Photo-Fenton Oxidation of Batik Making Textile Effluents

by

Ezzaini Bin Ramli

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

October 2004

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Photo-Fenton Oxidation of Batik Making Textile Effluents

by

Ezzaini Bin Ramli

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

Approved by,

(Mrs. Putri Nadzrul Faizura Megat Khamaruddin)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
OCTOBER 2004

CERTIFICATION OF ORIGINALITY

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

(EZZAINI BIN RAMLI)

ABSTRACT

The textile industry produces wastewater effluents that contain a high value of Chemical Oxygen Demand (COD). These effluents need to be treated before it is being discharged so that the discharge is safe to the environment. One of the attractive and economical alternatives is by utilizing Advanced Oxidation Processes (AOP). Photo-Fenton oxidation is one of those processes. Photo-Fenton oxidation includes an irradiation of an Ultraviolet light with the utilization of a Fenton's Reagent. In this project, Photo-Fenton oxidation is used to treat the wastewater sample taken from a Batik-making factory. The initial parameters of the sample such as the pH and COD values are measured and the Fenton's Reagent is prepared based on that initial measurement. The COD reading is measured using the HACH method which is using the DR4000 apparatus. COD is measured in mg/L. Fenton's Reagent consists of Iron (Fe) and Hydrogen Peroxide (H_2O_2). Different ratios of Fe and H_2O_2 are used to determine which composition ratio will produce the least value of COD value after a 2-hour experiment. From the results obtained, the Fenton's Reagent ratio of 1part Fe and 30 parts H_2O_2 yielded the least value of COD which is 114 mg/L after 60 minutes of the experiment. Thus, the optimum reaction time is determined to be at 60 minutes.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to my supervisor; Mrs. Putri Nadzrul Faizura Megat Khamaruddin, for supervising and giving me guidance throughout the duration of this project. This project would not have been successfully completed if not for her vast knowledge, support, attention and constant encouragement. I would also like to thank the Final Year Research Project Coordinator, Mrs. Yuliana for her moral support and immaculate coordinating skills in ensuring the milestones and flow of this project are appropriately abided. My gratitude also goes out to the Department of Chemical Engineering Head of Program, Dr. Hilmi Mukhtar, in allowing the students to fully utilize the equipments located in the various laboratories. I would also like to express my gratitude to the laboratory technicians in providing assistance and guidance on the operation of the various equipment and experimental procedures conducted in the laboratories. Without their help, this project would not have been successfully completed. I would also like to thank the various personnel form Kilang Batik Kam Ismail in allowing me to obtain the wastewater sample from their premises. My utmost gratitude also goes out to my friends and family who have provided assistance and support in every possible manner for me to complete this project. Last but not least, I would like to thank the various parties involved whether directly or indirectly in ensuring the completion of my Final Year Research Project and Dissertation.

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND NOMENCLATURES

AOP	Advanced Oxidation Process
M	Molar
ppm	Parts per million
mg/L	Milligrams per liter
COD	Chemical Oxygen Demand
wt/wt	Weight/Weight
°C	Degrees Celsius
L	Liter
mL	Milliliter
μL	Microliter
nm	Nanometer
UV	Ultraviolet

TABLE OF CONTENTS

CHAPTER 3: METHODOLOGY / PROJECT WORK

CHAPTER 4: RESULTS AND DISCUSSION

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

CHAPTER 6: REFERENCES

CHAPTER 1
INTRODUCTION

1.1 Background of Study

The textile industry produces large volumes of bleaching effluents that contain appreciable quantities of organic compounds which are not easily amenable to chemical or biological treatment. Furthermore, treatment cost of textile wastewaters has been scaling rapidly in recent years. Hence a search for more cost-effective treatment methods has practical application.

Recently, chemical treatment methods, based on the generation of hydroxyl radicals, known as advanced oxidation processes (AOPs), have been applied for pollutant degradation, due to the high oxidative power of the OH radical. The most widely studied AOPs include: heterogeneous photo catalytic oxidation, treatment with ozone (often combined with H_2O_2, UVA, or both), H_2O_2/UV systems, Fenton and photo-Fenton type reactions.

The photo-Fenton reaction, which is an irradiation of Fe(III) + H_2O_2 has been proven to enhance the reaction rate of oxidant production, through the involvement of high valence Fe intermediates responsible for the direct attack to organic matter. Absorption of visible light by the complex formed between Fe(III) and H_2O_2 seems to be the cause of formation of such high valence Fe-based oxidants.

1.2 Problem Statement

The textile industry produces large volume of colored effluents that contain organic compounds that cannot be treated easily by the norm wastewater treatment method. Advanced oxidation processes (AOP) is an attractive alternative. Fenton reaction is one example of AOP that has been identified to have potential in treating colored wastewater.

1.3 Significance of the Project

The project of Photo-Fenton Oxidation of Batik Making Textile Effluents is a method to increase the biodegradability and decrease the chemical oxygen demand (COD) value to ensure these effluents, when disposed, will not pose a significant threat or danger to the environment.

1.4 Objective and Scope of Study

This project involves an application of wastewater treatment according to the specified parameters which is COD. If the Photo-Fenton oxidation method is successful in increasing the quality of the wastewater discharged, then this method can be applied in treating the effluent from textile making or batik making specifically.

This project is feasible within the scope and time frame as the parameters determined are adequate and the length of time required for the experiments is sufficient for the whole length of the project implementation. The project which is related to wastewater treatment is also within the scope of the Chemical Engineering course undertaken in the university.

The specific objectives of this project of Photo-Fenton Oxidation of textile effluents are:

1. To determine the optimum reaction time.
2. To determine the optimum Fe : H_2O_2 ratio.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 General Information Concerning Textile Effluents

Textile production involves a number of wet processes that may use solvents. Emissions of volatile organic compounds (VOCs) mainly arise from textile finishing, drying processes, and solvent use. VOC concentrations vary from 10 milligrams of carbon per cubic meter (mg/m3) for the thermosol process to 350 mg carbon/m3 for the drying and condensation process. Process wastewater is a major source of pollutants. It is typically alkaline and has high BOD-from 700 to 2,000 milligrams per liter (mg/l)—and high chemical oxygen demand (COD), at approximately 2 to 5 times the BOD level.

Wastewater also contains solids, oil, and possibly toxic organics, including phenols from dyeing and finishing and halogenated organics from processes such as bleaching. Dye wastewaters are frequently highly colored and may contain heavy metals such as copper and chromium. Wool processing may release bacteria and other pathogens. Pesticides are sometimes used for the preservation of natural fibers, and these are transferred to wastewaters during washing and scouring operations. Pesticides are used for mothproofing, brominated flame retardants are used for synthetic fabrics, and isocyanates are used for lamination. The use of pesticides and other chemicals that are banned in some countries is discouraged and in general, is not acceptable. Wastewaters should be checked for pesticides such as DDT and PCP and for metals such as mercury, arsenic, and copper. Air emissions include dust, oil mists, acid vapors, odors, and boiler exhausts. Cleaning and production changes result in sludges from tanks and spent process chemicals, which may contain toxic organics and metals.

The treatment of wastewater from textile dyeing is an environmental problem that has received considerable attention. The effluent form textile processing is often discharged to municipal sewage treatment plants or directly to waterways. Textile dyes are not biodegradable, and consequently sewage treatment removes certain types of dye (particularly the so-called 'reactive' dyes). Reactive dye that remains in the effluent has been hydrolyzed during the dyeing process and therefore cannot be reused.

The reactive dyeing process produces two different waste streams. The initial concentration dye bath effluent id above 50°C, has a pH of at least 11, contains up to 0.6g/L unfixed dye and 40-80 g/L salt (NaCl or Na_2SO_4) and small quantities of other additives. Rinse water contains much lower concentrations of dye, salt and other additives.

Table 1: Textile Industries Wastewater Characteristics

Parameter	Maximum level
Ph	11
Initial dye concentrations	2.9×10^{-5} to 2.3×10^{-4} M
Chemical Oxygen Demand	450
Aspect	Red blue strong colored
Odor	Detergent scent
Total Suspended Solid	> 3500 ppm
Emulsion	No sedimentation tendency

(Source: Montserrat et al, 2001)

2.2 Pollution Prevention and Control

Pollution prevention programs should focus on reduction of water use and on more efficient use of process chemicals. Process changes might include the following:

1. Match process variables to type and weight of fabric (reduces wastes by 10–20%).
2. Manage batches to minimize waste at the end of cycles.

3. Avoid non-degradable or less degradable surfactants (for washing and scouring) and spinning oils.
4. Avoid the use, or at least the discharge, of alkylphenol ethoxylates. Ozone-depleting substances should not be used, and the use of organic solvents should be minimized.
5. Use transfer printing for synthetics (reduces water consumption from 250 l/kg to 2 l/kg of material and also reduces dye consumption).
6. Use water-based printing pastes, when feasible.
7. Use pad batch dyeing (saves up to 80% of energy requirements and 90% of water consumption and reduces dye and salt usage).
8. For knitted goods, exhaust dyeing is preferred.
9. Use jet dyers, with a liquid-to-fabric ratio of 4:1 to 8:1, instead of winch dyers, with a ratio of 15:1, where feasible.
10. Avoid benzidine-based azo dyes and dyes containing cadmium and other heavy metals. Do not use chlorine-based dyes.
11. Use less toxic dye carriers and finishing agents.
12. Avoid carriers containing chlorine, such as chlorinated aromatics.
13. Replace dichromate oxidation of vat dyes and sulfur dyes with peroxide oxidation.
14. Reuse dye solution from dye baths.
15. Use peroxide-based bleaches instead of sulfur and chlorine-based bleaches, where feasible.
16. Control makeup chemicals.
17. Reuse and recover process chemicals such as caustic (reduces chemical costs by 30%) and size (up to 50% recovery is feasible).
18. Replace non-degradable spin finish and size with degradable alternatives.
19. Use biodegradable textile preservation chemicals. Do not use polybrominated diphe-nylethers, dieldrin, arsenic, mercury, or pentachlorophenol in mothproofing, carpet backing, and other finishing processes. Where feasible, use permethrin for mothproofing instead.
20. Control the quantity and temperature of water used.
21. Use countercurrent rinsing.

22. Improve cleaning and housekeeping measures (which may reduce water usage to less than 150 m3/t of textiles produced).
23. Recover heat from wash water (reduces steam consumption).

2.3 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are a group of processes that are based on the generation of hydroxyl radicals, which are highly reactive oxidants. AOPs are able to oxidize a wide range of compounds that are otherwise difficult to degrade. The four AOPs that have been most widely studied are ozonation, UV/H_2O_2, Fenton's reagent (Fe^{2+}/ c) and UV/TiO_2.

Furthermore, AOPs for wastewater treatment include reactions with H_2O_2, with or without ultraviolet (UV) irradiation, ozonation and O_3/UV treatment. While ozone has a high oxidation potential ($E^o = +2.07$ V), ozone reacts very slowly with various compounds, such as with chlorinated alkanes, with chlorinated herbicides, such as 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), and also with the triazine herbicides, such as atrazine. Improved treatment methods involve the combination of ozone with UV light, generating the $^{\cdot}OH$ radicals, which are even more reactive oxidants ($E^o = +3.06$ V). (Halmann, M, 1996)

A major problem preventing the widespread use of ozone is the high cost of treatment. In contrast to the above AOPs in homogenous solutions, in which the oxidants are consumed, heterogenous photocatalytic oxidations use near-UV and visible light as the energy source to overcome the required activation energy. In this case, water or dissolved oxygen usually provides the necessary oxidant. The photocatalysts, such as TiO_2, may be reused or in a fixed-bed operation may be used for extended periods. Also, sunlight can be an inexpensive light source, particularly for well-insolated and arid regions. Modern efficient UV/visible light sources, such as the novel excimer lamps may enable economic application of photodetoxification also in poorly insolated regions. (Halmann, M, 1996)

Photocatalytic reactions are by definition exoergic processes, in which the absorption of light energy results in acceleration of reactions. Many compounds and materials of our environment, such as all organic molecules and most components of living systems are unstable toward oxidation – but their oxidative degradation is delayed and hindered by steric constraints and by high activation energies. Photochemical processes are of major importance in the chemistry of gaseous molecules in the upper atmosphere, regulating the interaction between oxygen, ozone, nitrogen oxides and nitrogen halides. In natural aquatic systems, in the earth's oceans, rivers and lakes, photochemical reactions are often masked by biological and photobiological processes. However, recent evidence indicated that abiological photoassisted reactions may also be important in natural waters. Photocatalytic reactions in aqueous solutions that involve oxidation of solutes may be enhanced by the presence of molecular oxygen. Such photochemical reactions pay an important role in the decontamination of organic pollutants in natural waters. An important advantage of photocatalytic processes is that they may be performed at low or ambiet temperatures, and usually complete mineraliation of the organic compounds may be achieved. Basic concepts in photocatalysis and strategies for photo-chemical treatment of wastewater have been discussed in several reviews. (Halmann, M, 1996)

2.4 Comparison of Photo-Fenton Oxidation Method with Other Methods Used to Treat the Effluents from Textile Making or Dyeing Process

There are several methods for treating wastewater in general or specifically, wastewater from textile dyeing. Some methods such as coagulation, adsorption and nano-filtration remove dyes from the wastewater and produce a secondary waste stream that requires further treatment or disposal. Other methods, namely anaerobic treatment and advanced oxidation processes, degrade dyes that are present in the effluent so that no further treatment of disposal dyes is required.

2.4.1 Ozonation

Ozone decomposes in water to form hydroxyl radicals. Ozone and hydroxyl radicals are both strong oxidants and are both able to oxidize compound such as dyes. The decomposition of ozone is faster at high pH and therefore the major oxidant in an alkaline solution is the more reactive hydroxyl radical, whereas oxidation by ozone is also significant in an acidic solution. Ozonation is used to treat dyehouse wastewater, and the color removal was more efficient at high pH. In the studies of ozonation of dye solutions conducted by Gahr and Shua and Huang, dye degradation was found to be faster at lower initial concentrations, and that the pH decreased during the reaction time.

Furthermore, ozonation is effective for the degradation of many organic compounds. However, the installation of ozonation requires considerable capital costs and electric energy consumption. Also the excess of unused ozone must be removed, to prevent the escape of this toxic gas to the atmosphere.

Ozonation by itself is ineffective for the oxidation of halomethanes, such as trichloroethylene and carboxylic acids (e.g., formic acid), and also of the triazine herbicides, such as atrazine. Ozone in combination with H_2O_2 or UV irradiation provides an effective of $^{\cdot}OH$ radicals for complete degradation and mineralization of most pollutants.

In natural waters containing a high concentration of bromide ions, which may occur due to the intrusion of saltwater into fresh-water supplies, ozonation causes formation of hypobromous acid, HOBr. This highly reactive brominating agent converts organic precursors in the water into brominated disinfection by-products (DBPs). Such brominated organic compounds include for carcinogenic and lachrymatory bromoform, bromoacetone, and various four- and five-carbon bromohydrins such as $(CH_3)_2C(OH)$-$CH(Br)$-CH_3 and dibromides, which probably are more toxic than the organic precursors.

2.4.2 Biodegradation

Biodegradation was shown to be hindered in the presence of certain xenobiotic compounds. Thus, methyl vinyl ketone, pentachlorophenol, and 2,4-dichlorophenol inhibited the respiratory activity of activated sludge. These compounds could be detoxified by sunlight exposure in the presence of TiO_2 (1 g/L). Complete mineralization was necessary, since the intermediates formed by partial degradation were even more toxic than the starting compounds for the biodegradation of xenobiotic substances; an important phase is the acclimation of the microorganisms. The degradation of recalcitrant compounds may often be facilitated by the use of mixed populations of bacteria. Photocatalytic oxidation of bioresistant substances has been proposed as a useful pre- or post- treatment for activated sludge treatment.

2.4.3 Radiolysis

A comparison was made of the γ-radiolysis of several chlorocarbon compounds in aerated aqueous solutions with the direct photolysis of these compounds under vacuum-UV illumination (184.9 nm). In order to make such a comparison, a 'photochemical G-value' that is, absorbed energy / quantum ($eVhv^{-1}$) was calculated for each compound, in analogy to the radiolytic G-value. The compounds tested were CH_2Cl_2, ClHC=CHCl, $ClHC{=}CCl_2$ and $Cl_2C{=}CCl_2$. The yields (G-values) of Cl^- release were in the case of the vacuum–UV irradiation about one order of magnitude larger than those due to radiation-induced degradation. The enhanced decomposition at 184.9 nm was explained by the combined effects of the direct excitation of the halocarbons at these wavelengths, in addition to the photolysis of water.

A pulsed electric discharge was used to decompose a variety of organic compounds dissolved in water, including benzene, toluene, xylene, styrene, phenol, p-benzoquinone, hydroquinone, and catechol. The decomposition was enhanced in the presence of H_2O_2.

2.4.4 Ultrasonic

Ultrasonic irradiation of water by sound waves at frequencies higher than 15 kHz causes the formation and collapse of microbubbles as a result of the acoustic cavitation caused by the expansion and compression waves. In the collapsing cavitation bubbles, temperatures of several thousand degrees Kelvin and pressures of several hundred atmospheres effect the thermal dissociation of water,

$$H_2O \longrightarrow {}^{\cdot}H + {}^{\cdot}OH$$

The resulting hydroxyl radicals are thus available for oxidation reactions.

The sonolysis of parathion was performed in a water-jacketed stainless steel cell operated at 20 kHz and ~75 W/cm^2, thermostated at 30°C. The initial sonolytic reaction was breakage of the P=S and P-nitrophenylate bonds, with the intermediate formation of 4-nitrophenol, sulfate and diethyl phosphate. At a slower rate, 4-nitrophenol degraded to hydroquinone, quinone, and 4-nitrocatechol, and eventually to nitrite and nitrate, oxalate, acetate and formate while diethyl phosphate hydrolyzed to ethanol and orthophosphate.

Up to 99.9% destruction of chlorinated C1 and C2 halocarbons in aqueous solutions at ambient temperature and pressure was achieved by ultrasonic irradiation. Sonication was performed at 20 kHz and 0.1 kW/L. Essentially, complete degradation and mineralization within 1 hour was obtained with methylene chloride, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-tricholoethane, trichloroethylene and tetrachloroethylene.

2.4.5 Corona Discharge

Water decomposition similar to that by electron bombardment and γ-radiolysis, with formation of hydroxyl and hydrogen radicals, hydrated electrons, and hydrogen peroxide may be achieved by a pulsed streamer corona discharge. In an oxygenated aqueous solution of an anthraquinone dye, rapid discolorization was achieved by such a discharge.

This method was applied to the degradation of phenol in aqueous solution, using a rotating spark gap power supply (peak voltage 25 to 40 kV; pulse width 500 to 1000 ns; repetition frequency 60 Hz). The discharge occurred between the tip of a hollow hypodermic needle (through which nitrogen or oxygen was bubbled) and a stainless steel round wide counter electrode. The degradation of phenol by the corona discharge was considerably accelerated by the presence of oxygen. This was attributed to the formation of ozone in the gas phase, followed by the diffusion of the ozone into the aqueous phase and its decomposition, with formation of additional $^{\cdot}OH$ radicals.

Further addition of $FeSO_4$ (~1mM), and breakdown then was complete in less than 15 minutes. The effect of Fe^{2+} was explained by a Fenton reaction on the H_2O_2 produced in the discharge, releasing $^{\cdot}OH$ radicals, which were the active oxidant species.

2.4.6 Electrochemical Oxidation

For the electrochemical oxidation of organic compounds in water it is necessary to choose low-resistivity anode materials with a high overvoltage for oxygen gas evolution. Among the known materials with high oxygen evolution overvoltage, PbO_2 and graphite are unstable under prolonged electrolysis, while Pt/Ti is expensive.

A stable and highly efficient SnO_2 was developed, using a spray hydrolysis method (spraying $SnCl_4$ and $SbCl_3$ in aqueous ethanol on a Ti plate at 500°C). SnO_2 is an n-type semiconductor with a direct band gap of about 3.5 eV, and doping is necessary to increase its conductivity. The best Sb-doped SnO_2 had a resistivity of 10^{-3} ohm cm. with such an anode and a platinized titanium counterelectrode, in a simple single-compartment beaker cell, with galvanostatic control at 30 mA/cm^2, an initially 1000 ppm phenol solution (and 0.5 N Na_2SO_4 at pH 12), the phenol disappeared after 1 Ah, while the total organic carbon (TOC) was destroyed in about 8 Ah. With the SnO_2 electrode, no quinone intermediates were observed during the oxidation of phenol. Presumably, such intermediates, if formed, were very rapidly mineralized.

This electrode was also applied to the oxidation of a large variety of aliphatic and aromatic compounds, including biorefractory substances such as sulfonic acid derivatives of benzene, naphthalene and anthraquinone. The SnO_2 electrode enabled about five times faster rates of oxidation of organic compounds than Pt electrodes. A pilot-scale undivided flow-through plate-and-frame electrochemical reactor was designed, with a SnO_2 anode and platinized titanium cathode.

At an operating current density of 30 mA/cm^2, the oxidation of organic compounds was not mass transfer limited, enabling a space-time yield of 6.4 kg COD $h^{-1}m^{-3}$. The power consumption was 40 to 50 kWh for the removal of 1 kg COD. The process was proposed to be competitive with other advanced oxidation processes for the removal of biorefractory pollutants.

2.4.7 Oxidation in Supercritical Water

The rapid and complete oxidation of organic compounds in supercritical water, in the temperature range of 380 – 390°C and pressures of 230 to 235 bar, was achieved in the presence of a commercial catalyst (12.1 wt% CuO and 22.7 wt% ZnO supported on a porous cement, pretreated for 2 hours at 860°C in an O_2 stream).

The reaction was performed by preheating (at 430°C) and then mixing aqueous solutions of these compounds with aqueous solutions of H_2O_2 (which decomposed to O2 and water), and then passing the mixed solution through the reactor in a 1m long (3.2 mm OD) stainless steel tube.

A residence time of 25 seconds was sufficient to cause reductions of TOC for 2-propanol, tert-butanol, acetic acid, 1-methyl-2-pyrrolidone, benzoic acid and phenol of

98, 87, 98, 51, 73 and 100% respectively. Without the catalyst, the rates of degradation were very much smaller. The catalytic oxidation in supercritical water may be attractive as a high-temperature solar0thermal process using concentrated sunlight.

With even higher temperatures, in the range of 700 to 1000°C, steam reforming of organic wastes was accomplished in a gas-solid reaction over a rhodium catalyst supported on a porous ceramic absorber, causing conversion of organic compounds to CO, CO_2 and H_2, and of chlorocarbons also to HCl.

2.5 Mechanism of Fenton's Reagent

Fenton's reagent treatment has been identified to be one of the most effective technologies to remove organic pollutants from aqueous solutions. It is well known that organic compounds can easily be oxidized. It consists in a mixture of Hydrogen Peroxide and Iron salts. There are chemical mechanisms that propose hydroxyl radicals as the oxidant species that are generated in the following chemical equation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\cdot \qquad (1)$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+}:

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

Fe^{3+} catalytically decomposes H_2O_2 following a radical mechanism that involves hydroxyl and hydroperoxyl radicals including equations (1) and (2):

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe - OOH^{2+} + H^+ \qquad (3)$$

$$Fe - OOH^{2+} \rightarrow HO_{2.} + Fe^{2+} \qquad (4)$$

$$Fe^{2+} + HO_{2.} \rightarrow Fe^{3+} + HO_2^- \qquad (5)$$

$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + H^+ + O_2$ (6)

$OH^\cdot + H_2O_2 \rightarrow H_2O + HO_2^\cdot$ (7)

Thus, it can be seen that the H_2O_2 used will be decomposed into water and hydrogen dioxide by the Iron used and this will not pose a threat to the discharged water after it has been treated with Fenton's Reagent.

2.6 Effects of Iron Type and Concentration on Fenton's Reagent

For the types of Iron used however, for most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction because the catalytic cycle begins quickly if H_2O_2 and organic material are in abundance. However, if low doses of Fenton's Reagent are being used, some research suggests Ferrous Iron may be preferred. Neither does it matter whether a chloride or sulfate salt of the Iron is used, although with chloride, chlorine may be generated at high rates of application.

It is also possible to recycle the Iron following the reaction. This can be done by raising the pH, separating the Iron floc and re-acidifying the Iron sludge. There have been some recent developments in supported catalysts that facilitate Iron recovery and reuse.

2.7 Effect of UV Light Irradiation on Fenton's Reagent

The UV Light in this experiment can play two different roles that would lead to an improvement of the reaction yields. First, it drives Photo-Fenton reaction, producing additional hydroxyl radicals and the recovery of Fe(II) needed in Fenton reaction. The Photo-Fenton reaction may involve direct photolysis of Ferric Iron or photolysis of Fe(III) peroxy complexes. Secondly, it can drive ligand to metal charge transfer in the potentially photoliable complexes formed by Fe(III) and organic compounds, a process that has been well proven for the complexes formed between Fe(III) and the carboxylic acid moiety. Large quantities of carboxylic acid are expected to be formed as degradation intermediates of the original organic substrate.

2.8 Effect of Temperature on Fenton's Reagent

The rate of reaction with Fenton's reagent usually increases with increasing temperature, with the effect more pronounced at temperatures below 20°C. However, as temperatures increase above 40 to 50°C, the efficiency of H_2O_2 utilization declines. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between 20 to 40° C.

However, it is also important to note that applications of Fenton's reagent for pre-treating high strength wastes may require controlled or sequential addition of H_2O_2 to moderate the rise in temperature which occurs as the reaction proceeds. Moderating the temperature is important not only for economic reasons, but for safety reasons as well.

2.9 Effect of pH on Fenton's Reagent

The optimal pH for a Photo-Fenton process occurs between pH 3 and pH 6. If the pH is too high, the iron used will precipitate as $Fe(OH)_3$ and catalytically decomposes the H_2O_2 to oxygen; potentially creating a hazardous situation.

In highly concentrated waste streams, (more than 10 g/L COD), it may be necessary to perform the oxidation in steps, readjusting the pH upwards to pH 4 or pH 5 after each step so as to prevent low pH from inhibiting the reaction.

2.10 Effect of Reaction Time on Fenton's Reagent

The time needed to complete a Fenton reaction will depend on many variables, most notably catalyst dose and wastewater strength. For complex or more concentrated wastes, the reaction may take several hours. In such cases, performing the reaction in steps (adding both iron and H_2O_2) may be more effective and safer than increasing the initial charges.

Determining the completion of the reaction may prove troublesome. The presence of residual H_2O_2 will interfere with many wastewater analyses. Residual H_2O_2 may be removed by raising the pH to pH7-10, or by neutralizing with bisulfite solution.

2.11 Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand (COD) test is used to measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in an acid solution.

Although it would be expected that the value of the ultimate carbonaceous Biological Oxygen Demand (BOD) would be as high as the COD, this is seldom the case. Some of the reasons for the observed differences are as follows:

1. Many organic substances which are difficult to oxidize biologically, such as lignin, can be oxidized chemically.
2. Inorganic substances that are oxidized by the dichromate increase the apparent organic content of the sample.
3. Certain organic substances may be toxic to the microorganisms used in the BOD test.
4. High COD values may occur because of the presence of inorganic substances with which the dichromate can react.

From an operational standpoint, one of the main advantages of the COD test is that it can be completed in about 2.5 hours, compared to 5 or more days for a BOD test. To reduce the time further, a rapid COD test that takes only about 15 minutes has been developed.

As new methods of biological treatment have been developed, especially with respect to biological nutrient removal, it has become more important to fractionate the COD. The principal fractions are particulate and soluble COD. In biological treatment studies, the particulate and soluble fractions are fractionated further to assess wastewater treatability. Fractions have been used include readily biodegradable soluble COD, slowly biodegradable colloidal and particulate (enmeshed) COD, non-biodegradable soluble COD and non-biodegradable colloidal and particulate COD.

The readily biodegradable soluble COD is often fractionated further into complex COD that can be fermented to volatile fatty acids (VFAs) and short chain VFAs. Unfortunately, as noted previously, there is little standardization on the definition of soluble versus particulate COD. Where filtration is the technique used to fractionate the sample, the relative distribution between soluble and particulate COD will vary greatly depending on the pore size of the filter. An alternative method used to determine the soluble COD involves precipitation of the suspended solids and a portion of the colloidal material. The COD of the clarified liquid corresponds to the soluble COD.

CHAPTER 3

METHODOLOGY / PROJECT WORK

3.1 Procedure Identification

The wastewater sample can be obtained from a batik making factory in Chemor, which is the Kilang Batik Kam Ismail. Several experiments and the necessary calculation must be performed and conducted to determine the optimum reaction time and dosing ratio. Identification of the components in the wastewater before and after treatment with Fenton reagent can also be done. The treatment efficiency will be based on the reduction of COD and also color.

3.2 Parameters

1. Chemical Oxygen Demand (COD)

3.3 Chemicals and Materials Required

1. Aluminium foils
2. Hydrogen Peroxide (H_2O_2)
3. Iron Sulphate ($FeSO_4$)
4. High range COD vials
5. Sample bottles
6. Gloves
7. UV light

3.4 Tools and Equipment Required

1. COD Reactor
2. DR4000
3. Water bath shaker
4. pH meter
5. Micropipettor
6. Erlenmeyer flask (250ml) (6 units)
7. Analytical balance
8. Volumetric flask (1 Liter) (2 units)

3.5 Preparation of Sampling Containers

The containers used to collect the sample of the wastewater effluent from the batik textile factory must first be rinsed with nitric acid. This is done to ensure that the containers are free from any other microorganisms that may be present in the containers as a result of various samples collected from previous usages. The concentration of nitric acid used is 0.1 M.

The calculation for the preparation of 0.1 M Nitric Acid is as below;

Moles of existing Nitric acid, HNO_3 , M_1

$$= \frac{\text{Specific gravity of } HNO_3}{\text{Molecular weight of } HNO_3}$$

$$= \frac{1.41g}{mL} x \frac{1mol}{63.01g} x \frac{1000mL}{1L}$$

$$= 22.37 \text{ mol/L}$$

Calculating the volume needed to prepare a 1 liter solution of 0.1 M Nitric acid, HNO_3

$M_1V_1 = M_2V_2$

$22.37 \text{ mol/L} (V1) = (0.1 \text{ mol/L})(1L)$

$V1 = 4.47 \times 10\text{-}3 \text{ L}$

$= 4.47 \text{ mL}$

The calculations above are repeated for each of the sampling containers.

The prepared Nitric acid are left in the sampling containers for 24 hours and after that, the containers are rinsed and dried in the laboratory oven with a minimal temperature setting.

3.6 Sampling

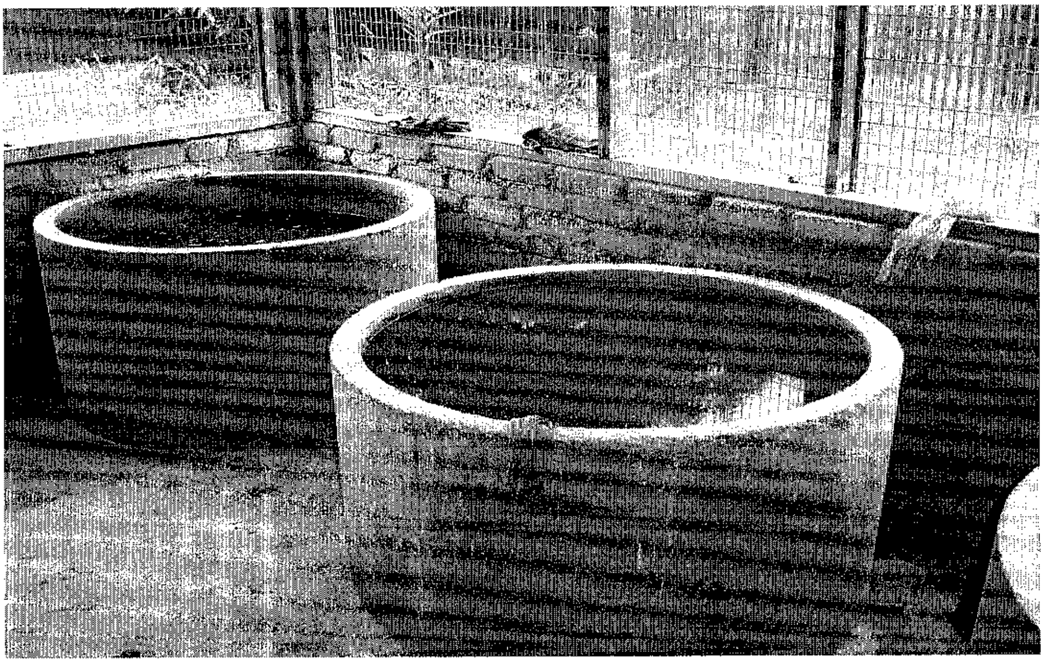

Figure 1: Effluent Ponds in the Batik Factory

The samples of effluent from the batik textile factory were taken using the prepared sampling containers inserted in a cooler to preserve its temperature. The batik factory in question is the Kilang Batik Kam Ismail located in Chemor, Perak. The total volume of samples taken is approximately 12 liters. At the textile factory, four ponds of effluent were utilized as a result of production on that day.

The first pond is where the textiles are soaked in boiling water and soda ash. The second pond is where the textiles are subjected to the first wash, to remove the excessive color, soda ash from the first pond and also the wax used in the dyeing of the textiles. The third pond is where the textiles are subjected to the second wash; whereby to remove the excessive color that was not completely removed during the first wash. The fourth and final pond is the final stage of the washing where apart form the removal of color from the textiles that was not completely removed during the first and second washes, the textiles are also soaked in fabric softener solution to soften the textile. The flow diagram of the ponds and the washing process is presented below:

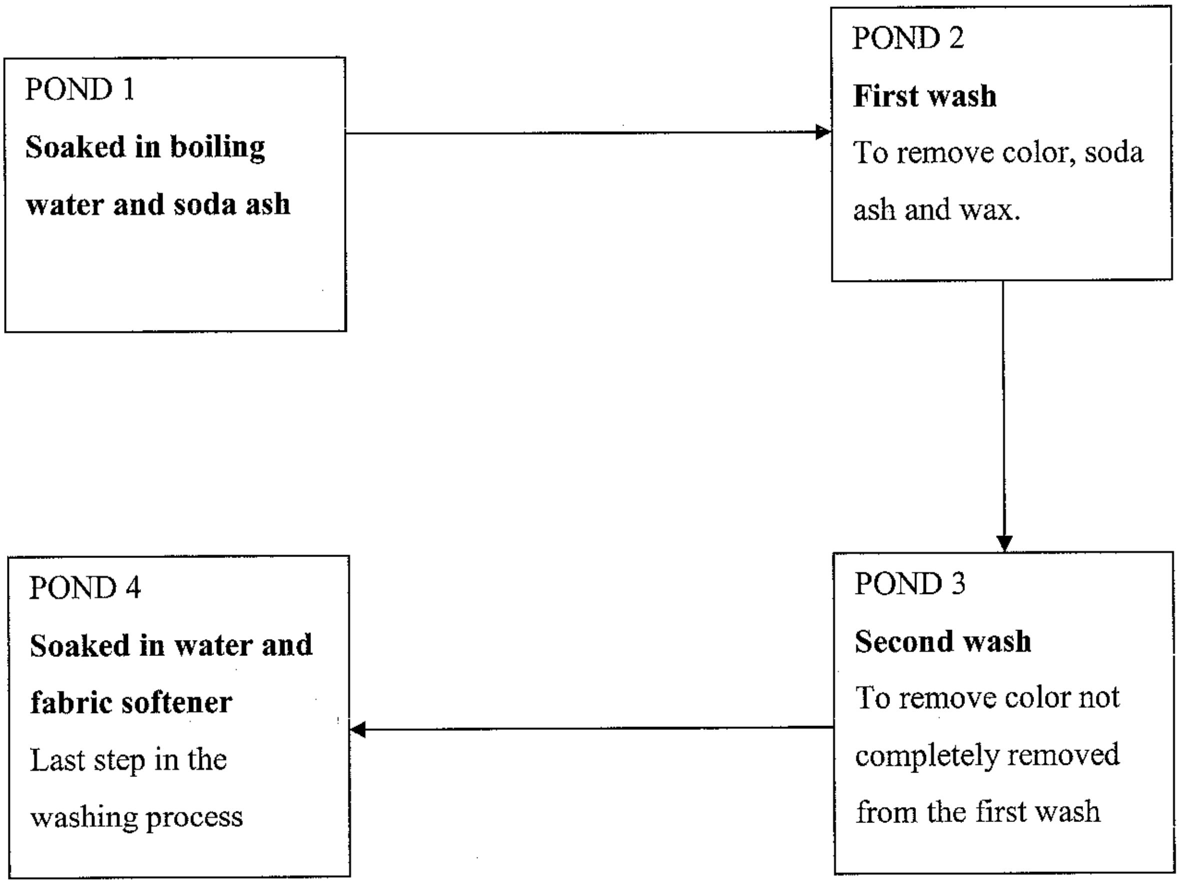

Figure 2: Washing Process for the Textiles

Equal amounts of samples are taken from each pond as the composition from all the ponds represent one stream of wastewater effluent produced from batik making in the textile factory. The samples are then refrigerated as a perseverance measure and then mixed together with the equal amount of wastewater from each pond collected.

The procedures for sampling method are as follows:

1. Sampling containers are rinsed in 0.1 M Nitric acid for 24 hours and dried afterwards. This is to ensure that the containers are free of contaminants that may interfere in the samples analysis.

2. Samples are taken from a batik making factory in Chemor. The samples are taken from four different ponds which represents the four stages of the rinsing of the textiles.

3. The samples are taken by dipping the sampling containers inside the effluent ponds.

4. To ensure that the samples are well preserved before they are being refrigerated, the samples are contained in an insulated cooler container filled with ice to maintain the samples at a low temperature.

5. The samples taken from four different ponds are then mixed with equal volumes from each pond.

6. Before conducting the experiment, the samples are refrigerated with a temperature of 4 °C to maintain their perseverance.

3.7 Preparation of Sample for Experiments (Measuring the Initial COD Level)

1. The initial COD level of the sample must be measured to determine the correct amount of Fenton's reagent needed.
2. To measure the COD value, high range COD vials are used, which measures COD values ranging from 0 to 1500 mg/L. These vials contain reagents that react with the samples.

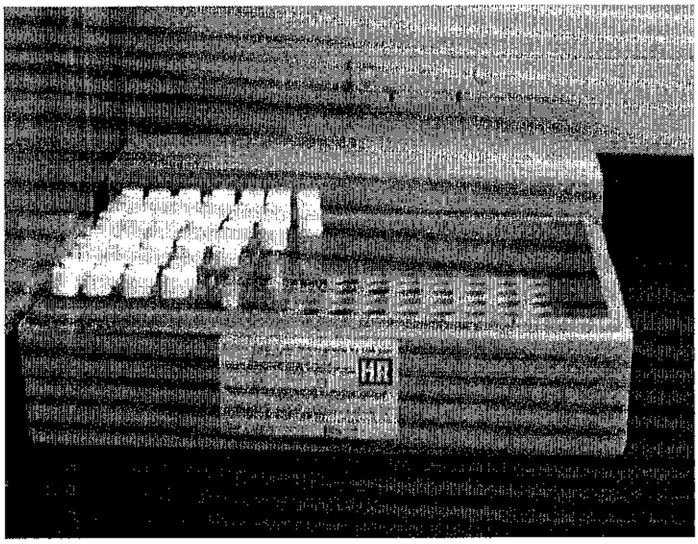

Figure 3: High Range COD Vials

3. A pipette is used to insert the water sample into the COD vials. Only 2 mL of water sample is inserted into each COD vial.

4. The COD reactor is heated to a temperature of 150 °C. Three COD vials containing the samples are used to obtain a more accurate reading based on the average of these three vials. One additional vial containing distilled water is also prepared as the blank.

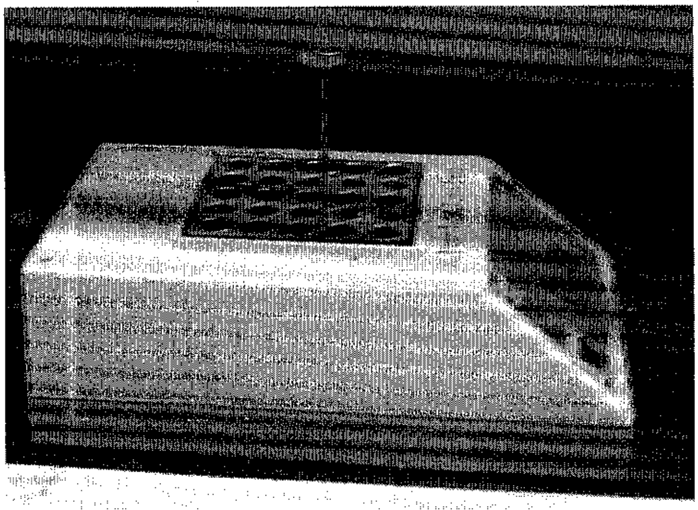

Figure 4: COD Reactor

5. The COD vials are inserted inside the COD reactor and timer is set for 120 minutes.

6. After 120 minutes, the COD vials are cooled off and the COD readings will be measure using the DR/4000 apparatus.

7. The DR/4000 apparatus is a measuring device manufactured by HACH that can measure various parameters of water analysis. Thus, the right program for measuring COD has to be chosen. The stored program number for high range and high range plus COD is selected by pressing 2720 with the numeric keys.

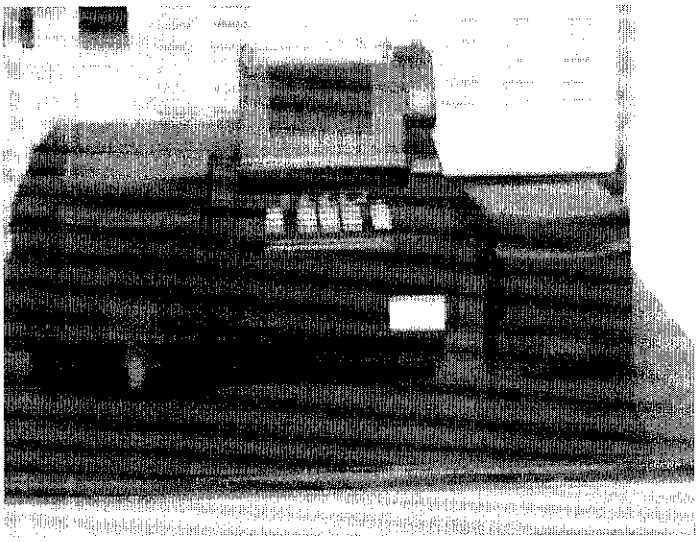

Figure 5: DR/4000 to Measure COD

8. The display will show: **HACH PROGRAM: 2720 COD, HR, HR PLUS**. The wavelength (λ), 620 nm, is automatically selected.

9. The Test 'N Tube Adapter is inserted into the sample cell module by sliding it under the thumb screw and into the alignment groves. It is fasten with the thumb screw.

10. The outside of the blank is cleaned and wiped with a damp towel, followed by a dry one, to remove fingerprints or other marks.

11. The blank is placed into the adapter with the HACH logo facing the front of the instrument. The light shield is then closed.

12. The ZERO key is pressed and the display will show: **0 mg/L COD**.

13. After the zero value is set in the apparatus, the samples are then measured. The outside of the sample vial is cleaned with a towel, similar to the procedure using the blank.

14. The sample vial is placed into the adapter with the HACH logo facing the front of the instrument. The light shield is closed. Results in mg/L COD (or chosen units) will be displayed.

3.8 Preparation of Fenton's Reagent

3.8.1 Determination of the Amount of Fe Needed

The initial COD value of the effluents is 361 mg/L.

To determine the amount of Fe needed in the Fenton's Reagent, the initial COD value must be divided with a value above the minimal threshold. A constant ratio of Fe: substrate (COD) must be taken into consideration whereby typically, 1 part Fe per 10-50 parts substrate, which produces the desired end products. For this experiment the ratio of Fe: substrate is determined as 1:20.

Thus, the amount of Fe needed:
= (Initial COD value) / 20
= 361 mg/L / 20
= **18.05 mg/L**

The amount of sample for each experiment is determined to be **200 mL**.

To obtain the amount of $FeSO_4.7H_2O$ needed in the experiment to achieve the concentration of 18.05 mg/L,
18.05 mg/L = (Amount needed) / 0.2 L
Amount needed = 3.61 mg

However, the chemical $FeSO_4.7H_2O$ does not constitute a hundred percent of Fe, thus, the real amount of $FeSO_4.7H_2O$ needed to achieve a concentration of 18.05 mg/L is:
= Amount of Fe calculated earlier / (MW of Fe / MW of $FeSO_4.7H_2O$)

= 3.61 mg / (55.85 / 277.92)
= 18.05 mg $\simeq$ **18 mg**

To increase the efficiency of the dosing method of the Fe, the solid Fe is diluted and prepared as a standard solution. A standard solution is prepared by diluting 1 g of $FeSO_4.7H_2O$ in 1000 mL of distilled water. Thus, by using a simple principle of ratio, to achieve a dosage of 18 mg if it is dosed in solid form, 18 mL of the standard solution is dosed for every experiment.

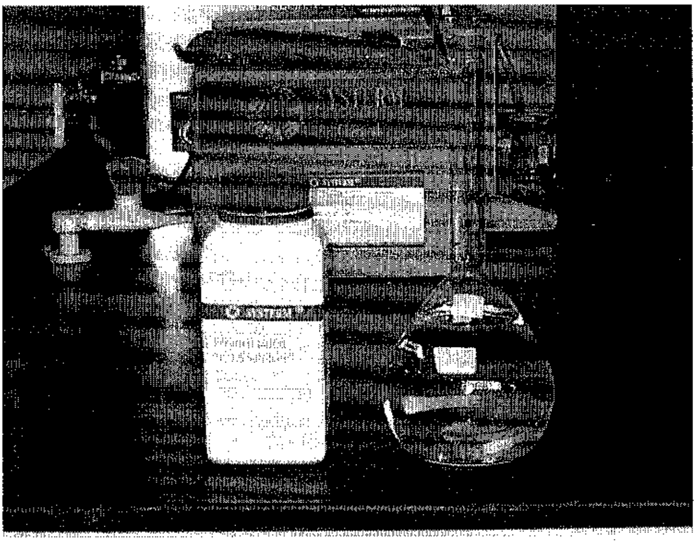

Figure 6: $FeSO_4.7H_2O$ in Solid Form and the Prepared Standard Solution

3.8.2 Determination of the Amount of H_2O_2 Needed

The H_2O_2 solution used is **30% in strength** and its density is **1110 mg/mL.**

Thus, considering the strength of 30%, the density is considered as:
= 30% x 1110 mg/mL
= 333 mg/mL

Fenton's Reagent involves a ratio of $Fe:H_2O_2$ (wt/wt). Thus, for a sample calculation of 1 part Fe with 10 parts H_2O_2 (1 Fe : 10 H_2O_2);

= 3.61 mg Fe : 36.1 mg H_2O_2

To obtain 36.1 mg of H_2O_2, the following calculation involving the density of H_2O_2 is performed,

36.1 mg / (Amount of H_2O_2 required in mL) = 333 mg/mL
Amount of H_2O_2 required = 0.108 mL

This calculation is repeated and simplified for various ratios of Fenton's Reagent that will be used in the experiment as displayed in the table below,

Table 2: Amount of Fe and H_2O_2 Needed According to the Determined Ratio

Ratio of Fe: H_2O_2 (wt/wt)	**Amount of Fe in mg**	**Amount of H_2O_2 in mL**
1:10	18.05	0.108
1:20	18.05	0.216
1:30	18.05	0.324
1:40	18.05	0.432
1:50	18.05	0.540
1:60	18.05	0.648
1:70	18.05	0.756
1:80	18.05	0.864
1:90	18.05	0.972
1:100	18.05	1.08

The concentration of Fe and H_2O_2 as it is dosed into 200 mL of the wastewater sample for each experiment according to the determined ratio is presented in the table below;

Table 3: Concentration of Fe and H_2O_2 in 200 mL of Wastewater Sample According to the Determined Ratio

Ratio of Fe: H_2O_2	Concentration of Fe in ppm	Concentration of H_2O_2 in ppm
1:10	90.25	180.5
1:20	90.25	361
1:30	90.25	541.5
1:40	90.25	722
1:50	90.25	902.5
1:60	90.25	1083
1:70	90.25	1263.5
1:80	90.25	1444
1:90	90.25	1624.5
1:100	90.25	1805

3.9 Photo-Fenton Experiment

After the ratio of the Fenton's Reagent and its amount is determined, the experiment can be carried out. Presented below are the experimental procedures:

1. The pH value of the wastewater sample is measured using a pH probe. The pH probe is first calibrated using a solution of having the standard pH value of 4 and 7.

2. The pH value obtained is 10.98 which is the typical value for textile effluent. However, the pH value must be reduced as if the pH is too high, the iron of the Fenton's reagent that is dosed will precipitate as $Fe(OH)_3$ and catalytically decomposes the H_2O_2 to oxygen; potentially creating a hazardous situation.

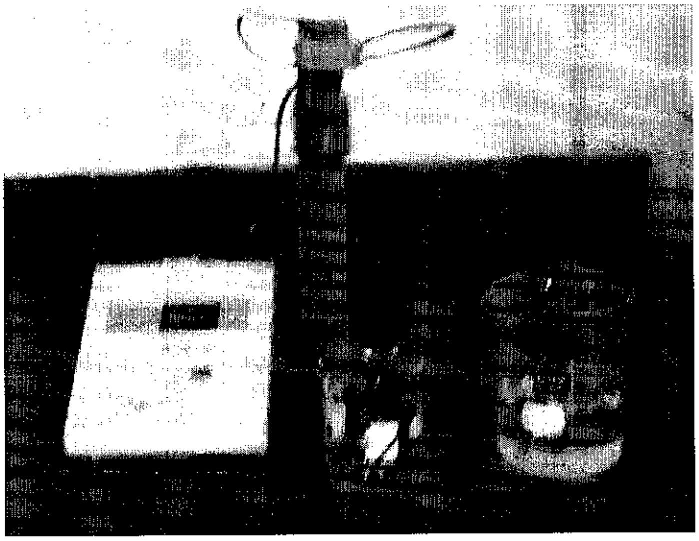

Figure 7: pH Probe and pH Meter

3. 1.0 M of H2SO4 is added to the sample until the pH value decrease to 4. The typical range of pH value for samples that will be dosed with the Fenton's Reagent is pH 3 to 5.

4. 200 mL of the wastewater sample is then poured into a 250-mL conical flask.

5. 18 mL of the diluted $FeSO_4.7H_2O$ solution is poured into the wastewater sample in the conical flask.

6. This conical flask is then put into the water bath shaker. The water temperature inside the water bath is set at 30°C. The water level is also checked to ensure that it is above the level of the wastewater inside the conical flask.

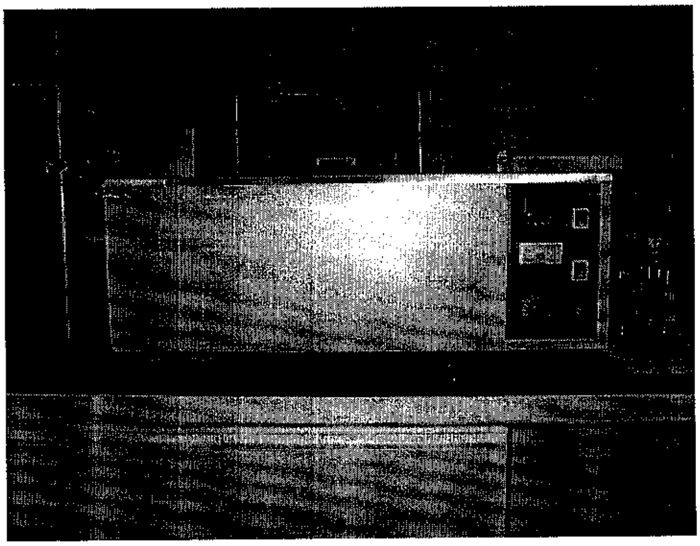

Figure 8: Water Bath Shaker

7. The power source for the UV light is located and a UV light with a wavelength of 365 nm is put on top of the conical flask with the light directed onto the sample inside the conical flask. This experiment is preferably carried out without the interference of other light sources.

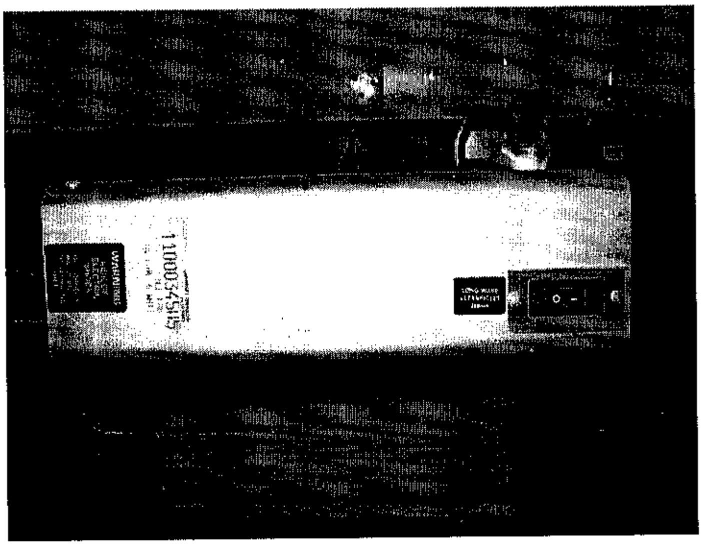

Figure 9: 365 nm Wavelength UV Light

8. 0.108 mL of the H_2O_2 solution is measured using the micropipettor. The micropipettor used has a range of 100 to 1000 μL.

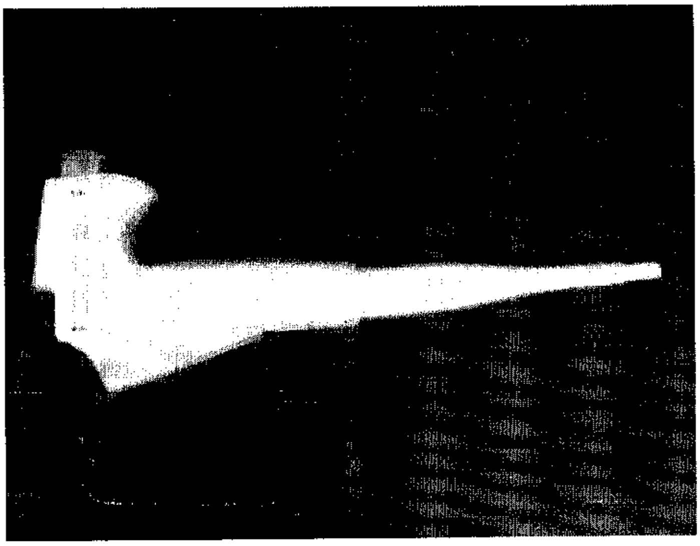

Figure 10: Micropipettor with a Range of 100 – 1000 μL

9. The water bath shaker is started and the UV light is switched on. The measured H_2O_2 solution is then dosed slowly into the wastewater sample inside the conical flask.

10. The wastewater sample is taken and inserted into COD vials (2mL for each vial) at these intervals of time: 5, 10, 15, 20, 30, 45, 60, 75, 90, 105 and 120 minutes.

11. After 120 minutes, the water bath shaker is stopped and the UV light is switched off. The COD vials containing the samples are put inside a COD reactor and the process of measuring COD is carried out similar to the procedures for measuring the initial COD of the wastewater sample.

12. This experiment is then repeated for the other ratios of the Fenton's Reagent.

13. The COD values obtained are then noted in a table and a graph of COD values against time is plotted for each experiment.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results

The following results were obtained from the experiments conducted;

4.1.1 Measurement of Initial COD and pH Value

Before conducting the experiments, the initial COD value of the wastewater sample is measured. The results are presented in the table below;

Table 4: Initial COD Value of the Wastewater Sample

Sample Readings	**COD Value (mg/L)**
First Reading	364
Second Reading	361
Third Reading	359
Average Reading	**361**

The initial COD value of the wastewater sample is measured using three High–Range COD vials, obtaining three readings to increase its accuracy. Form the table above, it can be seen that the average COD value calculated from the three readings is 361 mg/L.

The pH value of the wastewater sample must also be measured so that a reduction of pH can be done. This is important because if the pH is too high, the iron precipitates as $Fe(OH)^3$ and catalytically decomposes the H_2O_2 to oxygen; potentially creating a hazardous situation.

The initial pH value measured is **10.98**, and the reduction of pH is carried out until it reaches a pH value of 4.

4.1.2 Readings from the Photo-Fenton Experiment

The Photo-Fenton experiment is conducted using seven different ratios of the Fenton's Reagent, namely form 1:10 until 1:70. The values obtained from each experiment are presented in the tables below;

Table 5: Results for the Photo-Fenton Experiments (Fenton's Reagent Ratio 1:10 – 1:40)

Time (min)	COD Readings (mg/L)			
	Ratio 1 : 10 ($Fe:H_2O_2$)	Ratio 1 : 20 ($Fe:H_2O_2$)	Ratio 1 : 30 ($Fe:H_2O_2$)	Ratio 1 : 40 ($Fe:H_2O_2$)
0	361	361	361	361
5	335	316	315	310
10	279	263	264	270
15	254	231	228	235
20	233	213	209	211
30	208	196	182	188
45	174	152	143	144
60	142	122	114	132
75	133	118	114	125
90	128	118	115	128
105	130	117	114	123
120	128	117	114	125

Table 6: Results for the Photo-Fenton Experiments (Fenton's Reagent Ratio 1:50 – 1:70)

Time (min)	COD Readings (mg/L)		
	Ratio 1 : 50 ($Fe:H_2O_2$)	Ratio 1 : 60 ($Fe:H_2O_2$)	Ratio 1 : 70 ($Fe:H_2O_2$)
0	361	361	361
5	321	316	326
10	279	261	272
15	239	229	233
20	206	207	212
30	172	179	174
45	149	151	146
60	140	144	135
75	128	130	132
90	121	117	124
105	122	119	120
120	119	116	118

The graph tabulated from the data presented in the tables is plotted for each Fenton's Reagent ratio. The graph is presented below;

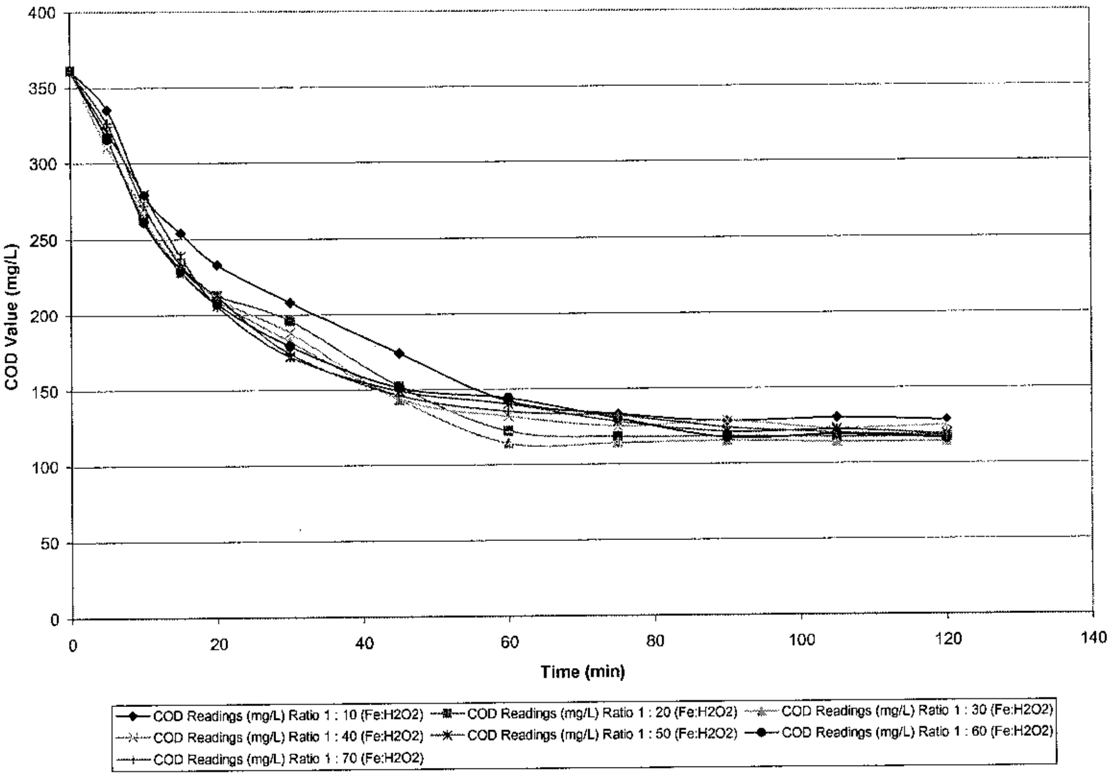

Figure 11: Graph of COD Value (mg/L) against Time (min) For All the Fenton's Reagent Ratios Used

From the final COD value obtained, a reduction percentage of COD value can be calculated for all the ratios used. The reduction percentage is presented in the table below;

Table 7: Reduction Percentage of COD Value

Fenton's Reagent Ratio (wt/wt)	Initial COD Value (mg/L)	End COD Value (mg/L)	Reduction Percentage of COD (%)
1 : 10	361	128	64.54 %
1 : 20	361	117	67.59 %
1 : 30	361	114	68.42 %
1 : 40	361	125	65.37 %
1 : 50	361	119	67.04 %
1 : 60	361	116	67.87 %
1 : 70	361	118	67.31 %

The graph tabulated from the data tabulated above is presented below;

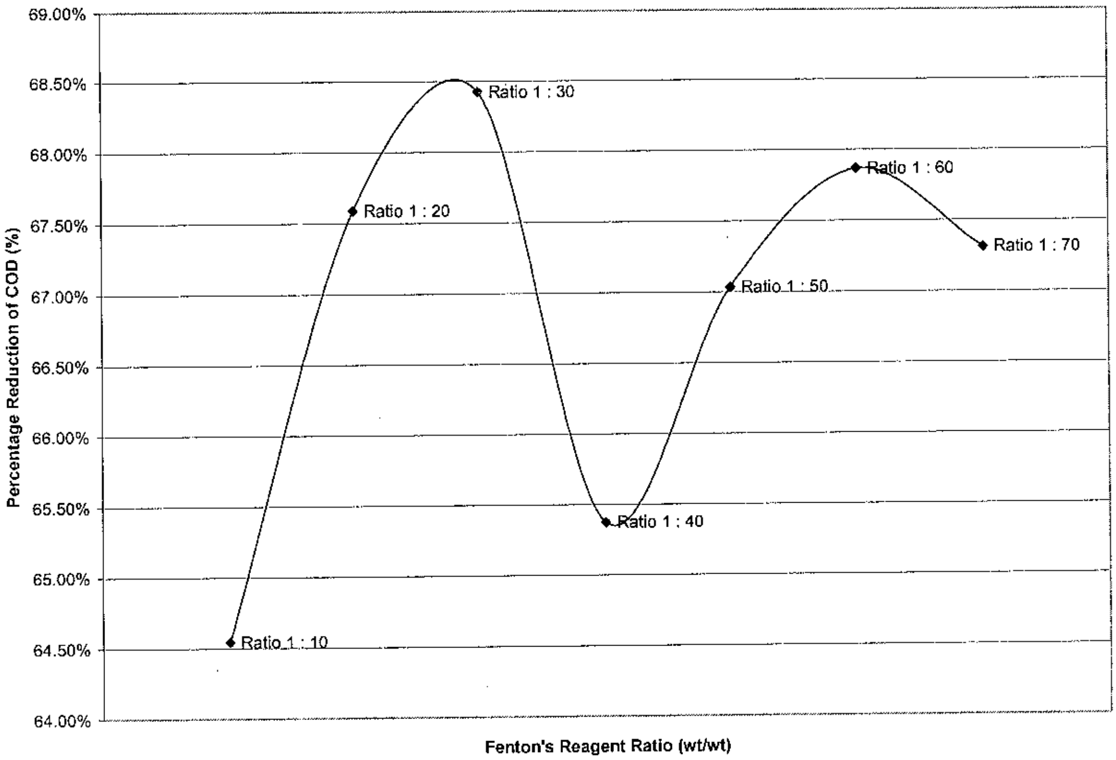

Figure 12: Graph of Reduction Percentage of COD Value against Fenton's reagent Ratios

4.2 Discussion

4.2.1 Discussion from the Graphs and Trending

From the data obtained and graphs plotted above, the Fenton's Reagent ratio used that produces the lowest COD value after 120 minutes of experimentation is the ratio of 1:30, whereby at 60 minutes of the experiment, the COD value decreases to 114 mg/L and stabilizes throughout the experiment until the 120 minutes are up. Thus, it can also be concluded that the optimum reaction time achieved is 60 minutes.

It is quite unusual to be noted that the increasing amount of H_2O_2 dosed for the ratios above 1:30 do not produce a lower amount of COD value. This can be amounted to the fact that the amount of Fe used, which is constant for all the experiments, is not enough to catalyze a larger dosage of H_2O_2 and thus, an optimum dosage ratio of 1:30 is achieved. Furthermore, the differences on the amount of H_2O_2 dosed is very small and although the Fenton's reagent dosage ratio of 1:30 yielded the least value of COD, the COD value for all the other experiments at the end of 120 minutes did not produce a large difference from 114 mg/L, which is the least value of COD yielded. This can be seen from the reduction percentage of COD values calculated, whereby the differences between the percentages calculated is very little. Theoretically, typical ranges of Fenton's reagent ratios are 1 part Fe per 5 to 25 parts H_2O_2, (Lenntech, 2003 and H2O2.com) thus the optimum value obtained in this experiment is approaching the theoretical values set.

However, it can also be noted that the COD values for the experiments utilizing the Fenton's Reagent ratios above 1:30 until 1:70 are still decreasing at the 120th minute of the experiment. Thus, if the experiments are to be conducted in a longer time scale, the COD values may decrease further and stabilize after a long period of time.

From all the experiments, it can also be noted that the decrement of the COD value is most prominent at the beginning of the experiment, from 0 to 5 and 10 minutes. This can be seen from all the graphs and trends that at the beginning, the slope is higher, and the decrement of the graphs gradually subsides as it reaches the end of the experiment. This is in agreement with the fact that Fenton reaction always dominates the first minutes of the process and a larger concentration of reactants will directly increase the reaction rate.

4.2.2 Discussion on the Value of COD Obtained

According to the Malaysian Environmental Standards, the COD value for wastewater discharge from industries is supposed to be below 100 mg/L. As it is displayed in the results, none of the Fenton's Reagent ratios used yielded a COD value of below 100 mg/L. This could be attributed to a number of factors, including the preparation of the sample itself before the experiment is being conducted. The results obtained could further be improved if the sample is thoroughly filtered to prevent any suspended solids interfering with the measurement of the COD value. A longer duration of time for the experiments could also be considered as for some of the Fenton's Reagent ratios used, the COD value is still decreasing even after the 120 minutes of the experiment are up, and are yet to stabilize.

4.2.3 Effect of Iron (Fe) Concentration and Iron Type

Generally, according to Perez, M; increasing initial quantities of iron in the solution produces increasing rates of degradation.

However, for the experiments conducted here, the amount of Iron dosed is constant for all the experiments; thus, a significant comparison cannot be made. However, it is important to note that the use of large quantities of Fe in solution has a negative effect from the applied point of view, since it implies the need of an additional treatment step for Fe removal. Theoretically, increasing initial quantities of iron in solution produce increasing rates

4.2.4 Effect of Hydrogen Peroxide (H_2O_2) Concentration

At the beginning of the experiment, from ratios 1:10 to 1:30, as the H_2O_2 concentration is increased, the degree of COD removal also increases. However, for ratios 1:40 until 1:70, the COD removal after 120 minutes varies from one another.

For this analysis, a comparison is made between this experimental result and three other literary sources. The first two sources, which is from the Reference Library of Peroxide Applications in h202.com, and from Lenntech.com, stated that the typical ranges of the Fenton's Reagent are 1 part Fe per 5-25 parts H_2O_2 (wt/wt). The third source, which is a research done by M.Perez et al, states that it is clear that increasing amounts of H_2O_2 lead to larger organic content removal, with no detrimental effects detected for the highest H_2O_2. However, he also states that the small difference in the organic content reduction for high concentration of H_2O_2 indicates that improvements of reaction rate may not compensate the large amounts of oxidants consumed.

From these literary sources, it can be seen that the experimental results generated are more similar to the first two sources, as the optimum ratio of Fenton's Reagent obtained from this experiment is 1 part Fe per 30 parts H_2O_2. This is not very far from the range specified which is 1part Fe per 5 to 25 parts H_2O_2. However, the results obtained are completely different if referred to the third source, saying that as the amount of H_2O_2 is increased, then further reduction of COD can be seen. This could also be attributed to a number of factors, including the condition of the water sampled and also the type of UV light used, which will be discussed in the next section.

4.2.5 Effect of the Usage of UV Light Irradiation

The intensity and the wavelengths emitted by the light source are key conditions when trying to describe the participation of the light-driven reaction. However, for this experiment, only one source of light and wavelength is used, which is the UV light with a wavelength of 365 nm, thus, a comparison between different sources and wavelengths of light cannot be made.

According to M.Perez et al, however, an intense irradiation favors the fast exhaustion of H_2O_2 through non-efficient reactions while mild irradiation consumes less oxidant in parallel and undesired photochemical reactions.

This could very well prove that a UV light source with a higher wavelength could produce a more effective result in terms of the decrement of the COD value. Types of light sources such as desk lamps and white fluorescent lights could also be used as they have a higher wavelength range if compared to a normal UV light.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

From the experiment conducted, it can be seen that the specific objectives stated which are to find the most optimum ration and most optimum reaction time has been achieved. The most optimum ratio of Fenton's Reagent used is 1 part Fe with 30 parts of H_2O_2, which yielded the lowest COD reduction and the most optimum reaction time achieved is 60 minutes for this particular ratio.

The experiment was carried out successfully and various parameters and their effect on the reaction such as H_2O_2 concentration, Fe concentration, temperature, the application of UV light, pH and reaction time are analyzed to determine the influence of all these parameters on the experiment conducted.

5.2 Recommendations

A few recommendations on this experiment can be made to further enhance and improve the desired results;

1. Different amounts of Fe could also be applied so that comparison between the effects on the amount or concentration of Fe used in a Photo-Fenton reaction can be analyzed.

2. The experiment time or duration could be increased to achieve a possible COD value that is much lower than the one achieved in this experiment.

3. Different wavelengths of UV light could also be applied so that the comparison between the effects of utilizing different wavelengths of UV light can be analyzed.

4. Variation of temperature within the permissible value could also be applied so that analysis of results conducted in different temperatures could be analyzed.

5. More variations of Fe to H_2O_2 ratio could be applied particularly in large differences in terms of amount and concentrations used so that a significant comparison can be made between the different ratios of the Fenton's Reagent.

6. Wastewater sample from different sources could be analyzed.

CHAPTER 6

REFERENCES

1. Aplin, R; Waite, T.D, *Comparison of Three Advanced Oxidation Processes for Degradation of Textile Dyes*; School of Civil and Environmental Engineering, The University of New South Wales, 2052, Australia; 2000.

2. Chamarro, E; Marco, A; and Esplugas, S; *Use of Fenton Reagent to Improve Organic Chemical Biodegradability*; Department d'Enginyeria Quimica I Metal.lurgia, Universitat de Barcelona C/Marti I Franques 1, Spain, 2000.

3. Final Year Research Project Guidelines for Supervisors and Students Semester July 2004, Chemical Engineering Department, Universiti Teknologi PETRONAS, 2004.

4. Gray, N.F; Water *Technology: An Introduction for Environmental Scientists and Engineers*; Viva Books Private Limited, New Delhi, 2000.

5. Hach Company, *DR/4000 Procedure: Oxygen Demand, Chemical*; United States of America, 1999.

6. Halmann, M.M, *Photo-degradation of Water Pollutants*, CRC Press, United States of America, 1996.

7. Lenntech, www.lenntech.com

8. Mallinckrodt Baker Chemicals, *Material Safety Data Sheet for Ferrous Sulfate ($FeSO_4.7H_2O$)*, United States of America, 2004.

9. Metcalf and Eddy; *Wastewater Engineering: Treatment and Reuse*, McGraw Hill, New York, 2003.

10. Novocostra Laboratories Limited, *Material Safety Data Sheet for Hydrogen Peroxide (H_2O_2)*, United Kingdom, 2003.

11. Perez, M; Torrades, F; Domenech, X and Peral, J; *Fenton and photo-Fenton Oxidation of Textile Effluents*, Universitat Politecnica de Catalunya and Universitat Autonoma de Barcelona, Spain; 2001.

12. World Bank, *Pollution Prevention and Abatement: Textiles Industry*, Draft Technical Background Document, Environment Department, Washington, July 1998.

CHAPTER 7

APPENDICES

Novocastra Laboratories Ltd

MATERIAL SAFETY DATA SHEET

ASTRA

IDENTIFICATION OF THE SUBSTANCE / PREPARATION AND OF THE COMPANY / UNDERTAKING

tification of the product

alogue code: Various

duct name: Paraffin and Frozen Kits for Immunohistochemistry

ponent name: Hydrogen peroxide

paration: Up to 30% by volume.

ufacturer / supplier identification

pany: **Novocastra Laboratories Ltd.**
Balliol Business Park West
Benton Lane
Newcastle upon Tyne
NE12 8EW, UK.

Telephone: 0191 215 0567
Fax: 0191 215 1152

COMPOSITION / INFORMATION ON INGREDIENTS

mical characterisation

id, colourless
w or equal to 30% by volume.

mical name: Hydrogen peroxide

number: 7722-84-1

-No: 231-765-0

HAZARDS IDENTIFICATION

ses severe burns to skin. Extremely irritating to respiratory system. Reacts vigorously with flammable liquids, gases oxidising substances.

FIRST AID MEASURES

contact: Irrigate thoroughly with water for at least 10 minutes. Obtain medical advice.

lation: Remove from exposure, rest and keep warm. In severe cases obtain medical advice.

contact: Drench the skin thoroughly with water. Remove contaminated clothing and wash before re-use. Unless osure has been slight, obtain medical attention.

stion: Wash out mouth thoroughly with water and give plenty of water to drink. Obtain medical advice.

FIRE FIGHTING MEASURES

cial risks: May evolve oxygen during decomposition.

able extinguishing media: Water

ACCIDENTAL RELEASE MEASURES

ar appropriate protective clothing. Inform others to keep a safe distance. If local regulations permit, mop up cautiously plenty of water and run to waste, diluting greatly with running water. Otherwise absorb on an inert absorbent, transfer suitable container and arrange removal by disposal company. Wash site of spillage thoroughly with water. Ventilate to dispel residual vapour.

HANDLING AND STORAGE

dling: Avoid contact with brass, iron, copper, metal and red lead sealing compounds.

rage: Store in a cool place, out of direct sunlight.

EXPOSURE CONTROLS / PERSONAL PROTECTION

ppropriate to quantity handled.

pirator: Self-contained breathing apparatus.

tilation: Extraction hood.

ves: Nitrile

protection: Goggles or face shield.

er precautions: Plastic apron, sleeves, boots - if handling large quantities.

PHYSICAL AND CHEMICAL PROPERTIES

m: Liquid

ur: Colourless

ur: Odourless

ting point: N/A

ing temperature: N/A

sity: N/A

our pressure: N/A

bility in water: Miscible in all proportions.

h point: N/A

losion limits: N/A

tion temperature: N/A

STABILITY AND REACTIVITY

dily decomposed by dust, metals, carbon, salts, etc. High pressure may develop in sealed containers. No reaction water.

TOXICOLOGICAL INFORMATION

ses severe burns to skin and eyes. Extremely irritating to respiratory system.

temic effect: If ingested, sudden evolution of oxygen may cause injury by acute distension of the stomach, and may se nausea, vomiting and internal bleeding. Has been found to cause cancer in laboratory animals. Evidence of mutaic properties.

ther data: LD50 1518 mg/kg oral, rat (data for 12%).

ECOLOGICAL INFORMATION

data available.

DISPOSAL CONSIDERATIONS

mical residues are generally classified as special waste, and as such covered by regulations which vary ording to location. Contact your local waste disposal authority for advice, or pass to a chemical disposal pany. Rinse out empty containers thoroughly before disposal.

TRANSPORTATION INFORMATION

-No.: 2014	ADR/RID: 5.1,1'(b)
): 5.1/2014	IMDG class: 5.1
A: 2014	Packaging group: II

rect technical name: Hydrogen peroxide, aqueous solution.

REGULATORY INFORMATION

elling according to EEC directives.

nbol: C corrosive

hrases: R34
uses burns.

hrases: **S3-36/37/39-45**

p in a cool place. After contact with skin, wash immediately with plenty of water. Wear suitable protective clothing, and /face protection. In case of accident or if you feel unwell, seek medical advice immediately (show the label where sible).

-No.: 231-765-0

al regulations:

exposure limits: OES, Long Term 1.5mg/ml.

OTHER INFORMATION

information contained in this Material Safety Data Sheet is believed to be accurate but it is the onsibility of the user or supplier to determine the applicability of the data to the formulation of necessary ty precautions. Novocastra Laboratories Ltd. shall not be held responsible for any damage resulting from use of the above product or the information contained in this Material Safety Data Sheet.

S Number: **F1802** * * * * * *Effective Date:* ***08/23/04*** * * * * * *Supercedes:* ***08/10/04***

MSDS *Material Safety Data Sheet*

24 Hour Emergency Telephone: 908-859-2151
CHEMTREC: 1-800-424-9300

National Response in Canada
CANUTEC: 613-996-6666

Outside U.S. and Canada
Chemtrec: 703-527-3887

From: Mallinckrodt Baker, Inc.
222 Red School Lane
Phillipsburg, NJ 08865

Mallinckrodt CHEMICALS J.T.Baker

NOTE: CHEMTREC, CANUTEC and National Response Center emergency numbers to be used only in the event of chemical emergencies involving a spill, leak, fire, exposure or accident involving chemicals.

All non-emergency questions should be directed to Customer Service (1-800-582-2537) for assistance.

FERROUS SULFATE

Product Identification

Synonyms: Iron (II) sulfate (1:1)ç; sulfuric acid, iron (2+) salt (1:1), heptahydrate
CAS No.: 7720-78-7 (Anhydrous) 7782-63-0 (heptahydrate)
Molecular Weight: 278
Chemical Formula: $FeSO_4 7H_2O$
Product Codes:
J.T. Baker: 2063, 2070, 2074
Mallinckrodt: 5055, 5056, 5401, 5572

Composition/Information on Ingredients

ngredient	CAS No	Percent	Hazardous
errous Sulfate	7720-78-7	99 - 100%	Yes

Hazards Identification

Emergency Overview

WARNING! HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. AFFECTS THE LIVER.

SAF-T-DATA$^{(tm)}$ Ratings (Provided here for your convenience)

Health Rating: 3 - Severe (Life)
Flammability Rating: 0 - None
Reactivity Rating: 1 - Slight
Contact Rating: 2 - Moderate
Lab Protective Equip: GOGGLES; LAB COAT; VENT HOOD; PROPER GLOVES
Storage Color Code: Green (General Storage)

Potential Health Effects

Inhalation:
Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath.

Ingestion:
Low toxicity in small quantities but larger dosages may cause nausea, vomiting, diarrhea, and black stool. Pink urine discoloration is a strong indicator of iron poisoning. Liver damage, coma, and death from iron poisoning has been recorded. Smaller doses are much more toxic to children.

Skin Contact:
Causes irritation to skin. Symptoms include redness, itching, and pain.

Eye Contact:
Causes irritation, redness, and pain.

Chronic Exposure:
Severe or chronic ferrous sulfate poisonings may damage blood vessels. Large chronic doses cause rickets in infants. Chronic exposure may cause liver effects. Prolonged exposure of the eyes may cause discoloration.

Aggravation of Pre-existing Conditions:
Persons with pre-existing skin disorders or eye problems, or impaired liver, kidney or respiratory function may be more susceptible to the effects of the substance.

---

irst Aid Measures

Inhalation:
Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Ingestion:
Induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. Get medical attention.

Skin Contact:
Immediately flush skin with plenty of soap and water for at least 15 minutes. Remove contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.

Eye Contact:
Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

Fire Fighting Measures

Fire:
Not considered to be a fire hazard.
Explosion:
Not considered to be an explosion hazard.
Fire Extinguishing Media:
Use any means suitable for extinguishing surrounding fire.
Special Information:
Use protective clothing and breathing equipment appropriate for the surrounding fire.

Accidental Release Measures

Ventilate area of leak or spill. Wear appropriate personal protective equipment as specified in Section 8. Spills: Pick up and place in a suitable container for reclamation or disposal, using a method that does not generate dust. US Regulations (CERCLA) require reporting spills and releases to soil, water and air in excess of reportable quantities. The toll free number for the US Coast Guard National Response Center is (800) 424-8802.

Handling and Storage

Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Maintain a constant temperature not to exceed 24 degrees centigrade (75 degrees fahrenheit). Fluctuating temperatures causes product oxidation. Do not use this product if coated with brownish-yellow basic ferric sulfate. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

Exposure Controls/Personal Protection

Airborne Exposure Limits:
-ACGIH Threshold Limit Value (TLV):
1 mg/m3 (TWA) soluble iron salt as Fe
Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures

below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

Personal Respirators (NIOSH Approved):

If the exposure limit is exceeded and engineering controls are not feasible, a half facepiece particulate respirator (NIOSH type N95 or better filters) may be worn for up to ten times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest.. A full-face piece particulate respirator (NIOSH type N100 filters) may be worn up to 50 times the exposure limit, or the maximum use concentration specified by the appropriate regulatory agency, or respirator supplier, whichever is lowest. If oil particles (e.g. lubricants, cutting fluids, glycerine, etc.) are present, use a NIOSH type R or P filter. For emergencies or instances where the exposure levels are not known, use a full-facepiece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection:

Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact.

Eye Protection:

Use chemical safety goggles and/or full face shield where dusting or splashing of solutions is possible. Maintain eye wash fountain and quick-drench facilities in work area.

---

hysical and Chemical Properties

Appearance:
Blue green crystals.
Odor:
Odorless.
Solubility:
48.6 g/100 g water @ 50C (122F)
Density:
1.90
pH:
No information found.
% Volatiles by volume @ 21C (70F):
0
Boiling Point:
> 300C (> 572F) Decomposes.
Melting Point:
57C (135F) Loses water
Vapor Density (Air=1):
No information found.
Vapor Pressure (mm Hg):
No information found.
Evaporation Rate (BuAc=1):
No information found.

Stability and Reactivity

Stability:
Stable under ordinary conditions of use and storage. Looses water in dry air and oxidizes upon exposure to moisture, forming a brown coating of extremely corrosive basic ferric sulfate.
Hazardous Decomposition Products:
Burning may produce sulfur oxides.
Hazardous Polymerization:
This substance does not polymerize.
Incompatibilities:
Alkalis, soluble carbonates, and oxidizing materials. Reacts in moist air to form ferric sulfate.
Conditions to Avoid:
Moisture.

. Toxicological Information

Oral rat LD50: 319 mg/kg. Investigated as a tumorigen and mutagen.

-------\Cancer Lists\--

	---NTP Carcinogen---		
ngredient	Known	Anticipated	IARC Category
errous Sulfate (7720-78-7)	No	No	None

. Ecological Information

Environmental Fate:
No information found.
Environmental Toxicity:
No information found.

. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be managed in an appropriate and approved waste disposal facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

Transport Information

Not regulated.

Regulatory Information

```
------\Chemical Inventory Status - Part 1\---------------------------------
gredient                                           TSCA  EC   Japan  Australia
-----------------------------------------------    ----  ---  -----  ---------
rrous Sulfate (7720-78-7)                           Yes  Yes   Yes      Yes

------\Chemical Inventory Status - Part 2\---------------------------------
                                                          --Canada--
gredient                                           Korea  DSL   NDSL  Phil.
-----------------------------------------------    -----  ---   ----  -----
rrous Sulfate (7720-78-7)                           Yes   Yes   No     Yes

------\Federal, State & International Regulations - Part 1\----------------
                                             -SARA 302-    ------SARA 313------
gredient                                     RQ    TPQ     List  Chemical Catg.
-----------------------------------------    ---   -----   ----  --------------
rrous Sulfate (7720-78-7)                    No    No      No          No

------\Federal, State & International Regulations - Part 2\----------------
                                                      -RCRA-    -TSCA-
gredient                                     CERCLA   261.33     8(d)
-----------------------------------------    ------   ------    ------
rrous Sulfate (7720-78-7)                    1000     No         No


ical Weapons Convention:  No     TSCA 12(b):  No     CDTA:  No
 311/312:  Acute: Yes      Chronic: Yes  Fire: No  Pressure: No
tivity: No          (Pure / Solid)
```

Australian Hazchem Code: None allocated.
Poison Schedule: None allocated.
WHMIS:
This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by the CPR.

Other Information

NFPA Ratings: Health: **1** Flammability: **0** Reactivity: **0**
Label Hazard Warning:
WARNING! HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO

SKIN, EYES AND RESPIRATORY TRACT. AFFECTS THE LIVER.

Label Precautions:

Avoid contact with eyes, skin and clothing.
Wash thoroughly after handling.
Avoid breathing dust.
Keep container closed.
Use only with adequate ventilation.

Label First Aid:

If swallowed, induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Wash clothing before reuse. In all cases, get medical attention.

Product Use:

Laboratory Reagent. Bulk pharmaceutical chemical.

Revision Information:

MSDS Section(s) changed since last revision of document include: 3.

Disclaimer:

****

Mallinckrodt Baker, Inc. provides the information contained herein in good faith but makes no representation as to its comprehensiveness or accuracy. This document is intended only as a guide to the appropriate precautionary handling of the material by a properly trained person using this product. Individuals receiving the information must exercise their independent judgment in determining its appropriateness for a particular purpose. MALLINCKRODT BAKER, INC. MAKES NO REPRESENTATIONS OR WARRANTIES, EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION ANY WARRANTIES OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE WITH RESPECT TO THE INFORMATION SET FORTH HEREIN OR THE PRODUCT TO WHICH THE INFORMATION REFERS. ACCORDINGLY, MALLINCKRODT BAKER, INC. WILL NOT BE RESPONSIBLE FOR DAMAGES RESULTING FROM USE OF OR RELIANCE UPON THIS INFORMATION.

****

Prepared by: Environmental Health & Safety
Phone Number: (314) 654-1600 (U.S.A.)