.493	32.2	2.00
400	956	0.421	37.9	2.50
300	728	0.321	47.7	3.33
200	578	0.255	55.6	5.00
150	463	0.204	62.5	6.67
100	384	0.169	67.7	10.00
60	286	0.126	74.8	16.67
50	288	0.127	74.7	20.00
30	251	0.11	77.5	33.33
10	208	0.092	80.9	100.00

Initial DIPA concentration which is 1000 ppm prepared earlier is diluted into different concentrations ranging from 700-10 ppm. Each blank sample is digested together with COD reagent for COD, absorbance and transmittance measurements. Besides, the dilution factor is also calculated based on the diluted concentration and the initial DIPA concentration, 1000 ppm. After measuring all the respective COD values, a graph of COD value (mg/L) versus blank DIPA concentration (ppm) is plotted as shown below which is used to study the trend and effect of DIPA concentration on its COD value. Note that there are two points highlighted in red with DIPA concentration of 1000 ppm and 700 ppm respectively are not included in any graph plotting since the COD measurement went out of range. It is not suitable to be considered in the calibration plot because it may literally affect the outcomes.

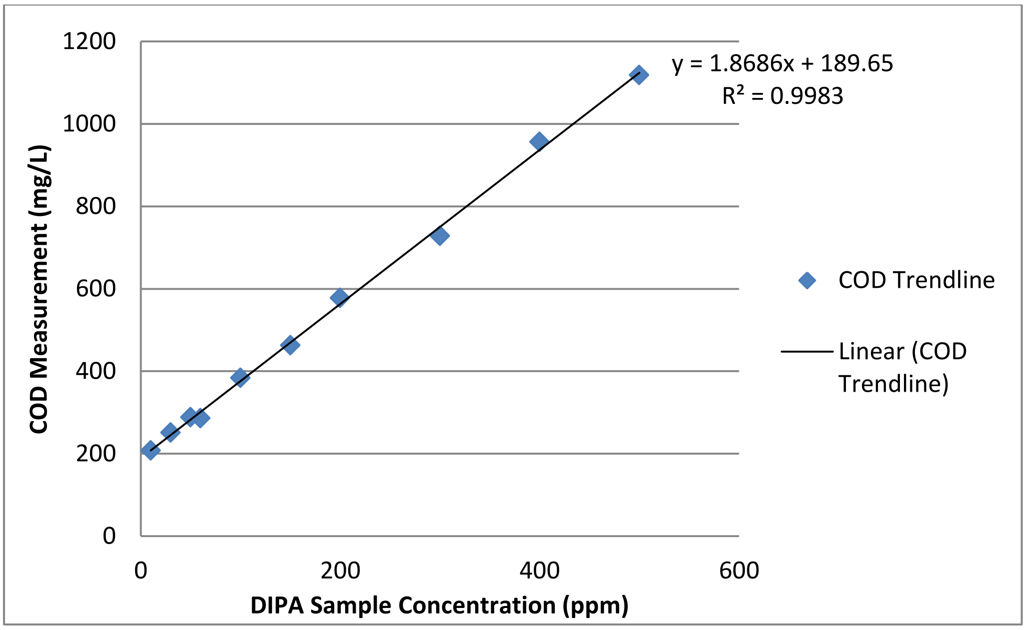


Figure 4.1.1 Calibration plot of COD measurement (mg/L) vs. DIPA concentration (ppm)

By utilizing this plot, COD value on a specific concentration of DIPA sample solution can be estimated using the linear equation provided:

$$y = 1.8686x + 189.65 \qquad (4.1)$$

where 'y' indicates the COD measurement value (mg/L) and 'x' as DIPA concentration in ppm.

From the plot above, we can clearly see the trend of variation in COD measurement values based on different level of DIPA concentration. As the concentration increases, the COD measurement gets increased in a linear pattern as well. This can be explained by the amount of organic pollutants available in the model waste are more when the concentration is high and more oxygen in mass is being consumed which indicated by the COD value. In another words, the greater the value of COD measurement, we can clarify the wastewater is more polluted.

In addition, a calibration curve is plotted based on the DIPA concentration and its absorbance which measured by Hach® DR 5000 as well. The absorbance value can be defined as the fraction of light source in Hach® DR 5000 being absorbed by the sample solution for COD measurement.

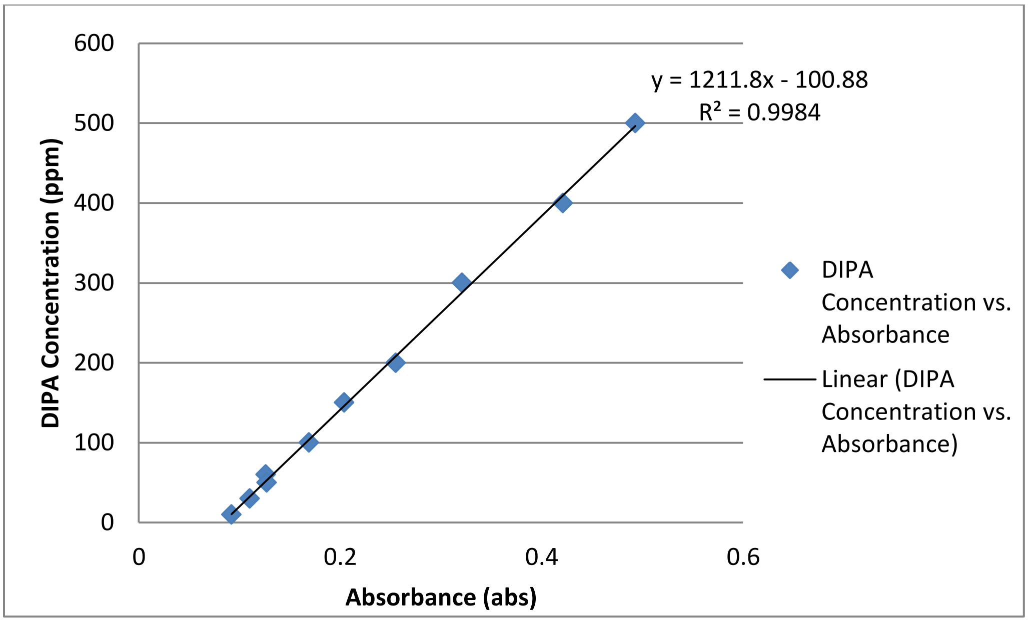


Figure 4.1.2 Calibration plot between concentration and absorbance

With the availability of linear expression, the actual concentration of DIPA sample can be calculated once the absorbance is obtained from the test after applying Photo-Fenton oxidation or degradation process.

$$y = 1211.8x - 100.88 \tag{4.2}$$

where ‘y’ represents the concentration of DIPA sample, whereas ‘x’ is the value of absorbance measured.

Due to the fact that concentration of DIPA sample after Photo-Fenton treatment is unknown and it cannot be measured directly, thus utilizing this calibration curve may assist in determining the approximate concentration of DIPA after degradation process. Since concentration is one of the most important data for reaction kinetic studies, so calibration plot is necessary before performing the experiments.

4.2 Optimizing H_2O_2 concentration (500 Watt Light)

For the entire research experiment, concentration hydrogen peroxide (H_2O_2) plays one of the major roles and contributes greatly to the final outcome since it’s the oxidizing agent that provide hydroxyl radicals during the advanced oxidation process.

As a kick start for the experiment configuration, three (3) different concentrations of H_2O_2 namely 0.01 M, 0.1 M and 1.0 M were put into tests by maintaining other parameters constant as discussed in the scope of study.

4.2.1 0.01 M of Hydrogen Peroxide (H_2O_2)

With all the other parameters kept constant, the experiment started with the first concentration of H_2O_2 which is 0.01 M. During the total duration of 60 minutes for the experiment, one sample is collected at every 15 minutes interval and undergone necessary procedures for COD measurement. Table below manage to summarize the findings for the system consisting 0.01 M H_2O_2 as the oxidizing agent.

Table 4.2.1.1 Data distribution for 0.01 M of Hydrogen Peroxide

Time (mins)	0	15	30	45	60
Water bath temp [C]	18.0	17.0	17.0	16.0	17.5
System temp [C]	25.0	26.5	27.0	26.0	27.0
COD (mg/L)	1118	1024	1000	808	760
COD removal (%)	-	8.41	10.55	27.73	32.02
Absorbance (abs)	0.493	0.451	0.441	0.356	0.335
Transmittance (%)	32.2	35.4	36.2	44.0	46.2
Degradation rate (ppm/min)	-	6.27	3.93	6.89	5.97

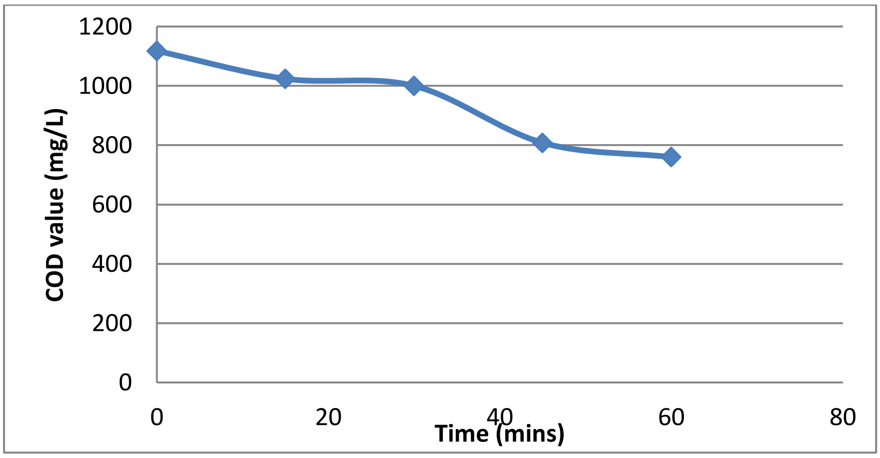


Figure 4.2.1.1 Plot of COD versus Time based on 0.01 M H_2O_2 (500 Watt)

For this set of experiment, the system temperature is successfully maintained under ambient condition ranging from 25-27 ^{o}C. The initial COD value for 500 ppm of sample is 1118mg/L and it managed to be degraded up to 760 mg/L at the end of 60 minutes. Furthermore, the percentage of COD removal is also calculated for each sample collected. However, the overall COD removal managed to achieve up till 32.02 % in total. Due to the fact that 0.01 M of H_2O_2 is the lowest concentration among all and it only able to produce limited amount of •OH in order to degrade DIPA. Thus, the overall COD removal percentage is considered quite low.

4.2.2 0.1 M of Hydrogen Peroxide (H_2O_2)

For this set of experiment, all the constant parameters were remaining unchanged. The only different is the concentration of hydrogen peroxide used is 0.1 M instead of the previous system with 0.01 M. In another words, the concentration of oxidizing agent has been increased by multiplication of 10 in order to observe the significant difference between their outcomes.

Table 4.2.2.1 Data distribution for 0.1 M of Hydrogen Peroxide

Time (mins)	0	15	30	45	60
Water bath temp [C]	18.0	20.0	20.0	18.0	17.0
System temp [C]	25.0	27.5	28.0	27.5	26.0
COD (mg/L)	1118	954	845	781	755
COD removal (%)	-	14.67	24.42	30.14	32.47
Absorbance (abs)	0.493	0.421	0.373	0.344	0.333
Transmittance (%)	32.2	38.0	42.4	45.2	46.5
Degradation rate (ppm/min)	-	10.93	9.10	7.49	6.05

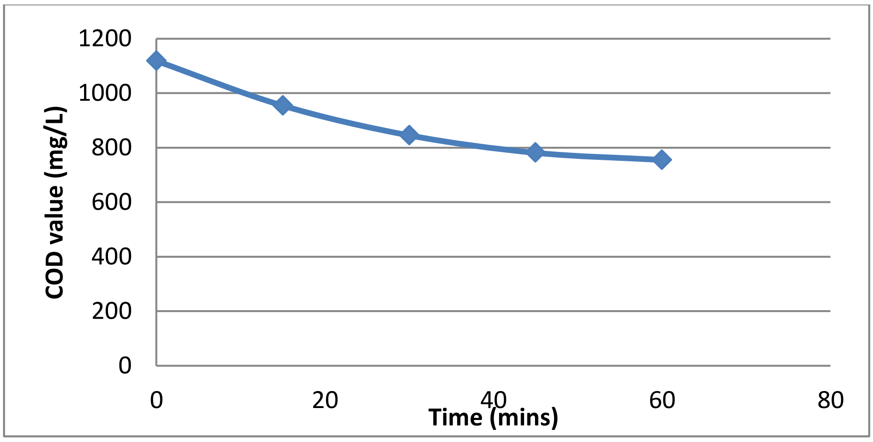


Figure 4.2.2.1 Plot of COD versus Time based on 0.1 M H_2O_2 (500 Watt)

Similarly, the initial COD concentration of DIPA model waste is 1118 mg/L and it is being degraded until 755 mg/L after 60 minutes duration. From the COD removal point of view, the overall degradation under the same experiment condition as above give a slightly higher percentage of COD removal (32.47 %) due to the usage of higher H_2O_2 concentration. This can be explained by more amount of hydroxyl radicals are being generated compared to the previous case since the concentration of H_2O_2 has increased from 0.01 M to 0.1 M. However, it is not considered as a significant increase in COD removal efficiency since both giving similar results although using different concentration of oxidizing agent. This might implies both 0.01 M and 0.1 M of hydrogen peroxide are not the most optimum parameter condition.

4.2.3 1.0 M of Hydrogen Peroxide (H_2O_2)

Last set of the experiment was carried out based on the highest concentration of H_2O_2 among all which is 1.0 M for degradation of DIPA under Photo-Fenton oxidation. With such concentrated oxidizing agent, it is believed that it can further degrade DIPA components in the sample compared to the previous concentrations. The following table summarizes the outcome of Photo-Fenton oxidation with 1.0 M of hydrogen peroxide in the system.

Table 4.2.3.1 Data distribution for 1.0 M of Hydrogen Peroxide

Time (mins)	0	15	30	45	60
Water bath temp [C]	18.0	18.0	19.0	17.5	17.5
System temp [C]	25.0	27.0	28.0	27.0	26.5
COD (mg/L)	1118	840	741	627	565
COD removal (%)	-	24.87	33.72	43.92	49.46
Absorbance (abs)	0.493	0.370	0.327	0.276	0.249
Transmittance (%)	32.2	42.6	47.1	52.9	56.3
Degradation rate (ppm/min)	-	18.53	12.57	10.91	9.22

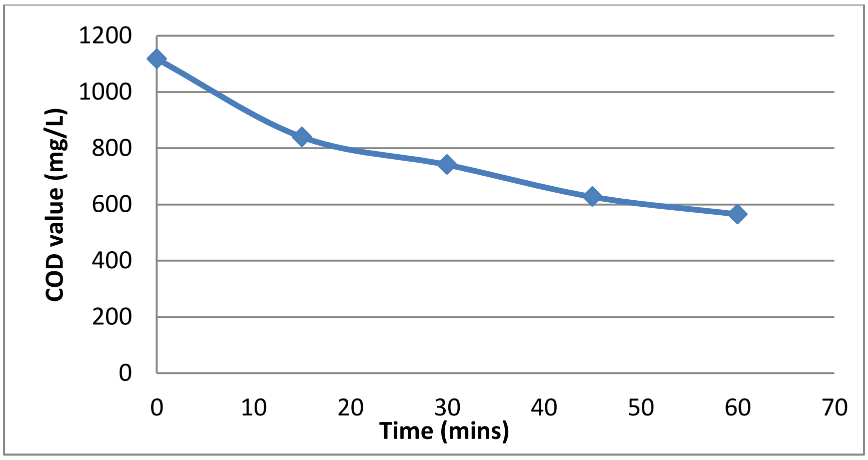


Figure 4.2.3.1 Plot of COD versus Time based on 1.0 M H_2O_2 (500 Watt)

By utilizing concentration hydrogen peroxide as oxidizing agent, the degradation process manage to be further enhanced where the COD concentration was reduced to almost half of its initial value which is from 1118mg/L to 565 mg/L. On top of that, the overall COD removal percentage achieved a new level of 49.46 % which is relatively high compared to the first two experimental conditions. Thus, a simple conclusion can be drawn where the high concentration of H_2O_2 is more suitable for degradation of DIPA samples because more free radicals are generated in order to degrade DIPA compounds. Since 1.0 M H_2O_2 is the highest concentration available, it is justified that it provides the greatest COD removal based on the radicals generated from this concentration in comparison with other two. Besides, this parameter condition will be carried forward for the optimization of DIPA concentrations for better findings. In another words, 1.0 M of hydrogen peroxide will be kept constant as one of the parameters for optimizing DIPA concentration in the following experiments. Lastly, all the data above are plotted in the graphs below for easy comparisons.

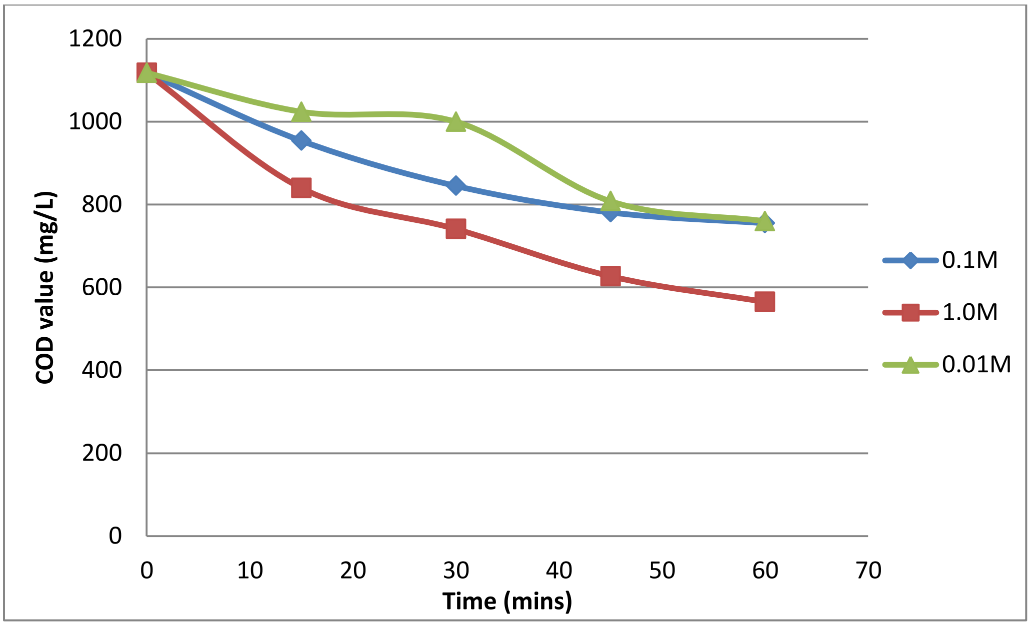


Figure 4.2.1 Degradation efficiency in terms of COD value (mg/L) by different concentrations of H_2O_2

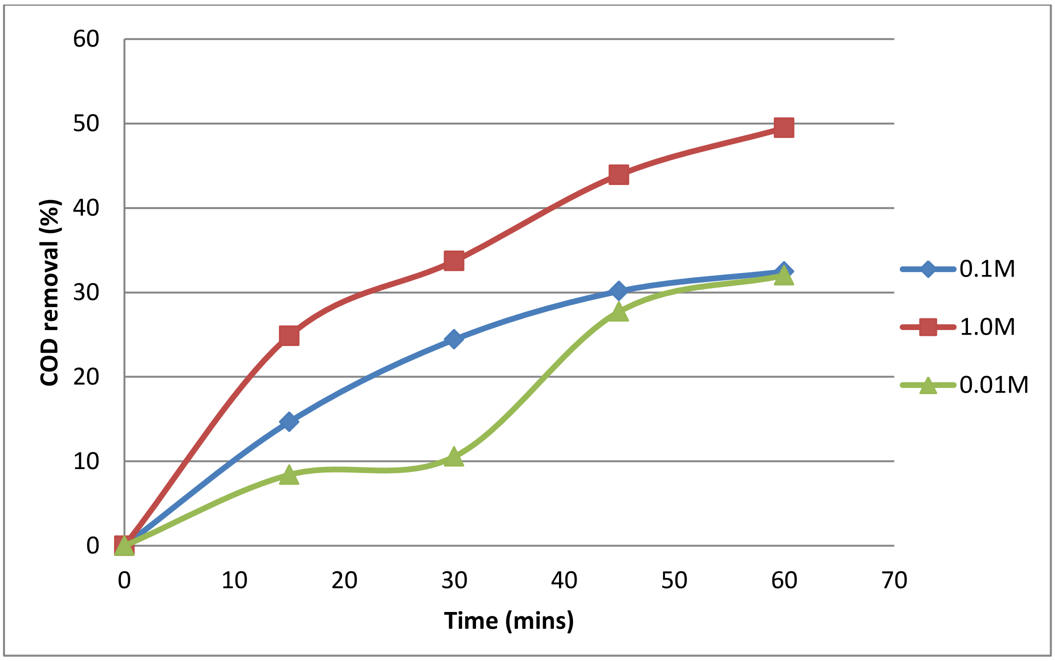


Figure 4.2.2 Degradation efficiency in terms of COD removal (%) by different concentrations of H_2O_2

Based on the two plots above, it is clearly shown that 1.0 M of hydrogen peroxide gives the best outcome among all. It reduces the most COD content (mg/L) from the initial condition, whereas 0.01 M and 0.1 M of H_2O_2 performed in a similar pattern and there is not much difference between their final COD value after degradation. On the opposite, 1.0 M H_2O_2 which produces most hydroxyl radicals and as a result, gave the highest percentage of COD removal which is close to 50 % whereas 0.01 M and 0.1 M H_2O_2 only managed to reduce slightly above 30 % of total COD content. Thus, in this case 1.0 M of hydrogen peroxide is said to be the most optimum condition for this particular parameter.

4.3 Optimizing DIPA concentration (500 Watt Light)

After the optimization of hydrogen peroxide concentration, next the optimization for initial DIPA concentration ranging from 100 ppm, 300 ppm and 500 ppm was also carried out based on the optimum hydrogen peroxide concentration which is 1.0 M, whereas other parameters were kept constant as usual.

4.3.1 100 ppm of Diisopropanolamine (DIPA) solution

Under this section of experiment, optimization of DIPA concentration is relative to the optimized concentration of hydrogen peroxide. Thus, it will further enhance the reliability of the outcome for this optimization process. The experiment was conducted with the similar procedures carried out before and a series of data was obtained for 100 ppm DIPA system.

Table 4.3.1.1 Data distribution for 100 ppm of DIPA solution

Time (mins)	0	15	30	45	60
Water bath temp [C]	17.5	17.5	17.0	17.5	17.0
System temp [C]	26.5	26.5	26.0	26.5	26.0
COD (mg/L)	384	274	234	208	225
COD removal (%)	**-**	**28.65**	**39.06**	**45.83**	**41.41**
Absorbance (abs)	0.169	0.121	0.103	0.092	0.099
Transmittance (%)	67.7	75.8	78.9	81.0	79.6
Degradation rate (ppm/min)	-	7.33	5.00	3.91	2.65

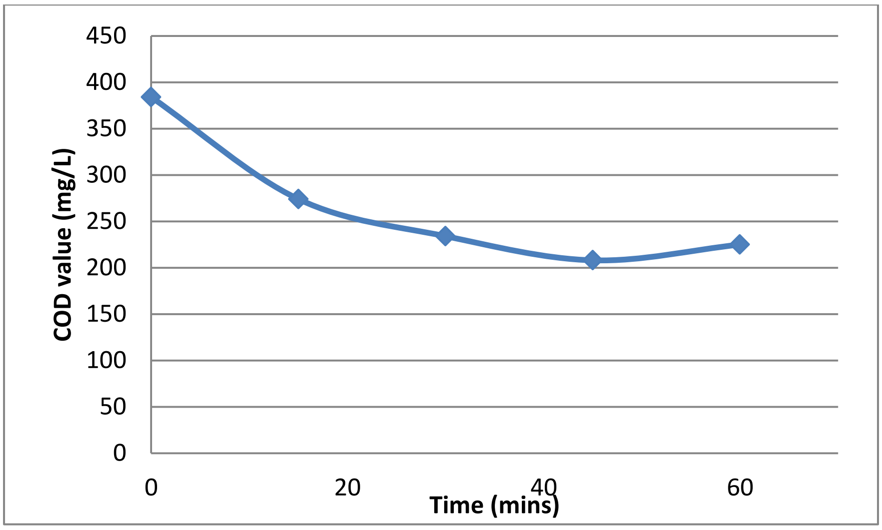


Figure 4.3.1.1 Plot of COD versus Time based on 100 ppm DIPA (500 Watt)

From the data obtained from COD analysis, the maximum percentage of COD removal is observed at 45 minutes of the reaction with total of 45.83 %. The degradation process managed to reduce the initial COD content from 384mg/L to the minimum level of 208 mg/L. However, a sudden increase in COD content at the end of the experiment is undesirable and opposes the normal trend of COD values in a degradation process. This phenomenon might be due to the incomplete boiling of sample solution after precipitation. There are still small amount of oxygen presents in the sample which then affected the final COD reading.

4.3.2 300ppm of Diisopropanolamine (DIPA) solution

In order to achieve the object of optimization, the experiment is continued by increasing the initial concentration of DIPA solution for the system. 300 ppm of DIPA concentration is used in the same reaction system to find out its degradation efficiency. Results obtained are tabulated in Table 4.3.2.1

Table 4.3.2.1 Data distribution for 300ppm of DIPA solution

Time (mins)	0	15	30	45	60
Water bath temp [C]	17.0	17.0	17.5	17.5	17.0
System temp [C]	26.5	26.5	27.0	27.0	26.5
COD (mg/L)	718	448	401	336	327
COD removal (%)	**-**	**37.60**	**44.15**	**53.20**	**54.46**
Absorbance (abs)	0.317	0.197	0.177	0.148	0.144
Transmittance (%)	48.2	63.5	66.6	71.1	71.8
Degradation rate (ppm/min)	-	18.00	10.57	8.49	6.52

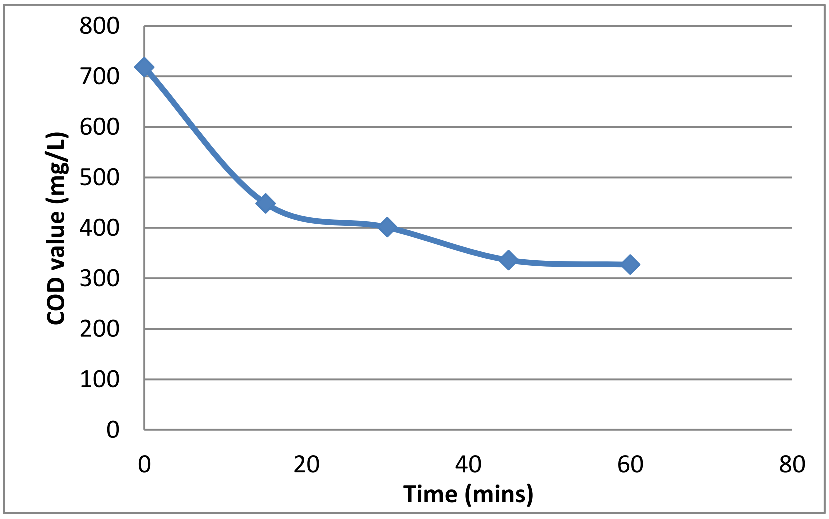


Figure 4.3.2.1 Plot of COD versus Time based on 300 ppm DIPA (500 Watt)

By utilizing DIPA concentration of 300ppm, the degradation process was further improved compared to the lower concentration system. With 300ppm of DIPA solution, the initial COD reading has been decreased from 718 mg/L to 327 mg/L together with the overall COD removal of 54.46 % which is so far the highest achievement among all experiment runs. More than half of the initial DIPA was managed to be degraded in this system. Based on the research done by R. Mahirah (2010), the effect of DIPA initial concentration on DIPA degradation is linear as in the increase in its concentration will lead to an increase in COD removal in terms of degradation. This may be due to the higher amount of DIPA compounds are being reacted with hydroxyl radicals and degraded.

4.3.3 500ppm of Diisopropanolamine (DIPA) solution

System with 500 ppm of initial DIPA concentration and 1.0 M of hydrogen peroxide at 500 Watt of light radiation has been carried out previously during the optimization of hydrogen peroxide. So the result outcome will be the same as the system explained above. COD value was lowered from 1118 mg/L to 565 mg/L with an overall COD removal of 49.46 %.

Two plots below (Figure 4.3.1 and 4.3.2) show the overall trend of COD measurement values based on separate initial DIPA sample solutions for 500 ppm, 300 ppm and 100 ppm respectively.

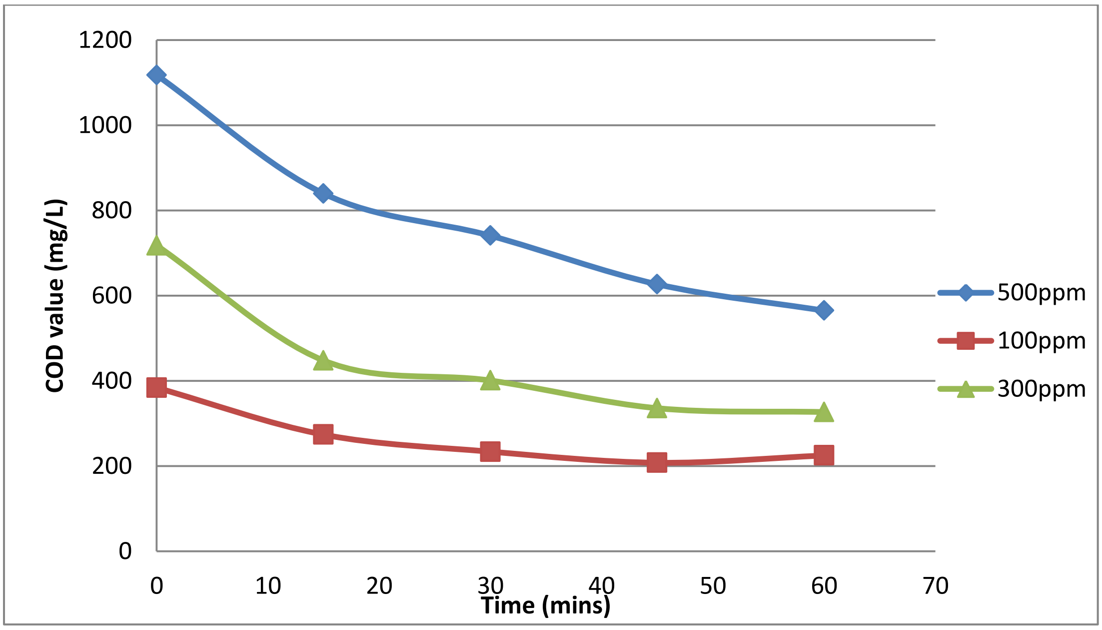


Figure 4.3.1 Degradation efficiency on different DIPA concentrations (500 Watt)

The first graph illustrates the decreasing of COD values with respect to time in minutes for each DIPA sample concentration. Unfortunately, it is not sufficient for us to identify which concentration gives the most efficient degradation with time.

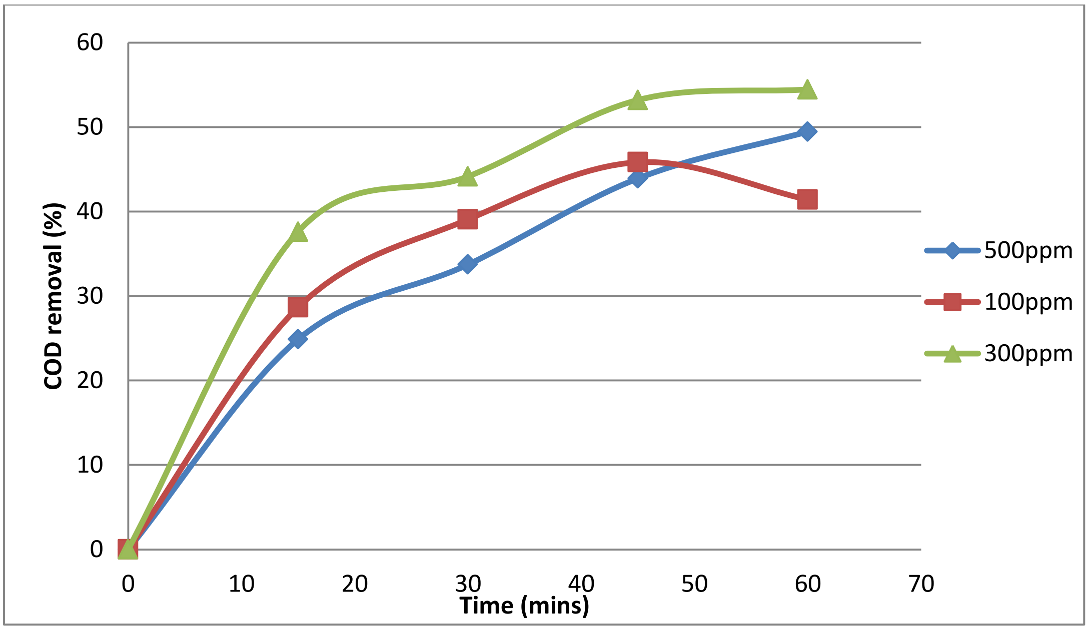


Figure 4.3.2 COD removal percentage on different DIPA concentrations (500 Watt)

With the availability of the second plot in terms of COD removal percentage, we are able to determine the most efficient degradation is based on 300 ppm since it has the highest trend of COD removal in terms of percentage.

4.4 Optimization of H_2O_2 Concentration (300 Watt Light)

Based on the same experimental setup, the experiment is carried out in the similar manner but under different visible light radiation, in this case will be 300 Watt of power instead of 500 Watt. This is to differentiate DIPA degradation rate between different visible light intensities in terms of COD removal as performed above. However, the optimization process cannot be excluded in order to find out the most optimum experimental condition under 300 Watt of visible light radiation. Similar to the previous sections, there are several parameters were kept constant as per scope of study.

4.4.1 0.01 M of Hydrogen Peroxide (H_2O_2)

With the same experimental procedures, the optimization process started with 0.01 M of H_2O_2 as the oxidizing agent under 300 Watt of visible light with the above constant parameters. Each sample is also obtained from the reactor system at every

15 minutes till the total reaction duration of 1 hour. The temperature was tired to be maintained within the range of ± 0.5 °C at each interval in order to reduce the effect of temperature on the reaction system. Temperature was maintained between 24.5-25.5 °C by circulating ice water in the water bath.

Table 4.4.1.1 Data distribution for 0.01 M of H_2O_2 system

Time (mins)	0	15	30	45	60
Water bath temp [C]	20.0	20.0	19.5	20.0	20.5
System temp [C]	25.0	25.0	24.5	25.0	25.5
COD (mg/L)	1125	1020	927	838	753
COD removal (%)	**-**	**9.33**	**17.60**	**25.51**	**33.07**
Absorbance (abs)	0.496	0.45	0.418	0.37	0.332
Transmittance (%)	31.9	35.5	40.6	42.7	46.6
Degradation rate (ppm/min)	-	7.00	6.60	6.38	6.20

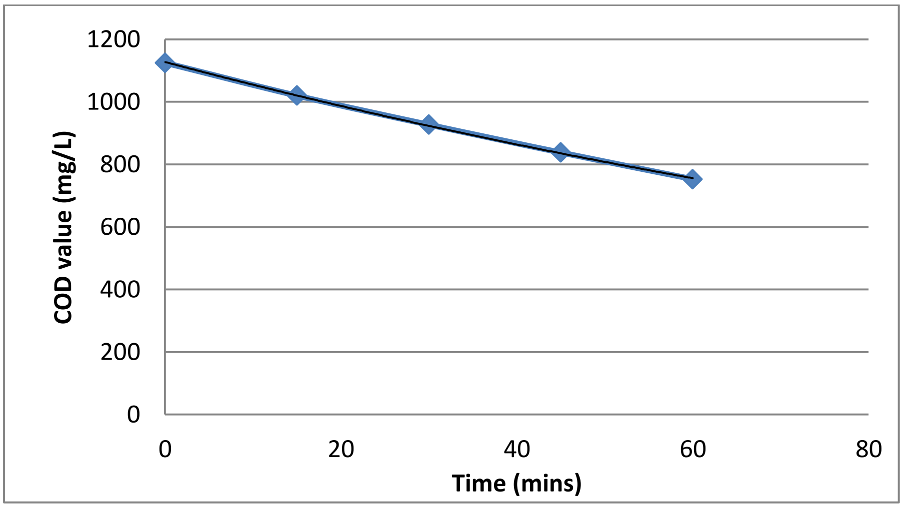


Figure 4.4.1.1 Plot of COD versus Time based on 0.01 M H_2O_2 (300 Watt)

Initially the COD value for this system was 1125 mg/L which being reduced to 753 mg/L. In terms of COD removal percentage, the maximum COD removal in this case only managed to achieve 33.07 % due to the low concentration of oxidizing agent which leads to a lesser amount of hydroxyl radical generation. Thus, lesser DIPA compound can be degraded compared to higher concentration of oxidizing radicals available.

4.4.2 0.1 M of Hydrogen Peroxide (H_2O_2)

Moving on with the optimization process of oxidizing agent, the concentration of hydrogen peroxide is then being increased to 0.1 M instead to find out the percentage of COD removal on DIPA waste sample under a 300 Watt of visible light source. By remaining all other parameters constant, the result of DIPA degradation in terms of its COD removal can be summarized in the table below.

Table 4.4.2.1 Data distribution for 0.1M of H_2O_2

Time (mins)	0	15	30	45	60
Water bath temp [C]	20.0	20.0	19.5	20.0	20.0
System temp [C]	25.0	25.0	24.5	25.0	25.5
COD (mg/L)	1125	681	653	646	597
COD removal (%)	**-**	**39.47**	**41.96**	**42.58**	**46.93**
Absorbance (abs)	0.496	0.300	0.288	0.285	0.263
Transmittance (%)	31.9	50.1	51.6	51.9	54.6
Degradation rate (ppm/min)	-	29.60	15.73	10.64	8.80

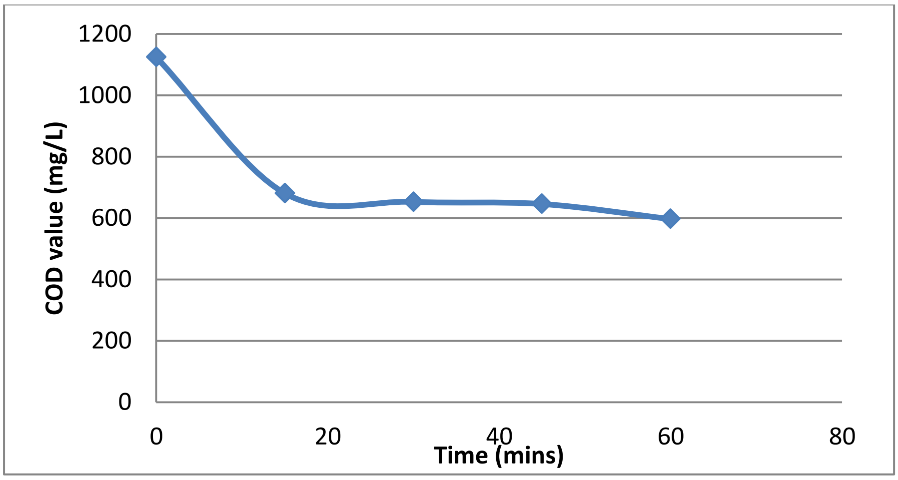


Figure 4.4.2.1 Plot of COD versus Time based on 0.1 M H_2O_2 (300 Watt)

In comparison with the results obtained prior to this system, the COD value of DIPA waste sample managed to further reduce to 597 mg/L from the same initial value of 1125 mg/L. In another words, the percentage of COD removal is further increased to a total of 46.93 %. This phenomenon can be explained by the higher concentration of hydrogen peroxide which produces more hydroxyl radicals under Photo-Fenton catalytic process. With more hydroxyl radicals available, the degradation of DIPA can thus be further enhanced.

4.4.3 1.0 M of Hydrogen Peroxide (H_2O_2)

Optimization process for hydrogen peroxide concentration under 300 Watt of visible light is ended with 1.0 M of H_2O_2 which was expected to provide the highest DIPA degradation among all due to its highest concentration compared to the previous two systems. Table below summarizes the outcome of using 1.0 M of hydrogen peroxide as the oxidizing agent.

Table 4.4.3.1 Data distribution for 1.0 M of H_2O_2

Time (mins)	0	15	30	45	60
Water bath temp [C]	18.0	19.0	19.0	18.5	19.0
System temp [C]	25.0	25.0	25.0	25.0	25.0
COD (mg/L)	1118	678	545	456	440
COD removal (%)	**-**	**39.36**	**51.25**	**59.21**	**60.64**
Absorbance (abs)	0.493	0.299	0.24	0.201	0.194
Transmittance (%)	32.2	50.3	57.5	62.9	63.9
Degradation rate (ppm/min)	-	29.33	19.10	14.71	11.30

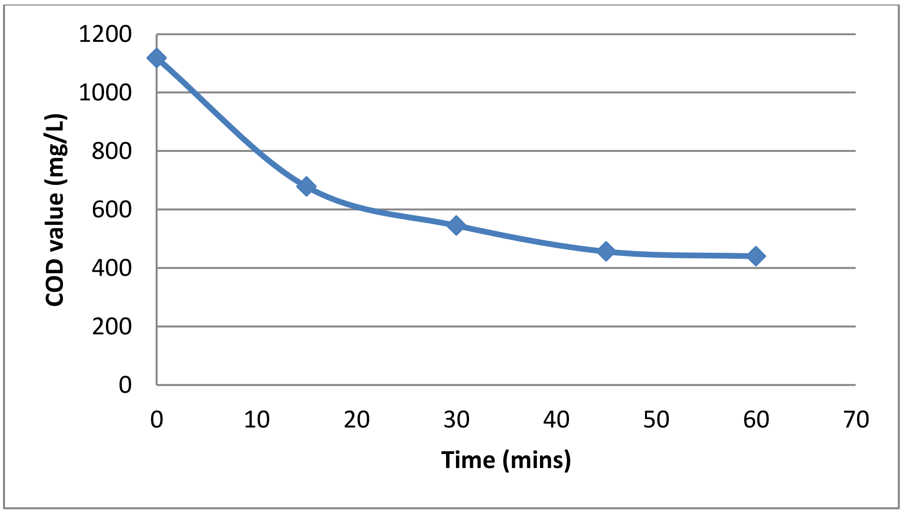


Figure 4.4.3.1 Plot of COD versus Time based on 1.0 M H_2O_2 (300 Wat)

As excepted, this system gives the best performance in degrading DIPA waste sample with H_2O_2 concentration of 1.0 M. By using 1.0 M of oxidizing agent, more oxidizing radicals managed to be generated and thus causing the initial value of COD managed to be reduced from 1118 mg/L down to 440 mg/L with the highest percentage of 60.64 % in COD removal. However, the general plot of COD removal can be observed from the figures below (Figure 4.4.1 and 4.4.2) in order to carry out comparisons between different hydrogen peroxide concentrations easily.

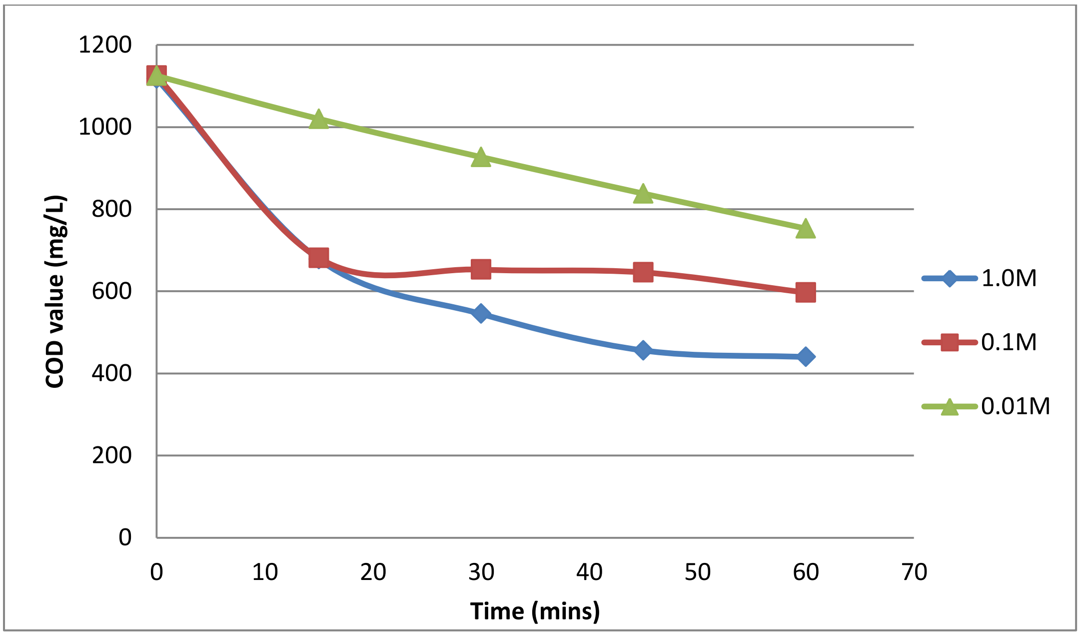


Figure 4.4.1 Overall plot of COD value vs. different H_2O_2 concentrations under 300 Watt visible light

From the plot above, the DIPA degradation trend can be clearly identified where 0.01 M of hydrogen peroxide removed least amount of COD value; whereas 1.0M of hydrogen peroxide removed most of the COD value from the initial DIPA waste sample due to the reason as discussed above. Nevertheless, the overall trend will be more significant by representing in terms of COD removal percentage (%).

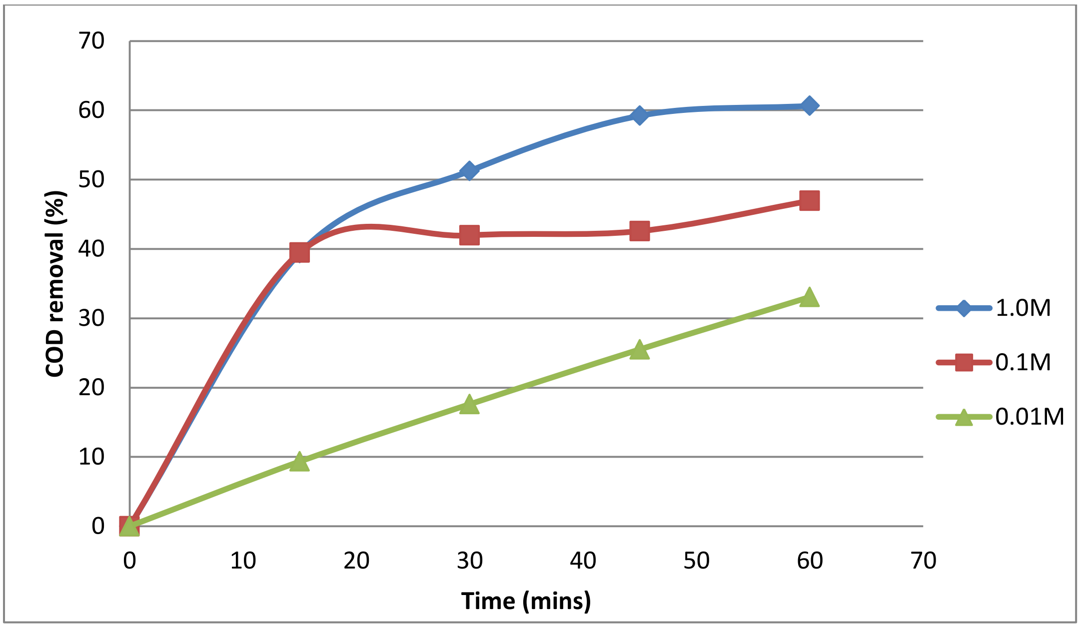


Figure 4.4.2 Overall plot of COD removal (%) vs. different H_2O_2 concentrations under 300 Watt visible light

As mentioned, 1.0 M of hydrogen peroxide gives the highest percentage of COD removal with 60.64 % in total; whereas 0.1 M and 0.01 M of hydrogen peroxide give a lower COD removal in terms of percentage namely 46.93 % and 33.07 % respectively. Even without reporting the actual percentage, it is clearly shown that the highest concentration of hydrogen peroxide (1.0 M) gives the highest trend line in degrading DIPA waste sample followed by 0.1 M and 0.01 M of H_2O_2 concentrations. In short, 1.0 M hydrogen peroxide will be again treated as the basis for optimization of DIPA concentration under 300 Watt visible light environments. Moving forward, the best system of DIPA degradation under 300 Watt of visible light will be identified via optimization of DIPA concentrations between 100 ppm, 300 ppm and 500 ppm respectively. The best system under this light radiation based on the optimized H_2O_2 concentration will be then compared with the best system obtained under 500 Watt visible light condition to find out which light intensity gives the most efficient DIPA degradation in terms of its COD removal percentage.

4.5 Optimization of DIPA Concentrations (300 Watt Light)

With the optimized hydrogen peroxide concentration, it is possible to determine the most optimum DIPA concentration under 300 Watt light source in a more precise manner. Without exception, the optimization process would be carried out with a set of constant parameters which is similar to the previous experiments.

4.5.1 100ppm Diisopropanolmaine (DIPA) Solution

The optimization process is again started with the lowest concentration of DIPA solution which is 100ppm but the visible light intensity has lowered to 300 Watt instead of 500 Watt. Different light intensities will definitely affect the outcome of DIPA degradation. Table below shows the result of degradation of 100ppm DIPA solution.

Table 4.5.1.1 Data distribution for 100ppm DIPA concentration under 300 Watt light

Time (mins)	0	15	30	45	60
Water bath temp [C]	20.5	20.5	20.0	20.5	20.0
System temp [C]	25.5	25.5	25.0	25.5	25.0
COD (mg/L)	314	238	232	217	196
COD removal (%)	**-**	**24.20**	**26.11**	**30.89**	**37.58**
Absorbance (abs)	0.138	0.105	0.102	0.096	0.086
Transmittance (%)	72.7	78.5	79.1	80.2	81.9
Degradation rate (ppm/min)	-	5.07	2.73	2.16	1.97

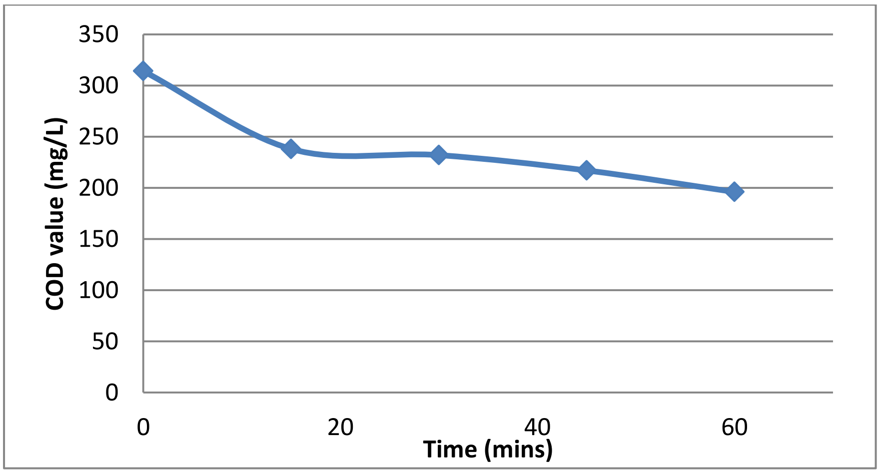


Figure 4.5.1.1 Plot of COD versus Time based on 100 ppm DIPA (300 Watt)

The initial COD value for 100 ppm DIPA solution was 314 mg/L which able to be degraded to 196 mg/L with an overall COD removal percentage of 37.58 %. However, the percentage seems to be lower compared to the same concentration of DIPA being treated under the 500 Watt visible light source. This might due to the incomplete degradation of 100 ppm DIPA under 300 Watt light radiation within 60 minutes of reaction time. This can be further explained with the plot below with the constant increment of COD removal percentage trend line even time exceeds 60 minutes. It is believed that the degradation process of DIPA is yet to be completed in this case and thus 37.58 % of COD removal at 60 minutes cannot be considered as the final outcome for this process. Thus, enhancement can be done for this system by increasing the reaction time in order to obtain more precise result.

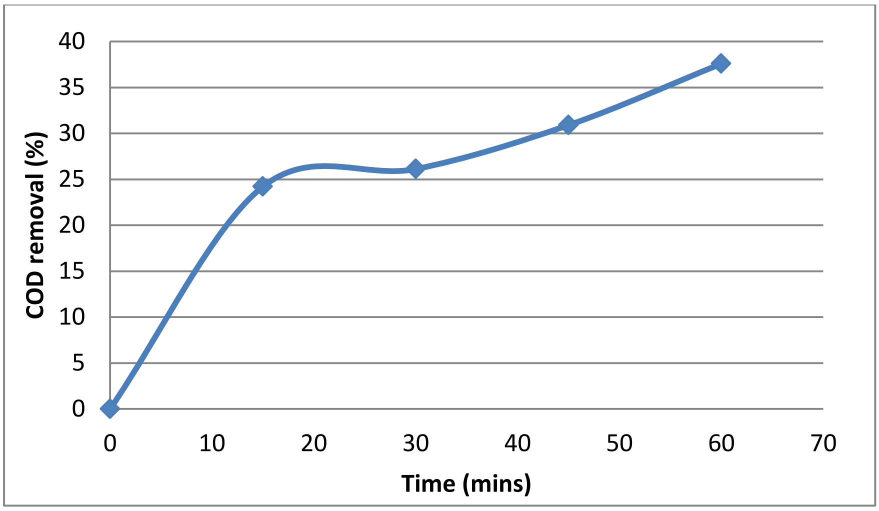


Figure 4.5.1.2 COD removal percentage against time for 100 ppm DIPA (300 Watt)

4.5.2 300ppm Diisopropanolamine (DIPA) Solution

Based on the previous study under 500 Watt visible light source, by increasing the concentration of DIPA solution will also tend to increase the efficiency of DIPA degradation in terms of COD removal. By carrying out DIPA degradation with Photo-Fenton oxidation with initial DIPA concentration of 300 ppm, the results obtained can be summarized in the table below.

Table 4.5.2.1 Data distribution for 300ppm DIPA solution under 300 Watt light

Time (mins)	0	15	30	45	60
Water bath temp [C]	20.5	21.0	20.5	20.0	20.5
System temp [C]	25.5	26.5	26.0	24.5	25.0
COD (mg/L)	718	364	335	317	313
COD removal (%)	**-**	**49.30**	**53.34**	**55.85**	**56.41**
Absorbance (abs)	0.317	0.16	0.148	0.14	0.138
Transmittance (%)	48.2	69.1	71.2	72.5	72.8
Degradation rate (ppm/min)	-	23.60	12.77	8.91	6.75

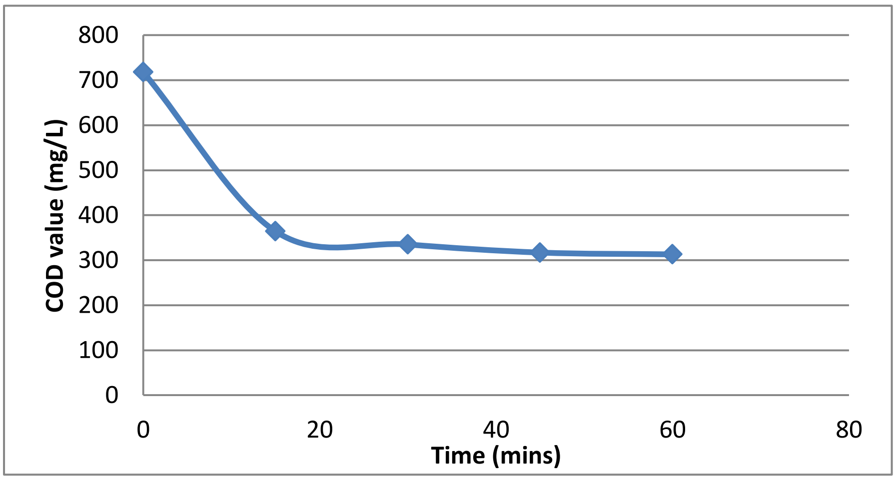


Figure 4.5.2.1 Plot of COD versus Time based on 300 ppm DIPA (300 Watt)

Indeed, the COD removal on a higher DIPA concentration is elevated and the initial COD value of 300 ppm DIPA managed to be reduced from 718 mg/L to 313 mg/L with an overall COD removal percentage of 56.41 %. This again proves that more DIPA compounds have been degraded as the initial concentration increases. It is found out to be higher compared to the same system conducted under 500 Watt light source which has the percentage of 54.46 % in terms of COD removal. The reason behind might be due to the tremendous intensity supplied by 500 Watt light source causing the evaporation rate of DIPA solution to be higher and lead to a higher concentration at the end of the degradation process. Higher final concentration of treated DIPA solution will tend to provide a higher value of COD measurement; in turn giving a lower percentage of COD removal.

4.5.3 500ppm Diisopropanolamine (DIPA) Solution

For the case of 500 ppm DIPA degradation using the optimized 1.0 M of hydrogen peroxide under 300 Watt of light radiation, the outcome will be the same as obtained in section 4.4.3 where the initial COD value is reduced from 1118 mg/L to 440 mg/L with the overall COD removal percentage of 60.64 % which is also the highest COD removal among all reaction systems. In addition, this system of course gives a higher removal in COD value compared to the same reaction system conduction under 500 Watt light source. However, the most optimum concentration of DIPA solution for its degradation with Photo-Fenton oxidation under 300 Watt light source is 500 ppm instead of 300 ppm obtained from 500 Watt visible light. Although the optimum DIPA concentrations for each light environment are different, but the comparison between DIPA degradation efficiency will be carried out between the most optimum conditions from two separate light sources. The overall plots of COD removal are shown in Figure 4.5.1 and 4.5.2.

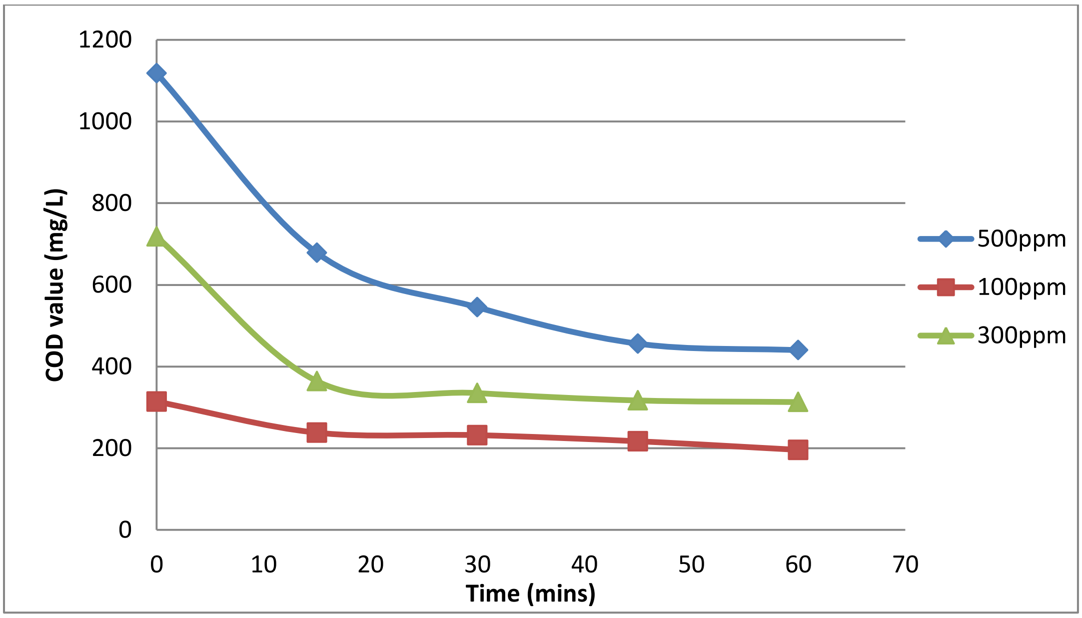


Figure 4.5.1 Overall plot of COD value vs. Time for all DIPA concentrations under 300 Watt light

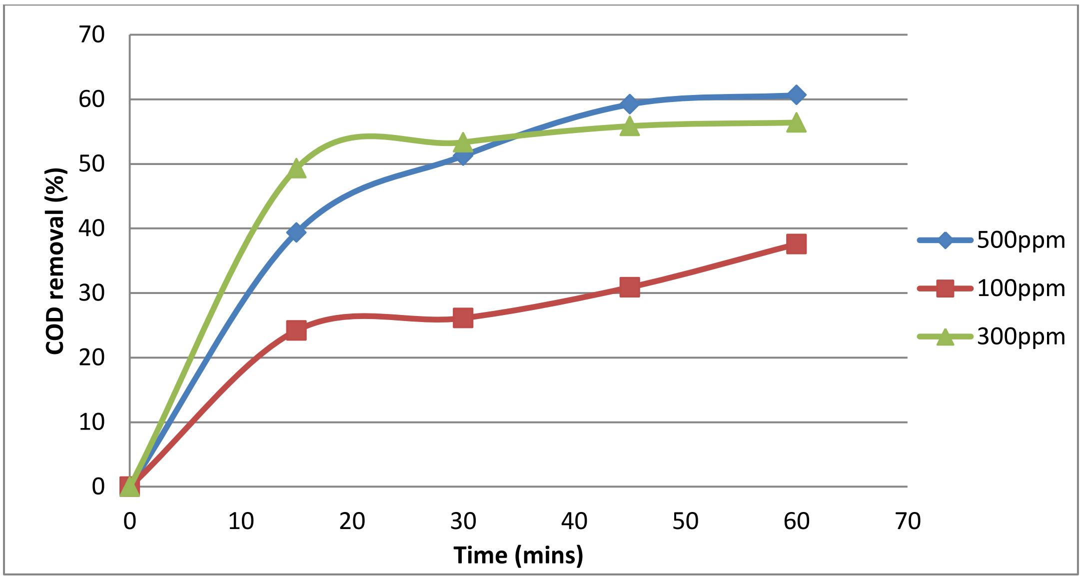


Figure 4.5.2 Overall plot of COD removal (%) vs. Time for all DIPA concentrations under 300 Watt light

In general, the increase in DIPA initial concentration will relatively lead to a higher degradation since more subject components undergone oxidation process. However, in the case of 500 Watt visible light, 500 ppm of initial DIPA concentration preformed lower than other two concentrations which is reversible to the norm. The low performance of the degradation might be caused by evaporation of reaction solution as 500 Watt of visible exposing high amount of heat energy to the system. In addition, the light source is placed directly above the reaction system in a near distance which will enhance the effect of evaporation even more. Nevertheless, normalization of the reaction system by adding distilled water after each sample is collected will tend to reduce the side effect of evaporation which causes the concentration of reaction system to increase tremendously. Furthermore, it is noticed that the reaction rates for the degradation of 300 ppm DIPA before 30 minutes time interval were higher compared to the ones with 500 ppm of DIPA. This can be seen from Figure 4.5.2 which COD removal percentage for 300 ppm reaches its maximum level at time 15 and 30 minutes before those under 500 ppm concentration. This might because of the variance in temperatures which leads to a higher rate of reaction. However, such hypothesis can only be verified when the research is further extended into the study of reaction kinetics and determining the activation energy for better justification of degradation efficiency.

4.6 Comparison between 300 Watt and 500 Watt Visible Light Sources

In order to clearly differentiate the efficiencies of DIPA degradation with Photo-Fenton oxidation under different light intensities, a comparison should be made between their COD removal percentage according to their respective DIPA concentration. Since the optimization of hydrogen peroxide concentration under both light radiation environment gives the same result, thus the comparison is made between different DIPA concentrations upon this basis. Table 4.6.1 summarizes the outcomes obtained from each optimization of DIPA concentration under different visible light intensities.

Table 4.6.1 Comparison of COD removal (%) based on different DIPA concentrations and light intensities

	COD Removal (%)	
DIPA Concentration	**300 Watt**	**500 Watt**
100 ppm	37.58	41.41
300 ppm	56.41	54.46
500 ppm	60.64	49.46

According to the results obtained, the COD removal percentage for each DIPA concentration under 300 Watt of visible light seems to be greater than those under 500 Watt light in general. However, there is an exception for 100 ppm of DIPA where the COD removal percentage obtained from 500 Watt light environment gives higher percentage which might due to the incompletion of degradation process for 300 Watt environment as explained before. In this case, we can conclude that a 300 Watt of light intensity is more effective in assisting DIPA degradation process with Photo-Fenton oxidation under visible light condition. Despite the general trend of COD removal percentage between different concentrations of DIPA solution, the statement above can be supported by the comparison of COD removal percentage between the two most optimum reaction systems under each light intensity. The most optimum system is defined by the highest percentage of COD removal for each light intensity regardless of the concentration of DIPA solution. In short, the most optimum reaction system for 300 Watt light intensity is 500 ppm of DIPA concentration with the COD removal percentage of 60.64 %; whereas the most optimum system under 500 Watt light is 300ppm DIPA concentration with COD removal percentage of only 54.46 %. This again shows the efficiency in degrading DIPA waste sample is more significant and promising by using a 300 Watt of visible light source. Since a 300 Watt is a better choice for Photo-Fenton oxidation of Diisopropanolamine waste, it will be highly recommended to utilize a lower power of light source such as 300 Watt compared to 500 Watt for similar process in order to reduce the consumption of energy; in another word reducing the cost of utility.

4.7 Fenton Oxidation Process WITHOUT Light Source

In order to further signify the effect on applying light radiation in Photo-Fenton process from ordinary Fenton process, this research study have also covered Fenton oxidation for DIPA degradation without the availability of light source for the two best reaction system with 300 ppm and 500 ppm of DIPA concentrations. However, the other parameter such as initial Fenton reagent concentration, pH value and concentration of hydrogen peroxide are kept constant as shown below. For the system of 300 ppm DIPA concentration, the DIPA waste sample was being degraded from the initial COD value of 718 mg/L to 528 mg/L with the percentage of 26.46 % only. In comparison with the same reaction system under light radiation, it is much lower. Thus, it proves that Photo-Fenton oxidation with the availability of light is more effective in degrading DIPA waste sample. Move over, the reaction system using 500 ppm of DIPA solution decreases the initial COD value from 1125 mg/L to 817 mg/L with an overall COD removal percentage of 27.38 % . Even the degradation rate is better for 500 ppm of initial DIPA concentration compared to 300 ppm, but it is still considered inefficient when in comparison with the existence of light radiations. Figure 4.7.1 shows a better comparison between COD removal with and without light under Fenton-oxidation processes.

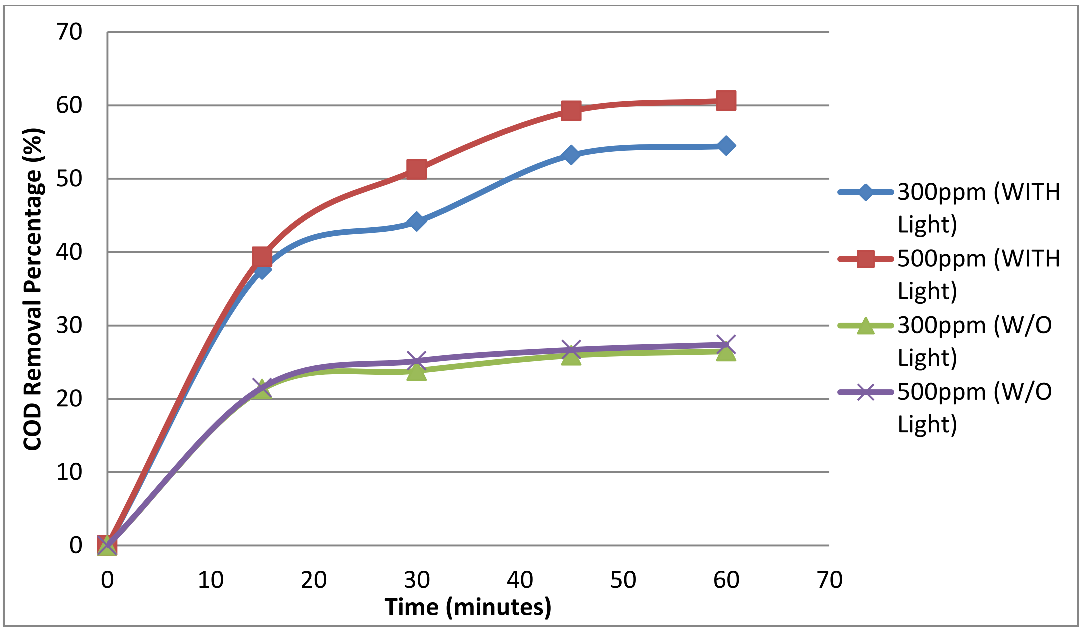


Figure 4.7.1 Comparison plot for systems with and without light

From Figure 4.7.1 above, it is clearly shown that the difference in trend line between the reaction systems with as well as without light radiation in terms of COD removal percentage for DIPA degradation under Photo-Fenton and Fenton oxidation respectively. It shows a significant difference between COD removal in terms of percentage for the both 300 ppm and 500 ppm initial concentration under Fenton reaction with and without the existence of light source. An average of 30 % difference between the COD removal for both initial DIPA concentrations under the reaction with and without visible respectively. Thus, we can ensure that Photon-Fenton oxidation is more effective compared to ordinary Fenton reaction without any assistance of light radiation.

4.8 Error and Recommendation

Errors

I. Diisopropanoamine (DIPA) tends to absorb water vapour from the air in the atmosphere. Weight of DIPA solid material will be affected by the absorbed water content during preparation of its standard solution and ultimately the concentration will be inaccurate.

II. Due to the continuous radiation of light from the light source, temperatures of reaction system and water bath will fluctuates. Precise temperature control is not efficient enough by only monitoring the temperature of the water bath.

III. Near distance between the light source and the reaction system causes reaction solution to vaporize and lead to increase in overall concentration as visible light exerting heat.

IV. 60 minutes of reaction time is still considered insufficient as some oxidation process is yet to reach its maximum level, especially the reaction system with lower DIPA concentration.

V. COD measurement becomes inaccurate due to the sample in COD vials are not being let to cool down to room temperature completely. Measurement easily went out of range during COD analysis.

Recommendations

I. In order to measure the accurate weight of DIPA solids, the weighing process should be carried out in a fume hood with proper air ventilation to prevent the absorption of water vapour by DIPA solids.

II. A better temperature monitoring can be achieved by placing one more thermometer into the reaction system directly in order to monitor and control the system temperature more effectively

III. Visible light source should be relocated and kept at certain distance away from the reaction system in order to avoid evaporation from occurring.

IV. Each experiment run should be given more time by extending the duration from 60 minutes to 90 minutes for the completion of degradation process.

V. All samples are recommended to be left overnight in order to completely cool down to room temperature after mixing with COD reagent and digestion process before proceeding into COD measurement using Hach® DR 5000.

4 .9 Gantt Chart

No.	Description	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14
1	Preparation of standard solutions	🟥	🟥												
2	Experiment setup run test		🟥												
3	Preparation of calibration curve			🟥											
4	Conduct H_2O_2 concentration optimization (500 Watt system)				🟥	🟥									
5	Conduct DIPA concentration optimization (500 Watt system)						🟥	🟥							
6	Preparation on Progress Report							🟥							
7	Conduct Photo-Fenton process with 300 Watt light source								🟥	🟥					
8	Conduct reaction kinetic studies with results obtained									🟥	🟥				
9	Preparation for Pre-SEDEX							🟥	🟥	🟥	🟥				
10	Preparation for final report and technical paper							🟥	🟥	🟥	🟥	🟥	🟥	🟥	
11	Submission of final report and technical paper													🟥	🟥

CHAPTER 5.0

CONCLUSION AND RECOMMENDATION

Photo-Fenton oxidation utilizes light source to literally speed up the generation of hydroxyl radicals for oxidation as well as to improve the overall oxidation efficiency. By conducting this research project, the ultimate aim is to evaluate and compare the degradation efficiency of Diisopropanolamine (DIPA) under different light intensities in Photo-Fenton oxidation process. In order to achieve the objective above, optimization of the most suitable parameter configurations of Diisopropanolamine (DIPA) degradation is important for more accurate outcomes. Parameters taken into consideration for optimization were the concentration of hydrogen peroxide and initial concentration of DIPA samples. Then, degradation of DIPA model waste was then conduction via Photo-Fenton oxidation with two different powers of light irradiations based on the optimized parameters.

At the beginning of the research work, calibration curve related to COD value (mg/L) against different DIPA concentrations was created. A linear relation was obtained between the concentration ranging from 10ppm to 500ppm and the measured COD values. The relation shows that as the concentration of DIPA increases, the COD measurement will increase as well.

Besides, optimization was carried out for different hydrogen peroxide (H_2O_2) concentration using 500 Watt of light source while maintaining other parameters constant. The result obtained shows the most effective concentration for DIPA degradation is 1.0M of H_2O_2 as the oxidizing agent. Moving forward, optimization of initial DIPA concentration (100ppm, 300ppm and 500 ppm) was carried out based on the optimum concentration of H_2O_2 under the same light source. As a result, 300ppm of DIPA turned out to be the most optimum concentration which gives the highest degradation with a COD removal percentage of 54.46% among all. In another words, reaction system with 1.0M of hydrogen peroxide and 300ppm DIPA solution under 500 Watt visible light source is said to be the optimum system which is used for the comparison between different light intensities. Moving forward, the same optimization process was also carried for hydrogen peroxide concentration then the DIPA concentration, but under the exposure of different light intensities namely 300 Watt. For the optimization of hydrogen peroxide concentration, the same outcome was obtained which 1.0M H_2O_2 is the optimum concentration for the oxidizing agent. However, optimization of DIPA concentration under 300 Watt visible light radiation turns out to be 500ppm instead of 300ppm which gives an overall COD removal of 60.64%. Thus, the optimum system under this light intensity is 1.0M of hydrogen peroxide with 500ppm of DIPA solution. By comparing both of the most optimum reaction systems under different light sources, 300 Watt of visible light tends to give better result on DIPA degradation under Photo-Fenton oxidation. Apart from that, the comparison between Photo-Fenton (with light) and Fenton (without light) oxidations was also carried out to prove the higher efficiency in degrading DIPA waste sample when light radiation is available. Lastly, we are able to draw to a conclusion that Photo-Fenton oxidation is more effective comparable to normal Fenton oxidation process. In addition, 300 Watt of light source is sufficient to provide efficient degradation of DIPA waste sample compared to a higher power light source which will eventually consume more energy. By utilizing 300 Watt light source is believed to be able to reduce unnecessary usage of energy.

5.1 Relevancy to objective

Based on the experimental layout, it is believed that the efficiency of DIPA can be effectively determined based on the COD measurements obtained over time by plotting the measurement values against time intervals of oxygen demand tests. Each set of data is being organized according to the respective light intensity under studied based on different power of light source. Towards the end of the analysis, all results gathered from different light intensities will be plotted together against time and the most optimum light intensity is then being suggested based on the efficiency of DIPA degradation while other parameters were kept constant throughout the entire project experiment. The suggested optimum light intensity can be utilized in the future in order to enhance Photo-Fenton oxidation process as well as to avoid wastage of power on the light source which is unnecessary.

5.2 Recommendation For Future Work

This particular project study can eventually be extended for further optimization of other experimental parameters based on the suggested optimum light intensity for a Photo-Fenton process on degradation of Diisopropanolamine (DIPA). Optimization is tedious if all the parameters are variable and reliability of such optimization process will be questionable as well. Thus, by applying the optimum possible light intensity, one of the major experimental parameters is taken care and accuracy of optimization will also be relatively higher. Apart from that, this project can also acts as a baseline for Photo-Fenton processes whereby future studies on Photo-Fenton related research using different type of light source or amine type can utilizes the findings obtained from this study as a reference or guideline. Despite the optimization of experimental parameters, the research on evaluating DIPA degradation efficiency can be further enhanced by extending the scope of study into reaction kinetics where activation energy (E_A) of each reaction system can be identified. Comparison of activation energy can help in determining the efficiency in a more precise and convincing manner. Thus, this project work is believed to be a good starting point for wider explorations on Photo-Fenton process if the findings obtained later are practical.

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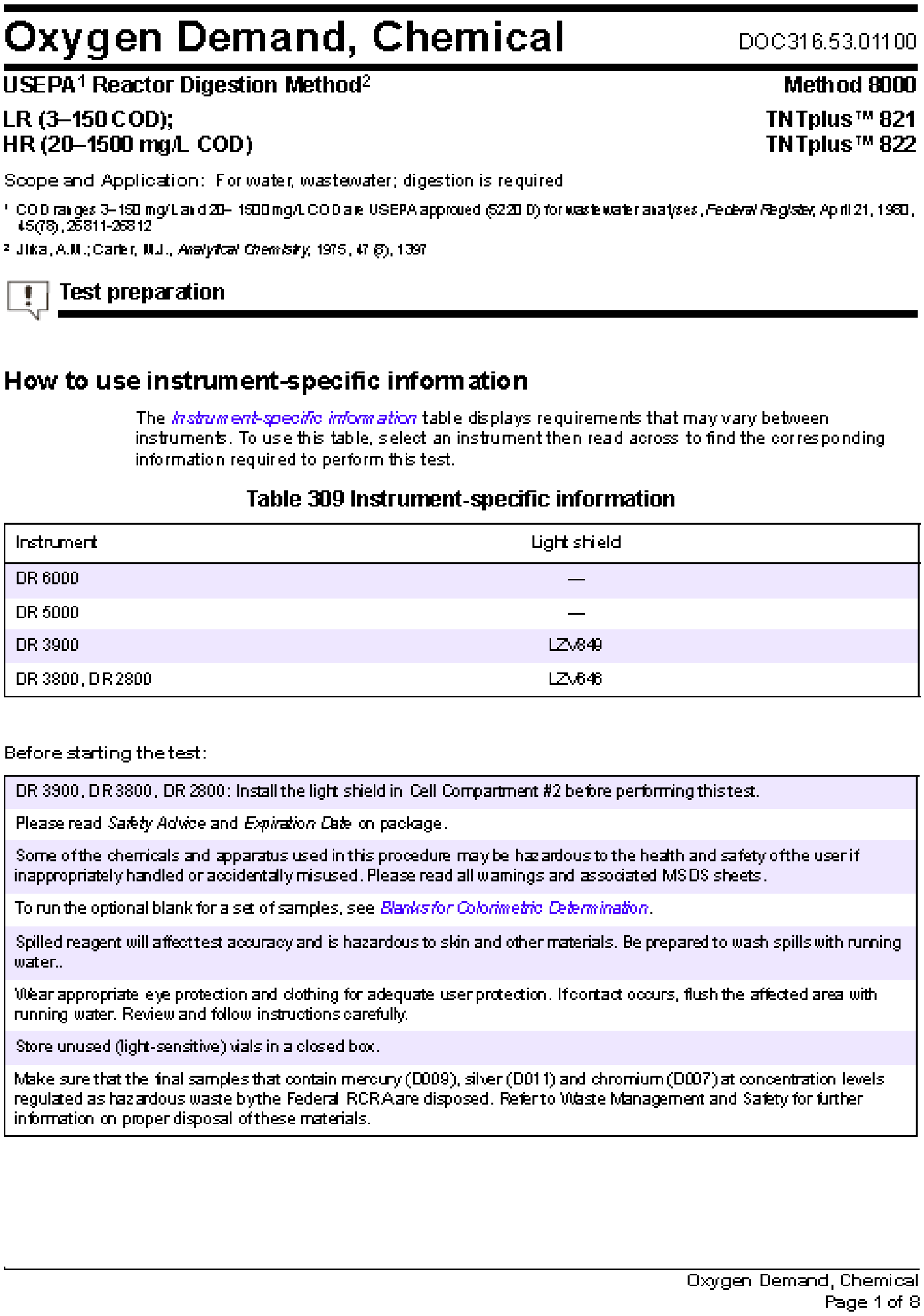
APPENDICES

Appendix A: User Manual of HACH® DR5000 Spectrophotometer



Oxygen Demand, Chemical

DOC316.53.01100

USEPA[1] Reactor Digestion Method[2] **Method 8000**

LR (3–150 COD); **TNTplus™ 821**
HR (20–1500 mg/L COD) **TNTplus™ 822**

Scope and Application: For water, wastewater; digestion is required

[1] COD ranges 3–150 mg/L and 20– 1500 mg/L COD are USEPA approved (5220 D) for wastewater analyses, *Federal Register*, April 21, 1980, 45(78), 26811-26812

[2] Jirka, A.M.; Carter, M.J., *Analytical Chemistry*, 1975, 47 (8), 1397

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 309 Instrument-specific information

Instrument	Light shield
DR 6000	—
DR 5000	—
DR 3900	LZV849
DR 3800, DR 2800	LZV646

Before starting the test:

DR 3900, DR 3800, DR 2800: Install the light shield in Cell Compartment #2 before performing this test.
Please read *Safety Advice* and *Expiration Date* on package.
Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and associated MSDS sheets.
To run the optional blank for a set of samples, see *Blanks for Colorimetric Determination*.
Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Be prepared to wash spills with running water..
Wear appropriate eye protection and clothing for adequate user protection. If contact occurs, flush the affected area with running water. Review and follow instructions carefully.
Store unused (light-sensitive) vials in a closed box.
Make sure that the final samples that contain mercury (D009), silver (D011) and chromium (D007) at concentration levels regulated as hazardous waste by the Federal RCRA are disposed. Refer to Waste Management and Safety for further information on proper disposal of these materials.

Oxygen Demand, Chemical
Page 1 of 8

Oxygen Demand, Chemical

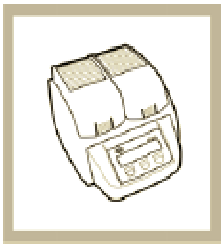
Collect the following items:

Description	Quantity
Blender	1
DRB200 Reactor with 13-mm wells (use adapters with 16-mm holes)	1
COD TNTplus™ vials for the appropriate concentration range	varies
Light Shield or Adapter (see Instrument-specific information)	1
Pipet for 2.0 mL Sample	1
Pipet Tip	1
Test Tube Rack	2

See Consumables and replacement items for reorder information.

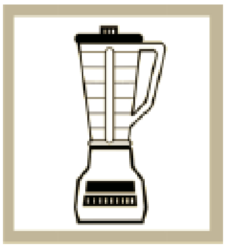
Reactor digestion method, TNTplus

Important Note: If the sample does not contain suspended solids, omit steps 2 and 3.

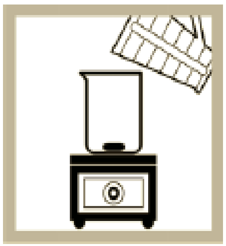


1. Turn on the DRB200 Reactor. Preheat to 150 °C.

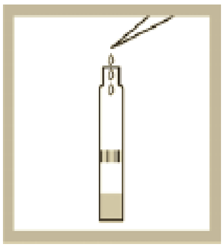
For DRB200 Reactors with 16-mm wells, insert a 16-mm to 13-mm adapter sleeve into each well before turning on the reactor.



2. Homogenize 100 mL of sample for 30 seconds in a blender. For samples containing large amounts of solids, increase the homogenization time.

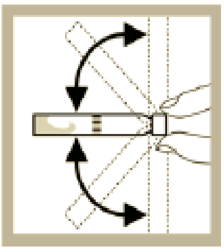


3. To help to make sure that a representative portion of sample is analyzed, pour the homogenized sample into a 250-mL beaker and gently stir with a magnetic stir plate.



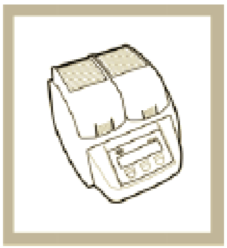
4. Carefully pipet 2.0 mL of sample into the vial. Cap and clean the outside of the vial.

Reactor digestion method, TNTplus (continued)

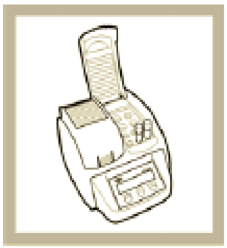


5. Hold the vial by the cap over a sink. Invert gently several times to mix. The sample vials will become very hot during mixing.

Place the vial in the preheated DRB200 Reactor. Close the protective lid

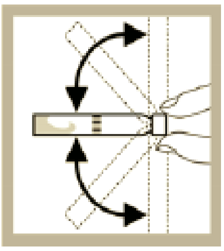


6. Heat for two hours.

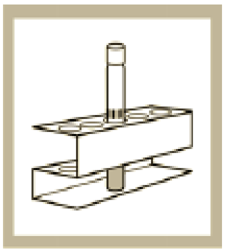


7. Turn the reactor off.

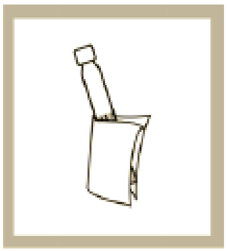
Wait about 20 minutes for the vial to cool to 120 °C or less.



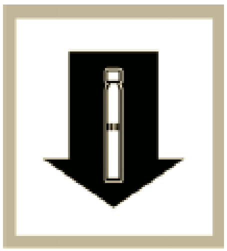
8. Invert the vial several times while still hot.



9. Place the vial into a rack to cool to room temperature.



10. Thoroughly clean the outside of the vial.



11. Insert the vial into the cell holder. Close the lid.

The instrument reads the barcode, then selects and performs the correct test.

Results are in mg/L COD.

Blanks for Colorimetric Determination

A reagent blank can be measured and the value subtracted from the results of each test performed using the same reagent lot number. The blank may be used repeatedly for measurements using the same lot of vials. Store it in the dark and monitor decomposition by measuring its concentration periodically.

To subtract the value of the blank from a series of measurements:

1. Measure the blank per step 11.
2. Turn on the instrument reagent blank feature.
3. The measured value of the blank should be displayed in the highlighted box. Accept this value.

4. The reagent blank value will be subtracted from all results until the function is turned off or a different method is selected.

Alternately, the blank can be recorded and entered at any later time by pressing the highlighted box and using the keypad to enter the value.

Interferences

Chloride is the primary interference when determining COD concentration. Each COD vial contains mercuric sulfate that will eliminate chloride interference up to 2000 mg/L Cl^-.

Sample collection, preservation and storage

- Collect samples in glass bottles.
- Use plastic bottles only if they are known to be free of organic contamination.
- Test biologically active samples as soon as possible.
- Homogenize samples containing solids to assure representative samples.
- Samples treated with sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C can be stored up to 28 days.
- Correct results for volume additions.

Accuracy check

Standard solution method for 3 to 150 mg/L COD range
Required for accuracy check:

- 1000 mg/L COD Standard Solution
- 100 mL Volumetric flask
- Deionized water
- 10 mL Volumetric Pipet and safety bulb

1. Prepare a 100-mg/L standard solution as follows:
    a. Pipet 10.0 mL of the 1000 mg/L COD standard solution into a 100 mL volumetric flask.
    b. Dilute to volume with deionized water and mix well.
2. Use 2 mL of this solution as the sample volume. Follow the *Reactor digestion method, TNTplus* test procedure. The expected result is 100-mg/L.

Standard solution method for 20 to 1500 mg/L COD range
Required for accuracy check:

- 300-mg/L COD Standard Solution

  OR

- 1000-mg/L COD Standard Solution
- Deionized water

1. Use 2 mL of either the 300-mg/L or the 1000-mg/L solution as the sample volume. Follow the *Reactor digestion method, TNTplus* test procedure. The expected result is 300 mg/L COD with the 300 mg /L standard or 1000 mg/L with the 1000 mg/L standard.

Alternate standard solution method for 20 to 1500 mg/L COD range
Required for accuracy check:

Use 2 mL of 300 mg/L, 800 mg/L or 1000 mg/L COD standard for accuracy check. Follow the *Reactor digestion method, TNTplus* test procedure. The expected result is 500 mg/L.

Method performance

Program	Method	Standard	Precision 95% Confidence Limits of Distribution
Barcode	TNTplus 822, HR	750	736–764 mg/L COD
	TNTplus 821, LR	75	72–78 mg/L COD

Summary of method

The mg/L COD results are defined as the mg of O_2 consumed per liter of sample under conditions of this procedure. In this procedure, the sample is heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). When the 3–150 mg/L colorimetric method is used, the amount of Cr^{6+} remaining is determined. When the 20–1500 mg/L colorimetric method is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst and mercury is used to complex chloride interferences. Test results for the 3 to 150 mg/L range are measured at 420 nm. Test results for the 20 to 1,500 mg/L COD range are measured at 620 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Select the appropriate TNTplus™ COD Digestion Reagent Vial:			
Low Range, 3 to 150 mg/L COD	1–2 vials	25/pkg	TNT821
High Range, 20 to 1500 mg/L COD	1–2 vials	25/pkg	TNT822

Required apparatus

Description	Quantity	Unit	Catalog number
DRB200 Reactor, 115 V, 9 x 13 mm + 2 x 20 mm (mono block)	1	each	DRB20001
OR			
DRB200 Reactor, 230 V, 9 x 13 mm + 2 x 20 mm (mono block)	1	each	DRB20005
Pipet, variable volume, 1–5 mL	1	each	BBP065
Pipet Tips, for BBP065 pipet	1	75/pkg	BBP068
Test Tube Rack, 13-mm	1	each	2497900

Recommended standards

Description	Unit	Catalog number
COD Standard Solution, 300-mg/L	200 mL	1218629
COD Standard Solution, 800 mg/L	200 mL	2672629
COD Standard Solution, 1000-mg/L	200 mL	2253929
Potassium Acid Phthalate, ACS	500 g	31534
Oxygen Demand Standard (BOD, COD, TOC), 10-mL ampules	16/pkg	2833510
Wastewater Influent Standard, for mixed parameters (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	2833149
Wastewater Effluent Standard, for mixed parameters (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	2833249

Recommended services[1]

Description	Unit	Catalog number
ez COD recycling service (mail-back program)	5-gallon container	2895405
ez COD recycling service (pick-up program)	5-gallon container	2895405P
ez COD recycling service	20-gallon container	2895420
ez COD recycling service	55-gallon container	2895455

[1] Available in U.S. only

Optional reagents and apparatus

Description	Unit	Catalog number
Beaker, 250 mL	each	50046H
Blender, 2-speed, 120 VAC	each	2616100
Blender, 2-speed, 240 VAC	each	2616102
DRB200 Reactor, 115 V, 21x13 mm + 4x20 mm (dual block)	each	DRB20002
DRB200 Reactor, 115 V, 15x13 mm +15x13 mm (dual block)	each	DRB20003
DRB200 Reactor, 115 V, 12x13 mm + 8x20 mm (dual block)	each	DRB20004
DRB200 Reactor, 230 V, 21x13 mm + 4x20 mm (dual block)	each	DRB20006
DRB200 Reactor, 230V, 15x13 mm+ 15x13 mm (dual block)	each	DRB20007
DRB200 Reactor, 230 V, 12x13 mm + 8x20 mm (dual block)	each	DRB20008
Stir Plate, magnetic	each	2881200
Stir Bar, octagonal, 28.6 x 7.9 mm	each	2095352
Analytical Balance, Analytical 80 g x 0.1 mg 115 V	each	2936701
Water, deionized	500 mL	27249
Weighing papers, 76x76 mm	500/pkg	1473800
Volumetric Flask; Class A, 1 L	each	1457453
pH Test Strip, 0–14 pH	100/pkg	2601300
Laboratory oven; 120 V 50/60 HZ	each	1428900
Laboratory oven; 240 V 50/60 HZ	each	1428902
Goggles, Safety Vented	each	2550700
Gloves, Chemical Resist 9-9 ½[1]	1 pair	2410104
COD Standard Solution, 300 mg/L	500 mL	1218649
Sulfuric Acid, ACS	500 mL	97949
TNTplus™ Reactor adapter sleeves, 16-mm to 13-mm diameter	5/pkg	2895805

[1] other sizes are available