Degradation of Alizarin Yellow R Using Ultraviolet/Hydrogen Peroxide (UV/H_2O_2) Advanced Oxidation Process

by

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Dissertation submitted in partial fulfilment of

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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The past 28 weeks of my enrolment in this final year project have been truly a valuable experience to me. Hence, I would like to take this opportunity to express my sincerest gratitude to a number of people that have helped me throughout this project.

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Last but not least, special thanks to my friends and family, and to anybody who has contributed directly and indirectly towards accomplishing the objectives of this final year project. In short, I feel blessed to have successfully completed my final year project.

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.

LAVANYAH NARAYANASAMY

ABSTRACT

The homogeneous advanced oxidation process of Ultraviolet (UV) radiation in presence of Hydrogen Peroxide (H_2O_2) was utilized to degrade Alizarin Yellow R, one of the most used azo dyes in the textile industry. The UV/H_2O_2 oxidation process is a feasible and efficient alternative for wastewater treatment from recalcitrant compounds such as azo dyes. In this study, the effects of initial hydrogen peroxide concentration, initial dye concentration, initial pH and temperature were examined to determine the optimum operating conditions that give the maximum rate of degradation. Complete decolourization was achieved in the relatively short time of 60-80 minutes of irradiation. The degradation efficiency increased with increasing initial concentration of H_2O_2 up to an optimum value. Faster decolourization was achieved at medium acidic and neutral pH environment ranging from p 5-7 and at high temperature. The degradation reaction was found to follow the first order kinetics with respect to the dye concentration. The Box-Behnken response surface methodology (RSM) was utilized for mathematical modelling for degradation rate and used to optimize the operating condition of this degradation process. The optimum operating conditions were initial H_2O_2 concentration of 0.25M, initial pH of 4.59 and temperature of 50°C. Under such conditions, the proposed model of Box-Behnken fitted very well with the experimental data with R^2 =0.989. In general, the result indicates that the UV/H_2O_2 technology proved to have good potential for removing dyestuff from wastewater but further treatment might be necessary to achieve complete mineralization of the organic intermediates.

CHAPTER 1

INTRODUCTION

1.1 Background Study

Globally, the increase in demand for textile products and the proportional rise in production and application of synthetic dyes have caused dye effluent to become one of the most important causes of environmental contamination (Santos *et al*, 2006). Synthetic dyes are usually categorized based on their prevalent chemical structures. Some of the different types of synthetic dyes that are available includes acidic, reactive, basic, disperse and azo. Most of these dyes have highly structured polymers which results in them having low biodegradability and thus possess a big threat to the environment (Bali *et al.*, 2004). It has been estimated that in every year, more than 10,000 various pigments and dyes are used in large quantities in numerous industries like textile, leather, food and cosmetics and more than 0.7 million tons of synthetic dyes are being produced worldwide (Nigam *et al*, 2000). Almost 200,000 tons of these dyes, especially from the textile industries are lost to effluents annually during the dyeing and finishing processes (Bali *et.al.*, 2004).

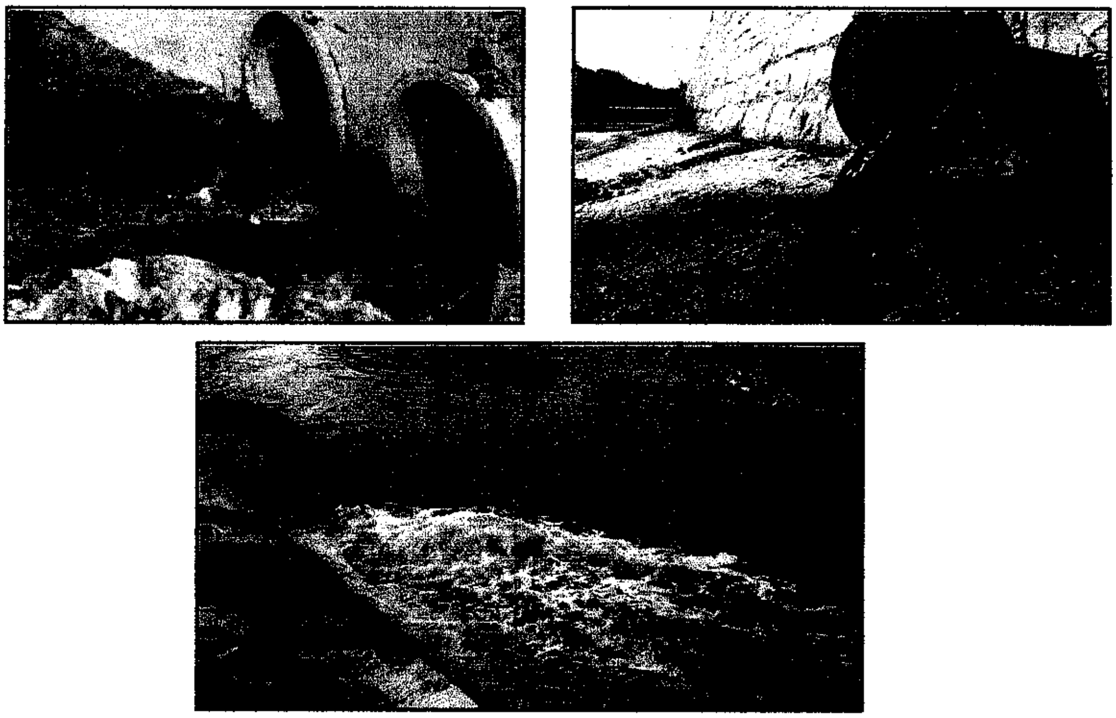


Figure 1.1: Untreated Dye in Effluent

Most of these dyes in the wastewater are carcinogenic in nature due to its complex structures and toxic products. For instance, azo dyes which are one of the most common synthetic dyes can be decomposed into carcinogenic amines (Bali *et al.*, 2004). In addition, it is more vital to treat these dye wastewater compared to treating other colourless organic compounds because even the presence of small amounts of dyes is clearly noticeable. Therefore removal of dyes from wastewater has become a major environmental issue and many countries are enforcing strict regulations concerning wastewater discharge by introducing various new environmental policies.

Advanced Oxidation Process (AOP) based on the Ultraviolet/Hydrogen Peroxide (H_2O_2/UV) system has proved high effectiveness in degrading certain types of dye that is present in the industrial wastewater. In our current project, we will be studying the degradation studies of Alizarin Yellow R using H_2O_2 in the presence of UV radiation.

1.2 Problem Statement

Untreated dye effluents from various industrial processes are highly coloured and possess dangerous characteristics like high level of toxic, naturally carcinogenic, not easily biodegradable, and decrease sunlight penetration. The discharge of these dye wastewaters into the ecosystem creates a significant source of pollution which also leads to eutrophication and perturbation of the aquatic life as it slows down the growth of aquatic microorganisms and threatens the stability of flora and fauna. Besides that, it can also result in intestinal cancer and cerebral abnormalities in foetuses for mammals particularly humans (Hammami *et al.*, 2007).

Numerous treatment methods and approaches have been employed to degrade the dye and minimize the high risk possessed by the untreated dye effluent. However, the practice of conventional methods such as activated carbon adsorption, coagulation/flocculation, ultrafiltration, sedimentation and membrane process does not fully degrade the dye. These methods simply transfer the pollutants (dyes) from liquid phase to solid phase (sludge) and this produces secondary contaminants that require additional treatments (Hammami *et al.*, 2007). The main reason most of these dyes gets away from conventional effluent treatment processes and stays in the environment is because of their high stability against light, temperature, water, detergents, chemicals, and microbial attack. The photo-oxidation reaction appears as a promising alternative for dye degradation because of the system's simplicity and the generation of highly reactive hydroxyl radicals which can lead to full degradation of dyes.

Moreover, the usual methods of studying the process variables by fixing the other parameters at a constant level cannot measure the combination effect of those parameters that affects the experiment results. It also takes more time and requires quite a number of experiments to represent the combinational effect of those variables. Response surface methodology (RSM) can be used to solve this problem where it can optimize the important parameters studied in a process. RSM is a combination of mathematical and statistical techniques used to develop, improve and optimize any processes. By utilizing the response surface model, RSM can determine the optimum conditions for the specified variables and predict the future response of the process.

Alizarin Yellow R dye are being used in various applications such as colouring of textile, leather, plastics, food and pharmaceuticals and also for manufacturing paints and lacquers. In spite of the various applications, research on its photolytic degradation using UV/H_2O_2 method is not yet available in literature. Therefore, it is very vital to initiate the study at it can cause a huge threat to the environment.

1.3 Objectives

1) To study the degradation of an azo dye (Alizarin Yellow R) by using UV/H_2O_2 method.
2) To investigate the effects of important process variables like initial dye concentration, initial H_2O_2 concentration, initial pH, and temperature on degradation performance.
3) To optimize the degradation of Alizarin Yellow R using statistical approach.

1.4 Scope of Study

The scope of work can be divided into three stages based on the objectives. For the first stage of the project, the author will focus on research and literature review on previous studies related to this topic. This includes deciding on the dye and the parameters that is going to be studied. The second stage is conducting the experiments. The lab experiment would be conducted by varying few parameters such as initial dye concentration, initial H_2O_2 concentration, effect of initial pH and temperature and keeping the parameters constant. The final stage would be in finding the optimum condition that gives the maximum rate of degradation of the dye using the experimental design and Response Surface Methodology (RSM).

1.5 Relevancy and Feasibility of the Project

This project is relevant to the author's field of study since environmental sustainability is one of the focus areas in Chemical Engineering. Environment Engineering is one of the sub-disciplinary in Chemical Engineering where Chemical Engineers develop strategies and designs to reduce pollution at the source and treat waste that cannot be eliminated by applying chemistry theories in order to create methods of environmental sustainability, conservation and protecting efforts. As a chemical engineer, the author has evaluated the conventional dye wastewater treatment to find the most promising solution where she has proposed UV/H_2O_2 system as an alternative method for degradation of dye in wastewater.

The project is feasible since it is within the scope and time frame. The author has planned to complete the research and literature review by the end of the first semester while purchasing the material after the mid-semester break. She plans to dedicate the first six weeks of final year project II (FYP II) to conduct the experiment to evaluate the effects of the various parameters while the other four weeks to determine the optimum conditions based on statistical approach. Besides that, the photo-reactor and other tools are readily available at the university Lab (Block 4 and 5) and thus there is no wastage of time in ordering and waiting for their arrival.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes

2.1.1 General Overview

Dyes which are extensively used in various industrial processes such as the fabric, textile, and printing industries are an essential class of chemicals. (Rauf *et al.*, 2007). In general, a dye can be defined as a coloured substance that has an attraction to the substrate to which it is being applied. Usually, the dye is applied in an aqueous solution and sometimes it requires a mordant to increase the fastness of the dye on the fiber. The reason dyes seem to be coloured is because they absorb certain wavelengths of light preferentially. Figure 2.1 show how dyes are normally available in market for textile application.

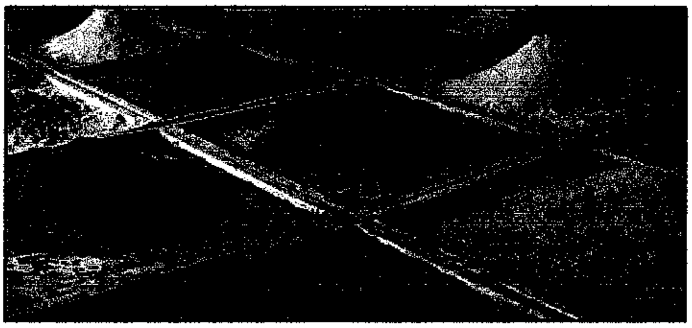


Figure 2.1: Dyes used in Textile Industry

There are two types of dyes, natural and synthetic dye. Natural dyes refer to the dyes which are produced from animals, plants or minerals, with very little or no processing at all. Till today, many parts of a plant especially the roots, berries, bark, leaves and even wood have been used to produce natural dyes. However, only a few of these dyes have been commercialized.

In contrast, synthetic dyes are artificial dyes which are extensively used in most industrial applications currently. These dyes have very complex chemical bonding which cannot be degraded easily using biological methods. Some of the different types of synthetic dyes available in the market are azo dyes, anthraquinone, direct dyes, quinine, mordant, disperse dyes, vat dyes, xanthenes, and nitro dyes. By design, dyes are very resistant chemicals and are not easily degraded using conventional treatment processes. Thus, this imposes a strong challenge for industrial wastewater systems. Besides that, many biodegradability efforts and studies on dyes have proved that they are not easily biodegradable (Bali, 2004). This is mainly due to the highly structured polymers in most of the dyestuffs (Rauf *et al.*, 2008). Most dyes also have molecules such as nitrogen, chlorine, and sulphur. The oxidation products of these components are even more toxic than the original molecule (Chen *et al.*, 2005). On the whole, synthetic dyes contribute to special environmental concern due to their degradation products such as aromatic amines which are considered as highly carcinogenic substances (Bali *et al.*, 2004).

2.1.2 Alizarin Yellow R

Alizarin Yellow R or also known as Mordant Orange 1 is an azo mordant dye, made by the diazo coupling reaction. Azo compounds are those compounds having the functional group R-N=N-R', where R and R' can refer to either aryl or alkyl. It is commonly used for the dyeing of wool and nylon (Bahl *et al.*, 2007). It normally exists as a sodium salt. It is a rust-coloured solid in its pure form (Lide, 2008). Its molecular formula is $C_{13}H_8N_3 NaO_5$ (Na salt) with the molecular weight of 309.21 while its λ_{max} is 373 nm. Figure 2.2 shows the molecular structure of Alizarin Yellow R where it has an N=N bond.

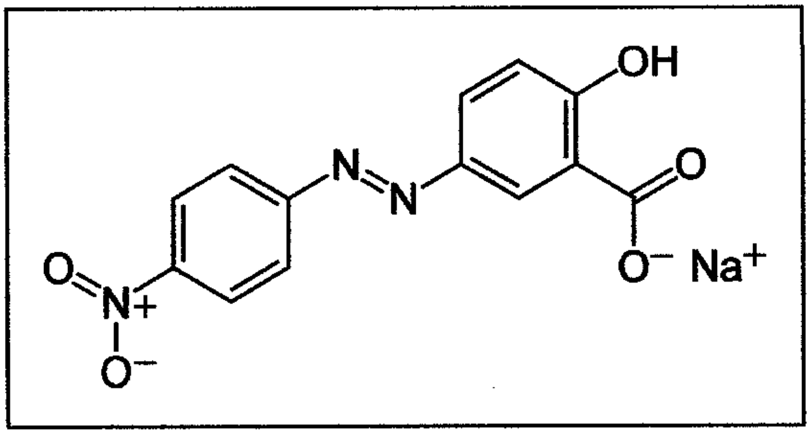


Figure 2.2: Molecular Structure of Alizarin Yellow R

This slightly brown powder is soluble in cold water and it is like any other azo dye which gives bright and high intensity colours, much more than anthraquinones, the next most common dye category. They have quite good fastness properties which means it has good ability to retain the colours when washed, cleaned or exposed to sun light. Cost-effectiveness is the biggest advantage of this dye which is due to the processes involved in its production process. However, this dye can cause irritation to the eyes, skin, digestive tract, and respiratory tract. Figure 2.3 below shows the dye powder which will be used in this experiment.

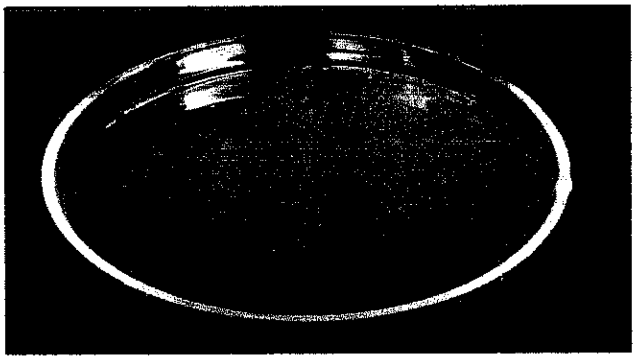


Figure 2.3: Alizarin Yellow R Dye

2.2 Dye Treatment Methods

2.2.1 Conventional Methods

Numerous efforts have been employed to develop treatment methods that are capable in reducing the dangerous effects caused by dye wastewater. The various existing treatment methods which are currently applied to treat the industrial textile effluent can be classified into three main groups which are biological, chemical and physical (Robinson *et al.*, 2001).

Biological Methods

Compared to chemical and physical treatments, usually biological treatments are considered as eco friendly as it can manage to degrade organic contaminants effectively at very low cost. Biodegradation techniques like microbial degradation, fungal decolourization, adsorption by (living or dead) microbial biomass and bioremediation systems are normally used in the treatment of industrial effluents because these microorganisms like bacteria, yeasts, algae and fungi can accumulate and break down the different pollutants (McMullan *et al.*, 2001 and Fu & Viraraghavan, 2001). Figure 2.4 shows the white-rot fungi which have been widely studied as dye decolourizing microorganisms.

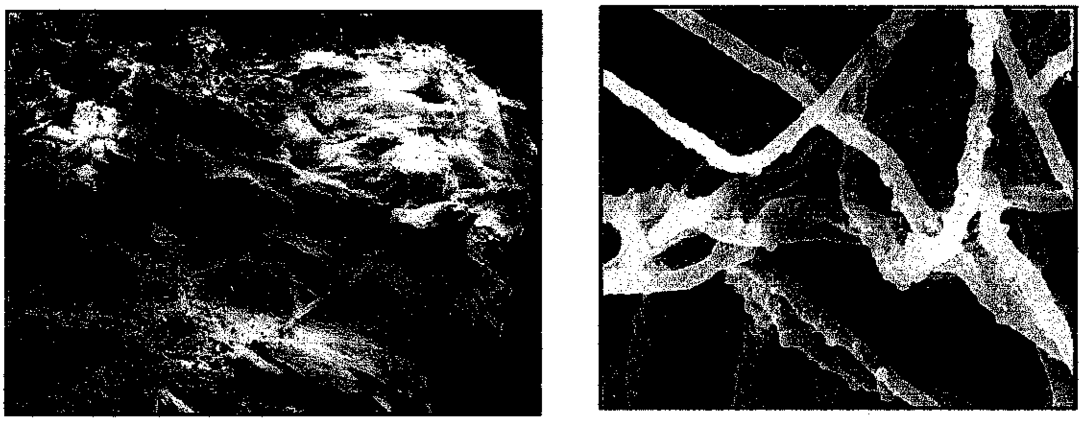


Figure 2.4: White-rot fungi

However, due to technical constraints, their application is often limited. As stated by Bhattacharyya and Sharma, (2003), biological method needs a huge land area and has less flexibility in its design and process. It is also inhibited by toxicity of some chemicals. Furthermore, it is unable to obtain satisfactory colour removal with existing conventional biodegradation techniques (Robinson *et al.*, 2001). Although many organic compounds are degraded through this method, there are many others especially pollutants like azo dyes which are recalcitrant due to their complex aromatic structures xenobiotic nature (Ravi Kumar *et al.*, 1998). They normally require a complicated anaerobic and aerobic process to achieve a complete demineralization (Sugumar & Thangam, 2012).

Physical Methods

Various physical treatments such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption techniques are also extensively used. The main drawbacks of the membrane processes is that the lifetime of the membrane is very limited as membrane fouling can happen and the regular is a serious consideration in any economic viability analysis. From the environmental viewpoint, adsorption technique is an excellent method to treat wastewaters compared to other conventional process (Ravikumar *et al.*, 2006). This is mainly because of the lower initial cost, flexibility and simplicity of design, ease of operation and its insensitivity to toxic contaminants.

Many different adsorbents like peat, wood chips, fly ash and brown coal have been used as dye adsorbents (Nigam *et al.,* 2000; Robinson *et al.,* 2001). However, activated carbon is the most common adsorbent for colour removal and is has been proven to be very effective in adsorbing cationic, mordant and acid dyes (Nasser and El- Geundi, 1991). Carbon is being used as an adsorbent (shown in Figure 2.5) because of its high efficiency in treating the organic materials in effluents. Although it has very high efficiency, but the increase in the price of the activated carbon results in higher cost of operation (Khattri and Singh, 2000).

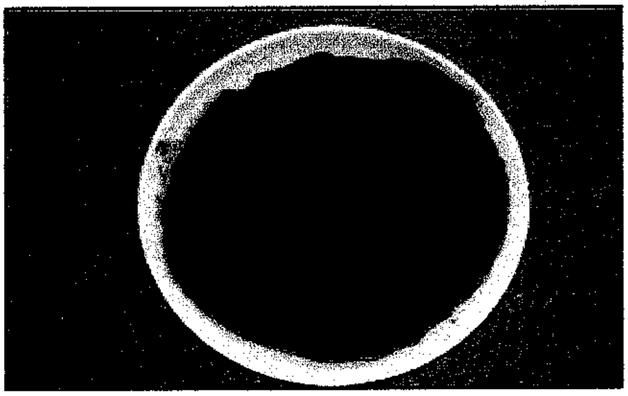


Figure 2.5: Activated Carbon as Adsorbent

Therefore, it can be concluded that even though, adsorption is capable to decolourize textile wastewaters effectively, it has certain limitations such as high cost of adsorbents and it usually requires large volume of wastewater (Robinson *et al.*, 2001).

Chemical Methods

Some of the common chemical treatments methods are coagulation flocculation combined with flotation and filtration, precipitation-flocculation with Fe(II)/Ca(OH)2, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. The process flow diagram for a typical coagulation/flocculation process is shown in Figure 2.6. These chemical methods are slightly costly and although it removes the dyes, the accumulated concentrated sludge creates a disposal challenge. Due to the excessive chemical use, it is also possible to have a secondary pollution problem. Recently, other promising alternatives also known as advanced oxidation processes have been found to be very effective in the degradation of dye pollutants. This technology involves the generation of very powerful oxidizing agents such as hydroxyl radicals to degrade the complex structures of the dyes.

In conclusion, degradation of dyes in wastewater in a cost-effective way remains as a big problem for textile industries. Though these conventional methods of effluent treatment can eradicate the main organic compounds, but the biochemical decomposition is not sufficient enough to fully decolorize and degrade dye effluents (Çatalkaya and Sengul, 2006). Thus, it is necessary for dyes based industries to reconsider upon the alternative methods in their effluent treatment.

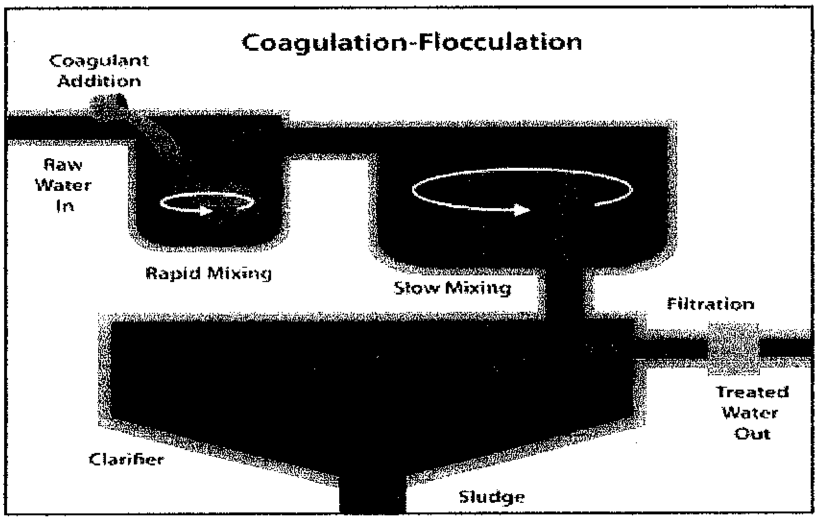


Figure 2.6: Coagulation and Flocculation Process Flow

2.2.2 Advanced Oxidation Processes

Advance Oxidation Processes (AOP) is an alternative way to reduce wastewater effluents produced by industries and it is very efficient for dye decolourisation and degradation (Alhamedi *et al.*, 2009). According to Behnajady *et al.*, (2006), AOPs' are an excellent physical water treatment processes because they are able to remove the compound rather than changing it to another phase or medium such as solid waste or sludge. The AOP destroys the chromophoric structure of the dye (Kurbus et al., 2002) and eventually achieves a complete colour removal, hence advanced oxidation processes are being considered as an emerging technology to deal with large amount of textile wastewater. The application of different AOPs' such as UV/H_2O_2 (Korbahti and Rauf, 2008), photocatalytic (Attia *et al.*, 2008), Fenton processes (Çatalkaya and Sengul, 2006) has proven potential outcomes as these processes seems to have the capability to fully decolourize and partially degrade the dyes from textile industry in short reaction time (Rauf *et al.*, 2008) and (Bali *et al.*, 2004).

Generation of very reactive free radicals is the main function mechanism of AOPs'. These hydroxyl radicals (HO•) are efficient in breaking down the organic chemicals because they are highly reactive electrophiles (electron preferring) that react very quickly and nonselectively with practically all electron-rich organic compounds. They have an oxidation potential of 2.33 V and demonstrates more rapid rates of oxidation reactions comparing to conventional oxidants such as H_2O_2 or $KMnO_4$ (Stasinakis, 2008). The hydroxyl radicals once generated, can attack organic compounds by radical addition (Eq. 1), hydrogen abstraction (Eq. 2) and electron transfer (Eq. 3). R is used to describe the reacting organic compound in the following reactions:

$$R + HO\bullet \rightarrow ROH \qquad (1)$$

$$R + HO\bullet \rightarrow R\bullet + H_2O \qquad (2)$$

$$R_n + HO\bullet \rightarrow R_{n-1} + OH^- \qquad (3)$$

There are many different methods which fall under the broad definition of AOPs'. Most of them utilize a combination of powerful oxidizing agents like H_2O_2 and O_3 with catalysts (e.g. transition metal ions) and irradiation (e.g. ultraviolet, visible). Among the many different available processes of generating hydroxyl radicals, hydrogen peroxide/UV light process, titanium dioxide/UV light process, and Fenton's reactions ($Fe^{2+)}$ appears to be some of the most common technologies for dye effluent treatment as demonstrated by the great amount of information available in the literature. Table 2.1 shows a list of different combinations of AOPs' and the type of dye that have been studied by various authors.

Table 2.1: Types of Dye Studied and Treatment Method Used

Author	Dye Studied	Treatment Method
Bali *et.al.* (2004)	Direct Red 28	$UV/H_2O_2/Fe^{2+}$
Sohrabi *et.al* (2008)	Direct Red 23	UV/TiO_2
Alshamsi *et.al* (2006)	Crystal Violet	UV/Fe^{2+}
T.Kurbus *et al*	C.I. Reactive Black 5 C.I. Reactive Black 5	O_3/H_2O_2
Rauf *et.al*	Rose Bengal	UV/ H_2O_2
U.Bali (2004)	Remazol Black B	UV/ H_2O_2
Shu *et al*	Acid Black 1	UV/ H_2O_2
S.Hammami *et al.*, (2008)	Direct Orange 61	$O_3/H_2O_2/Fe^{2+}$

2.2.3 UV/H_2O_2 System

From the efficiency and relative ease of operation's point of view, UV/ H_2O_2 is one of the best known AOPs'. This process consists of using the combination of UV radiation and H_2O_2 and it characterised by the production of strong hydroxyl radicals (Behnajady *et al.*, 2006). UV wavelengths of 200 – 280 nm lead to dissociation of H_2O_2 and mercury lamps emitting at 254 nm are those mostly used.

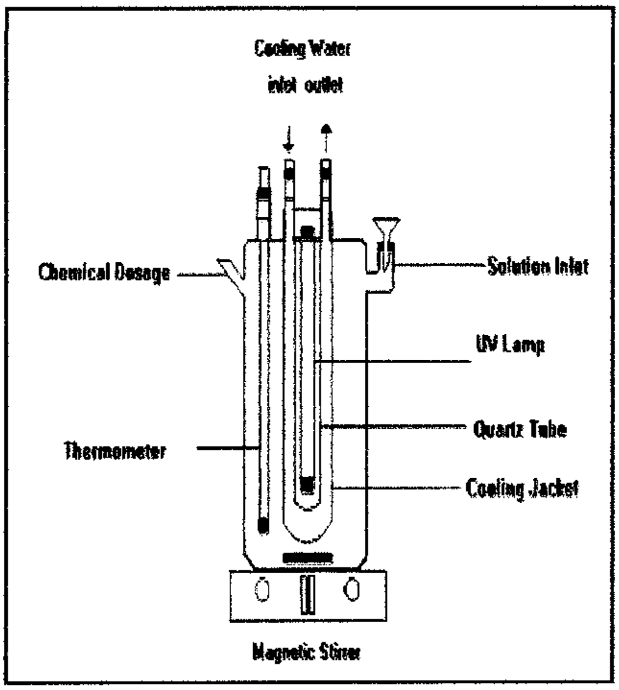


Figure 2.7: Schematic diagram of the laboratory photo-chemical installation

UV/H_2O_2 systems produce hydroxyl radicals (•OH) which are very strong oxidizing agents. These hydroxyl radicals are able to oxidize organic compounds (RH) and leads to the generation of organic radicals (•R), which are also very reactive and can be oxidized further (Bali *et al.*, 2004). Then, these radicals will attack the dye molecules and it will go through a sequence of reactions in which the organic molecules will be removed or changed into simpler or less harmful molecules (Alhamedi *et al.*, 2009). The major reaction that happens during the UV/H_2O_2 oxidation process is as follows:

$$H_2O_2 + UV \rightarrow 2OH\bullet \qquad (4)$$

$$H_2O_2 \leftrightarrow HO2- + H^+ \qquad (5)$$

$$RH + OH\bullet \rightarrow H_2O + R\bullet \rightarrow \text{further oxidation} \qquad (6)$$

where R is the carbon chain.

Once produced the powerful hydroxyl radicals will react randomly and very quickly with most organic molecules to form organic radicals. These generated organic radicals then will react with oxygen to initiate another sequence of degradative oxidation reactions. This leads to end products such as CO_2 H_2O and low molecular weight aliphatic acids (Çatalkaya and Sengul, 2006). Hydrogen abstraction, electrophilic addition and electron transfer reactions are the other probable reactions that may take place during the UV/H_2O_2 process (Behnajady *et al.*, 2006).

Even though AOPs' have many advantages in treating dye effluent, one main problem in AOPs' is that it has high operational cost due to the high demand for energy needed for the UV lamps. Therefore, it is essential to optimize the pH condition, temperature and chemical concentration in order to reduce the reaction time, energy consumption, and operational cost. (Çatalkaya and Sengul, 2006). The application of experimental design is the best solution for this problem where it will be used to optimize the important variable that affect the effectiveness of the dye degradation.

2.3 Experimental Design

2.3.1 Introduction

In an experiment, one or more process variables are normally varied in order to examine the consequences the changes have on one or more response variables. The (statistical) design of experiments is an effective method to plan the experiments so that the results gained can be analyzed and a valid conclusion can be obtained. Experimental design's main aim is to improve the experimental works. Experimental design application is usually used to choose which experiment has to be conducted in order to have more data on the specific chemical processes or products. Based on the results, it can be determined which parameters have a significant effect on the final outcome of the process. Besides that, it is also aimed to know the number of experiments that have to be conducted in order to get enough information to do the analysis (Kurbus *et al.*, 2003).

Therefore, it can be summarized that the main purpose of the experimental design methodology is to decide the effect of the different parameters and their combination effect on the outcome of the process with less number of experiments (minimum effort). Statistical techniques like analysis of variance (ANOVA) need to be used to decide which factors and/or interactions are statistically significant for that particular process.

2.3.2 Screening of Process Parameters

Kurbus et al., (2003) has stated that there are a few methods s of experimental design are which includes full factorial, fractional factorial design, box-behnken, D-optimal design, and uniform design. The choice of the experiments has a specific effect on the system. The characteristics of the product named as a response. The factors that affecting the product are called independent variables while the product or the response is called dependent variables. So, experimental design can be defined as a set of carefully planned experiments.

In experimental design process, firstly the type of experimental design is determined. Then, the next step is to choose the initial factors and response and to select the experimental domain. Once screening process is done, insignificant factors are discarded. After determining which factors have minimal or insignificance on the response, the optimum settings of the significant parameters levels that produce the best response need to be performed.

2.3.3 Optimization

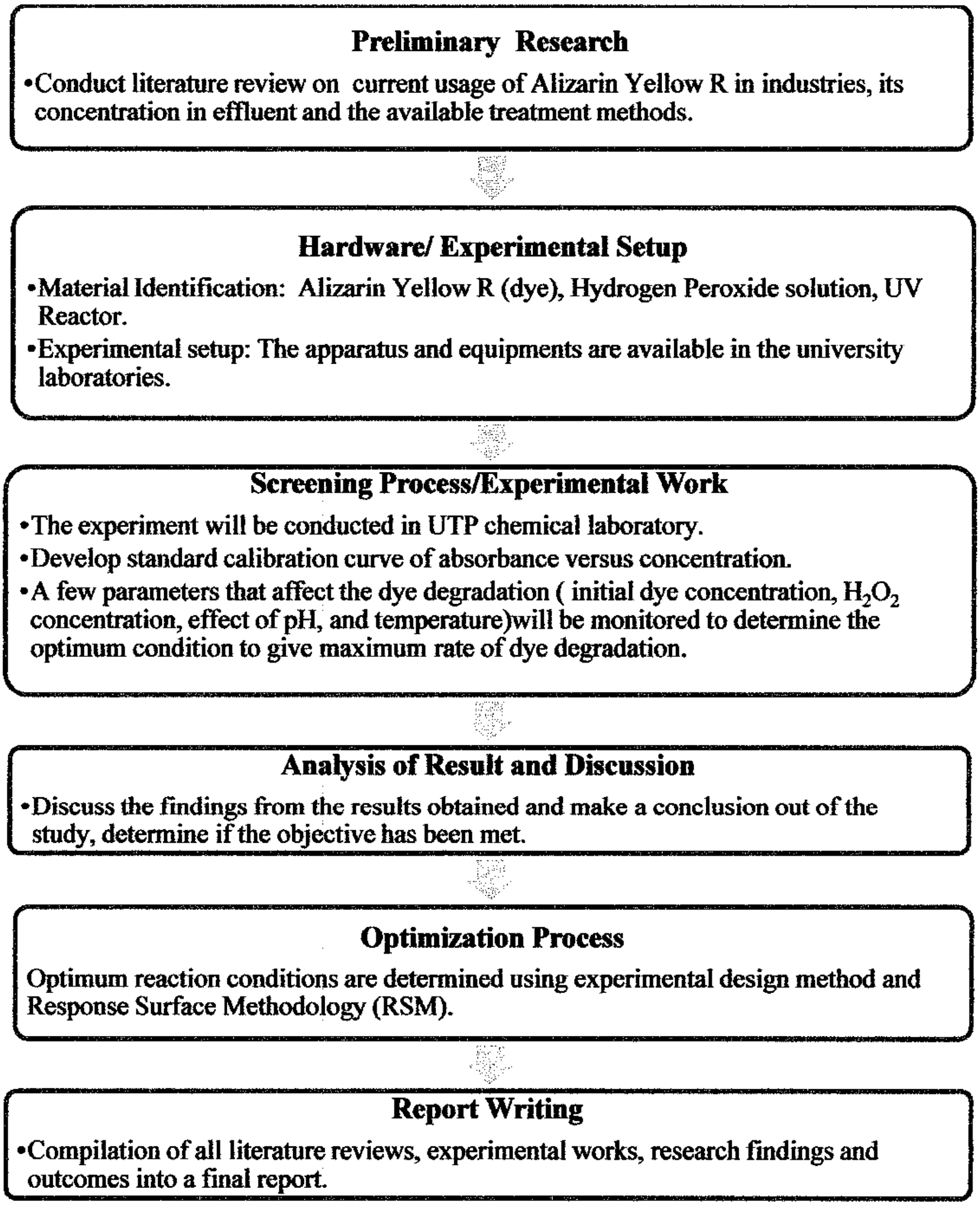
According to Çatalkaya and Sengül, (2006), response surface methodology (RSM) is utilized to find the optimum operating conditions and to examine the effect of important process parameters of dyes degradation. Basically, RSM is the set of mathematical and statistical methods normally used to design experiments, build models, evaluate the effect of variables, and determine the optimum conditions of parameters to forecast the target responses (Myers and Montgomery, 2002). It is an important branch of experimental design and a critical tool in developing new processes, optimizing their performance, and improving design and formulations of new products (Körbahti and Rauf, 2008a). RSM is used for the analysis of dependent variables as functions of independent variables. It is also used to find the optimum operating conditions or to determine a region for the factors at a certain operating specification (Rauf et al., 2008).

CHAPTER 3

METHODOLOGY / PROJECT WORK

3.1 Project Flow

The experiments conducted are based on the equipment provided by the university laboratories. The methodology for the experimental work will further be explained in the next subtopic.



Preliminary Research

- Conduct literature review on current usage of Alizarin Yellow R in industries, its concentration in effluent and the available treatment methods.

Hardware/ Experimental Setup

- Material Identification: Alizarin Yellow R (dye), Hydrogen Peroxide solution, UV Reactor.
- Experimental setup: The apparatus and equipments are available in the university laboratories.

Screening Process/Experimental Work

- The experiment will be conducted in UTP chemical laboratory.
- Develop standard calibration curve of absorbance versus concentration.
- A few parameters that affect the dye degradation (initial dye concentration, H_2O_2 concentration, effect of pH, and temperature)will be monitored to determine the optimum condition to give maximum rate of dye degradation.

Analysis of Result and Discussion

- Discuss the findings from the results obtained and make a conclusion out of the study, determine if the objective has been met.

Optimization Process

Optimum reaction conditions are determined using experimental design method and Response Surface Methodology (RSM).

Report Writing

- Compilation of all literature reviews, experimental works, research findings and outcomes into a final report.

Figure 3.1: The Methodology of the Project

3.2 Laboratory Experiment

There are four main experiments that will be conducted in chemical laboratory.

a) Experiment 1 (Effect of initial H_2O_2 concentration)
Manipulated parameter: Initial H_2O_2 concentration (0.06M-0.30M)
Constant parameters: Initial dye concentration (250ppm), Initial pH (5), Temperature (30°C)

b) Experiment 2 (Effect of initial dye concentration)
Manipulated parameter: Initial dye concentration (100ppm -300ppm)
Constant parameters: Initial H_2O_2 concentration (0.24M), Initial pH (5), Temperature (30°C)

c) Experiment 3 (Effect of Initial pH)
Manipulated parameter: Initial pH (3-11)
Constant parameters: Initial H_2O_2 concentration (0.24M), Initial dye doncentration (250ppm), Temperature (30°C)

d) Experiment 4 (Effect of Temperature)
Manipulated parameter: Temperature (20°C -50°C)
Constant parameters: Initial H_2O_2 concentration (0.24M), initial dye concentration (250ppm), Initial pH (5)

3.3 Experiment Procedure and Analytical Method

3.3.1 Reagent

The main reagents used for the experimental work in this project are Alizarin Yellow R dye, Hydrogen Peroxide (30%) solution, sodium hydroxide, hydrochloric acid and distilled water. The Alizarin Yellow R salt was obtained from Acros Organics, Hydrogen Peroxide (30%) from Systerm while NaOH and HCl were purchased from Merck (Germany). Aqueous solutions of azo dyes were prepared by dissolving required quantity of the dye in distilled water. Figure 3.2 shows the prepared aqueous solution of dye to be tested.

Figure 3.2: Prepared sample of dye solution

3.3.2 Experiment

All experiments were carried out in a 400 mL well stirred, jacketed, glass reactor. The outside of the reactor is covered with an aluminium sheet. The reaction zone is a cylindrical borosilicate glass tube of 14 inch long with internal diameter of 2 inches. At the top, the reactor has inlets for feeding reactants and withdrawing samples. A magnetic stirrer is placed in the bottom to provide proper mixing. The radiation source is a UV lamp (8 W, UV-C, manufactured by Philips, Holland) which was protected by a quartz tube. Figure 3.3 shows the setup of the photoreactor in the lab.

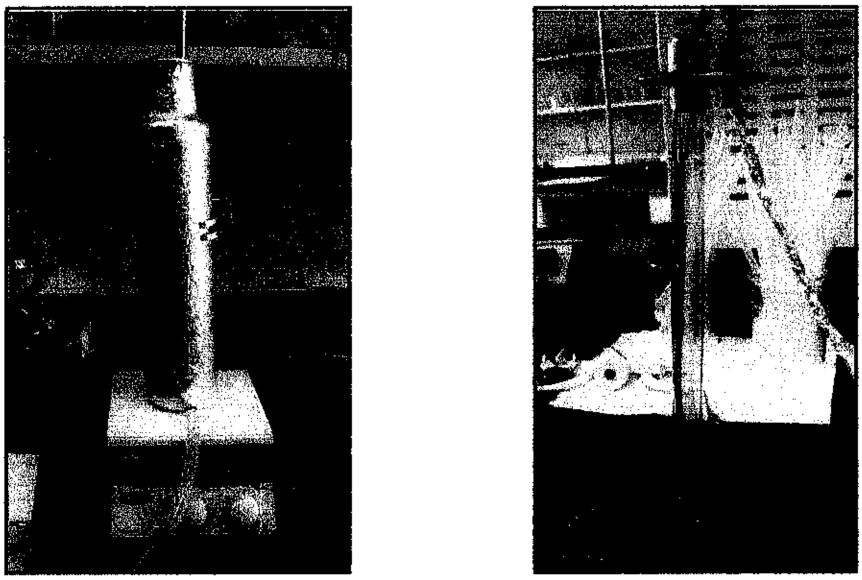


Figure 3.3: Experiment setup in lab (a) reactor coated with aluminium foil (b) UV lamp used for radiation

In each experiment, 400 mL of the dye solution with known concentration of dye will be used. At certain reaction intervals, 5 ml of sample will be withdrawn and analyzed with a UV–Vis spectrophotometer for its absorbance value. The pH adjustment was made using sodium hydroxide (NaOH) and hydrochloric acid (HCL). The temperature was maintained by circulating cooling water through the jacket.

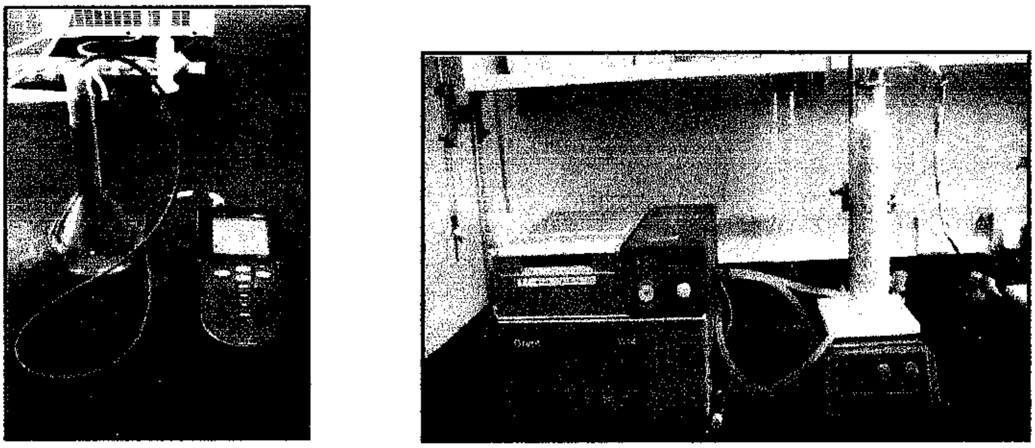


Figure 3.4: Equipment used in lab (a) pH meter to measure the pH of the solution, (b) Thermostatic bath to control the temperature of the system

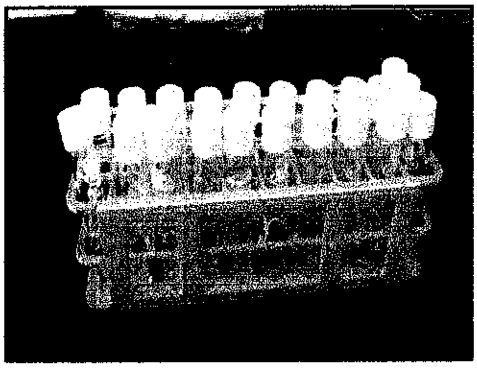


Figure 3.5: Samples taken every 10 minutes for UV-VIS analysis

3.3.3 Analysis

The decolourization of Alizarin Yellow R will be measured with UV–Vis spectrophotometer (Shimadzu model) at 373 nm (λ_{max}). The spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the colour, or more specifically, the wavelength of light. It measures the intensity of light passing through a sample (1), and compares it to the intensity of light before it passes through the sample (I,). Figure 3.4 below shows the UV-VIS spectrophotometer available in the lab in Block 4 which is used for the sample's absorbance measurement.

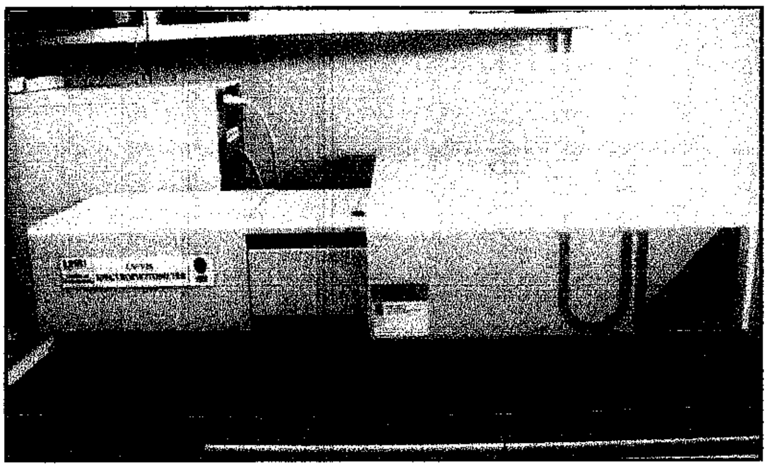


Figure 3.6: UV-VIS Spectrophotometer

Calibration plot based on Beer–Lambert's law is first established by relating the absorbance to the concentration and is shown in Figure 3.5

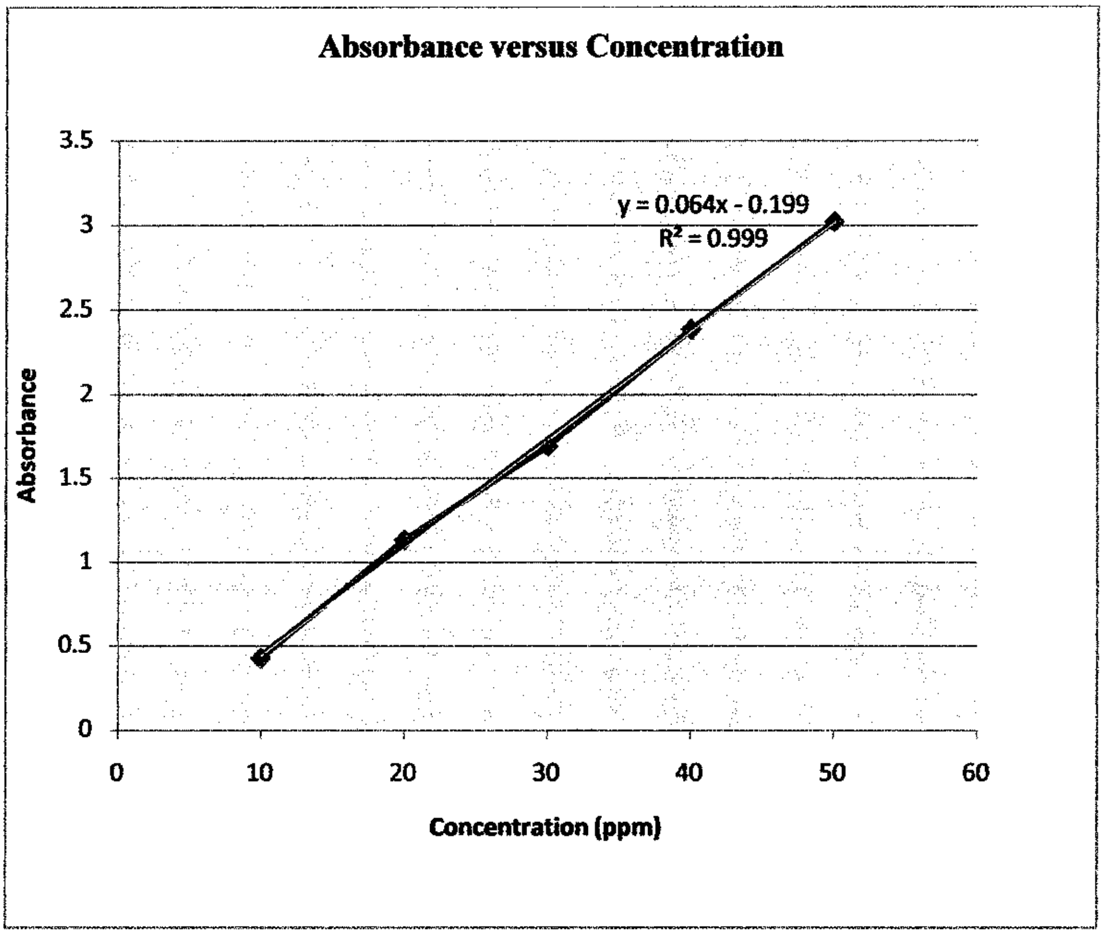


Figure 3.7: Calibration Plot of Absorbance vs. Concentration

Percentage decrease in absorption will be calculated as the equation follows:

$$\textbf{\% degradation effciency} = \frac{(A_f - A_i)}{A_i} \times 100 \qquad (7)$$

where A_i and A_f are the initial and final absorbance values of solution before and after irradiation.

The degradation of Alizarin Yellow R is tested using the Fourier Transform Infrared Analysis where it is a technique to identify organic molecules. In this case FTIR analysis is done to determine whether the azo compound (N=N bond) is being degraded by the end of the oxidation process and this is done by using a FTIR spectrometer. The technique uses an infrared signal to excite an organic compound. The functional groups on the compound will vibrate at specific frequencies when they are excited. An infrared (IR) signal, therefore, that passes through an organic compound will have a characteristic energy that can be transformed into a unique spectrum.

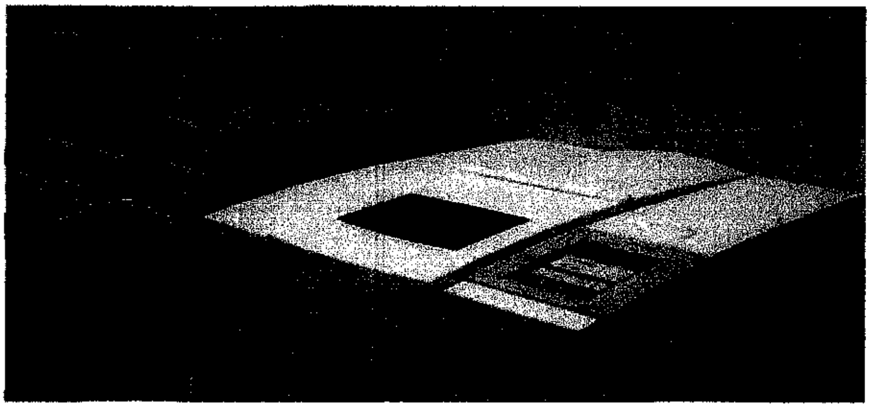


Figure 3.8: FTIR Spectrometer in lab

3.4 Statistical Design Experiment (Optimization)

A Box-Behnken design with three factors and three levels was used for fitting a second order response model. The fit quality of the polynomial model equation can be evaluated by coefficient of determination R^2. According to Box-Behnken design, the initial H2O2 concentration (X1), initial pH (X2) and temperature of the system (X3) were selected as the independent variables because they were three important parameters affecting Alizarin Yellow R's degradation using UV/H_2O_2, and percentage degradation (Y) was considered as the response. The initial dye concentration was kept constant at 250ppm. Experimental range and levels of independent variables for the degradation of Alizarin Yellow R by UV/H_2O_2 were presented in Table 1. For this optimization study, fifteen experiments were conducted.

Table 3.1: Experimental Region Investigated for Alizarin Yellow R degradation

		Range Levels		
Independent Variable	Factors	1	0	-1
Initial H_2O_2 concentration (M)	X1	0.18	0.24	0.30
Initial pH	X2	3	5	7
Temperature	X3	30	40	50

3.5 Analysis by RSM

Response Surface Methodology is used to model and analysis this process where the response (percentage degradation) is influenced by several factors. The objective of this method is to optimize the response. The experimental response is normally represented by a linear polynomial model with interaction:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{ij} \sum \beta_{ij} x_i x_j + \varepsilon \qquad (8)$$

Where

Y = predicted response

x_i = coded factors

β_o = constant terms

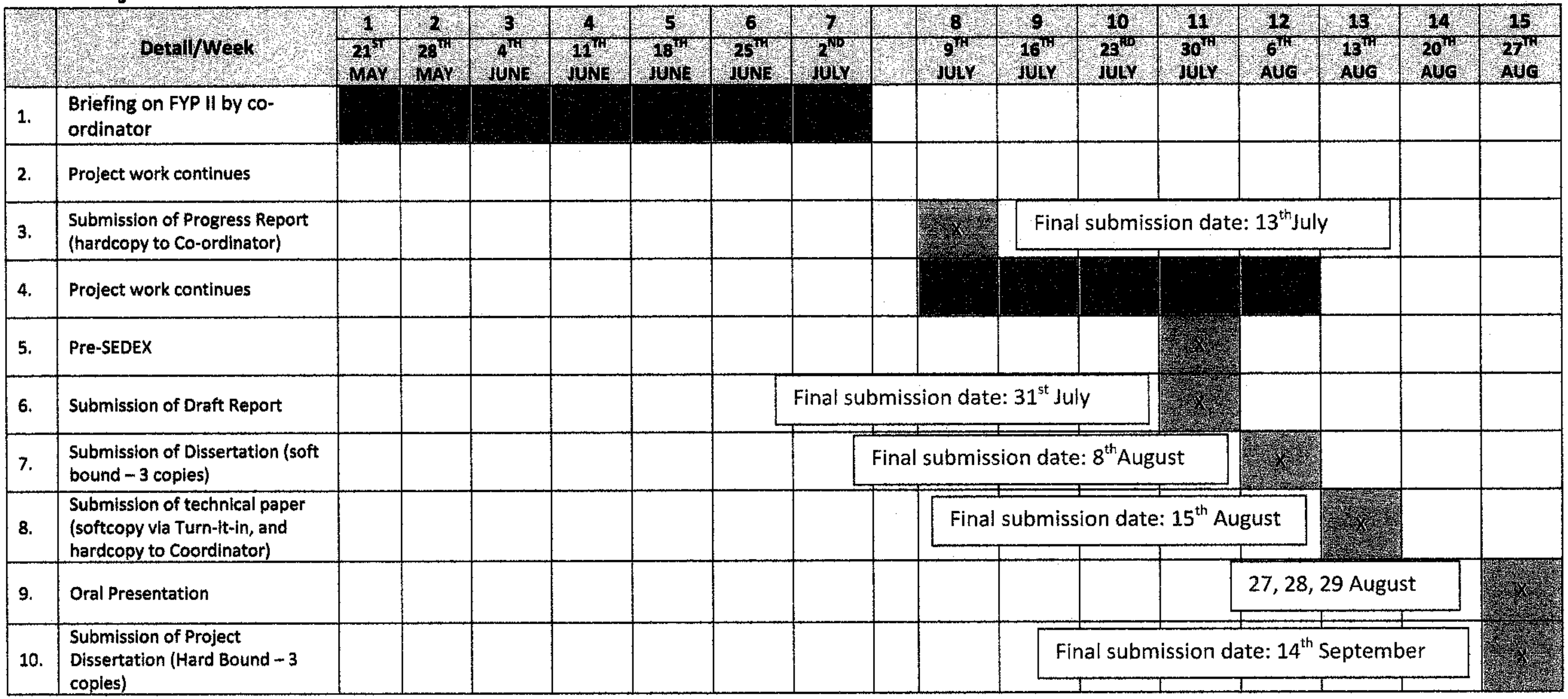
β_i = the linear effect

β_{ii} = the squared effect

β_{ij} = the interaction effect

Experimental results were analyzed using Portable Statgraphics Centurion 15.2.11.0 statistical software to approximate the response of dependent response variable and to find the effects coefficients, standard deviation of coefficients as well as the other parameters of the model.

3.6 Project Activities



	Detail/Week	1 21ST MAY	2 28TH MAY	3 4TH JUNE	4 11TH JUNE	5 18TH JUNE	6 25TH JUNE	7 2ND JULY		8 9TH JULY	9 16TH JULY	10 23RD JULY	11 30TH JULY	12 6TH AUG	13 13TH AUG	14 20TH AUG	15 27TH AUG
1.	Briefing on FYP II by co-ordinator	■	■	■	■	■	■	■									
2.	Project work continues																
3.	Submission of Progress Report (hardcopy to Co-ordinator)									X	Final submission date: 13th July						
4.	Project work continues									■	■	■	■	■			
5.	Pre-SEDEX												X				
6.	Submission of Draft Report							Final submission date: 31st July					X				
7.	Submission of Dissertation (soft bound – 3 copies)								Final submission date: 8th August					X			
8.	Submission of technical paper (softcopy via Turn-it-in, and hardcopy to Coordinator)									Final submission date: 15th August					X		
9.	Oral Presentation													27, 28, 29 August			X
10.	Submission of Project Dissertation (Hard Bound – 3 copies)										Final submission date: 14th September						X

Figure 3.9: Gantt Chart

compared to hydroxyl radicals (OH•). Therefore, any increase in H_2O_2 does not seem play a role in the degradation of the Alizarin Yellow R.

$H_2O_2 + UV \rightarrow 2HO\bullet$ (9)

$H_2O_2 + HO\bullet \rightarrow H_2O + HO_2\bullet$ (10)

$HO_2\bullet + HO\bullet \rightarrow H_2O + O_2$ (11)

Figure 4.3 summarizes the percentage degradation of Alizarin Yellow R for the various H_2O_2 concentrations. From the chart, 0.24M appears to be the optimal concentration for the Alizarin Yellow R degradation.

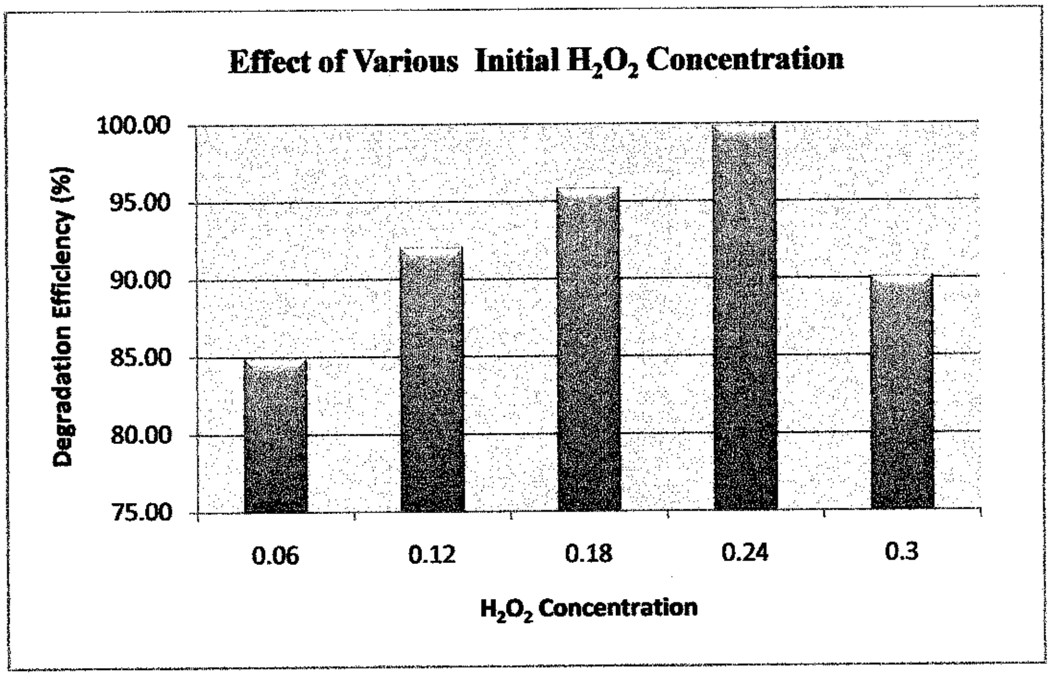


Figure 4.3: Effect of Various H_2O_2 concentrations on the percentage degradation

4.3 Effect of Initial Dye (Alizarin Yellow R) Concentration

Various initial dye concentrations were also tested to see the effect on degradation of Alizarin Yellow R using the UV/ H_2O_2 method. The results are presented in Figure 4.4 for a H_2O_2 concentration of 0.24M and pH 5.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of UV Radiation in the Presence on H_2O_2

Initially, the experiments were carried out with UV radiation only, hydrogen peroxide without UV radiation and UV radiation plus hydrogen peroxide. Figure 4.1 shows the concentration of Alizarin Yellow R against irradiation time for these experiments. When the irradiation was conducted in the absence of H_2O_2, there was no significant loss of the dye and the degradation of the dye was very small in the absence of UV radiation. However, when the sample subjected to UV light in the presence of H_2O_2, the results shows a significant decrease in the dye concentration. This reduction can be linked with the generation of hydroxyl radicals, which is a strong oxidizing agent.

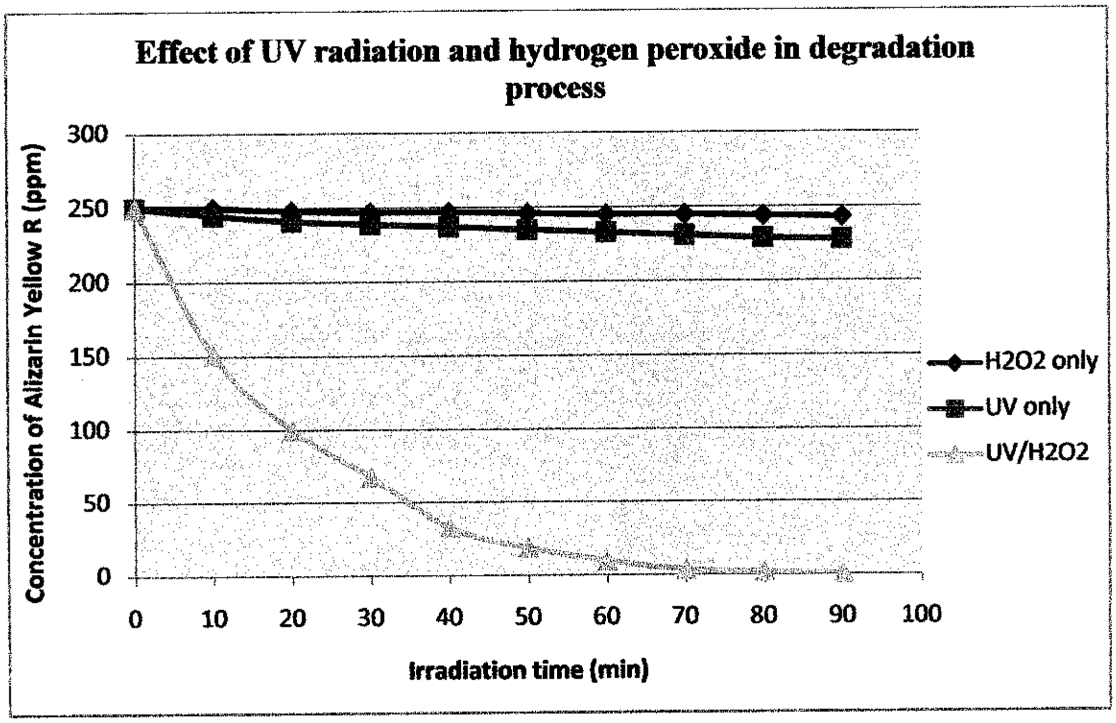


Figure 4.1: Effect of UV Radiation and Hydrogen Peroxide in degradation of Alizarin Yellow R [Initial dye concentration = 250ppm, H_2O_2 = 0.24M, pH = 5]

4.2 Effect of Initial H_2O_2 Concentration

Different concentrations of H_2O_2 (0.06M – 0.30M) were added to the prepared dye solutions to investigate the effect of H_2O_2 concentration on the degradation's efficiency. Figure 4.2 shows the concentration of Alizarin Yellow R dye as a function of UV irradiation time for various initial H_2O_2 concentrations.

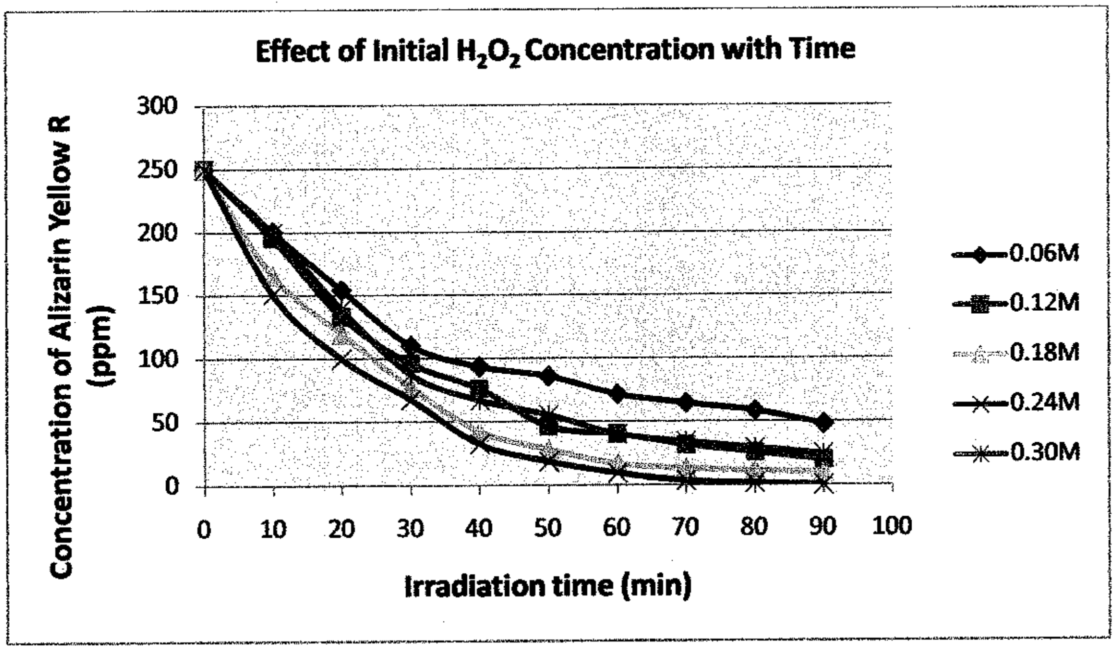


Figure 4.2: Effect of different initial H_2O_2 concentration with time [Initial dye concentration = 250ppm, pH=5, Temperature = 30°C]

Generally, the concentration of dye decreased along with time in the presence of H_2O_2 and UV. As can be seen from the graph, the degradation percentage increased as the initial concentration of H_2O_2 increases from 0.06M until 0.24M. However, further increase in H_2O_2 concentration from 0.24M to 0.30M decreases the degradation percentage. The degradation rate was limited at low H_2O_2 concentration, as there was insufficient production of hydroxyl radicals. As the H_2O_2 concentration increases, more hydroxyl radicals were formed to attack the aromatic structures leading to a faster oxidation rate (Equation 7 and 8). However, above 0.24M, these hydroxyl radicals preferred to react with the excess of H_2O_2 rather instead of reacting with the dye molecules (Legrini et al., 1993, Galindo & Kalt, 1999). The product of this competitive reaction hydroperoxyl radicals (HO2•) which are less reactive

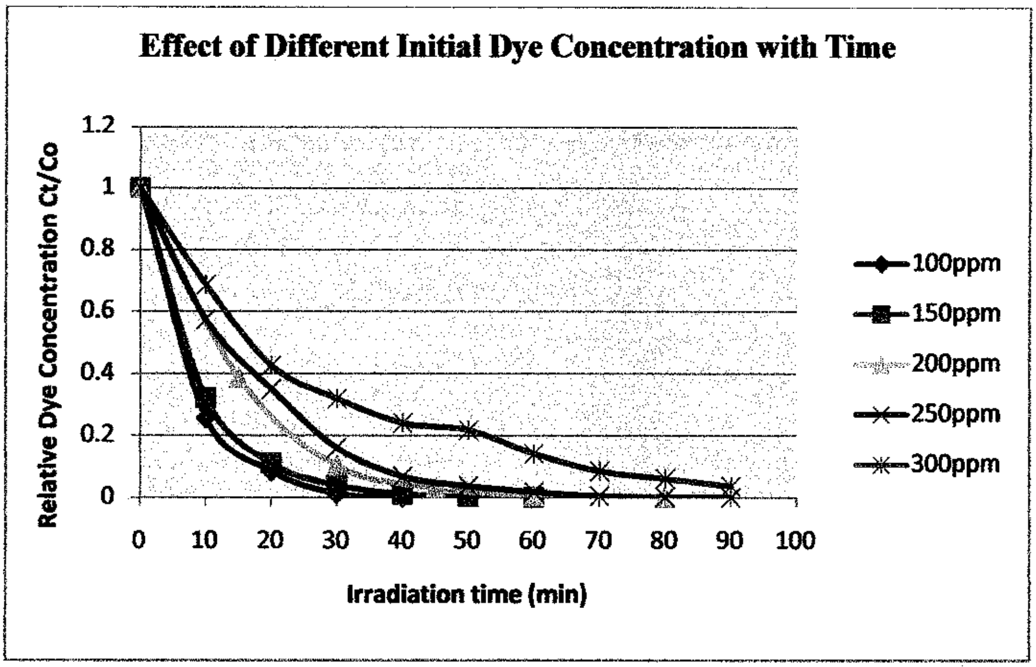


Figure 4.4: Effect of different initial dye concentration with time [$H_2O_2 = 0.24M$, pH = 5, Temperature = 30°C]

It can be seen that the degradation percentage decreased from 100% to only 35% in 40 minutes as initial dye concentration increased from 100 to 300 ppm, although the initial H_2O_2 concentration was the same.

This can be explained by considering that, as the dye concentrations increased, the absorption of UV radiation also increases, therefore the availability of UV light for reactions with H_2O_2 decreases and this subsequently results in lesser production of hydroxyl radicals in the tested solution (El-Dein et al., 2003). Based on the graph, it can be observed that the degradation rate fits the first order kinetics with respect to the concentration of azo dye as the rate constant changes when the initial concentration of Alizarin Yellow R is varied.

$$\frac{-dC}{dt} = k_{obs}C_t \qquad (12)$$

Where C_t is the concentration of the dye at a certain irradiation time (t), and k_{obs} is the first order rate constant.

$$\ln\left(\frac{C_o}{C_t}\right) = -k_{obs}t \qquad (13)$$

Integration of Equation 10 with the restriction of $C_t = C_o$ at $t = 0$ will lead to Equation 11. The results of the first order rate constants of Alizarin Yellow R degradation are presented in Table 4.1.

Table 4.1: First order rate constants of Alizarin Yellow R Degradation (80 min)

Initial Dye Concentration (ppm)	k_{obs}	r^2
100	0.154	0.986
150	0.119	0.992
200	0.086	0.995
250	0.075	0.993
300	0.034	0.987

It can be seen that the increase in dye concentration decreases the first order rate constant. The linear semi-log charts of C_t/C_o against time confirmed the first order reaction kinetics of the dye degradation rate with respect to the dye concentration. The slopes of the linear regression lines shown in Figure 4.5 were used to determine observed the initial first order rate constants for degradation of the dye. Different initial concentrations of the dye caused incomparable reaction conditions (Keller *et al.*, 2005) resulting in different k_{obs} values.

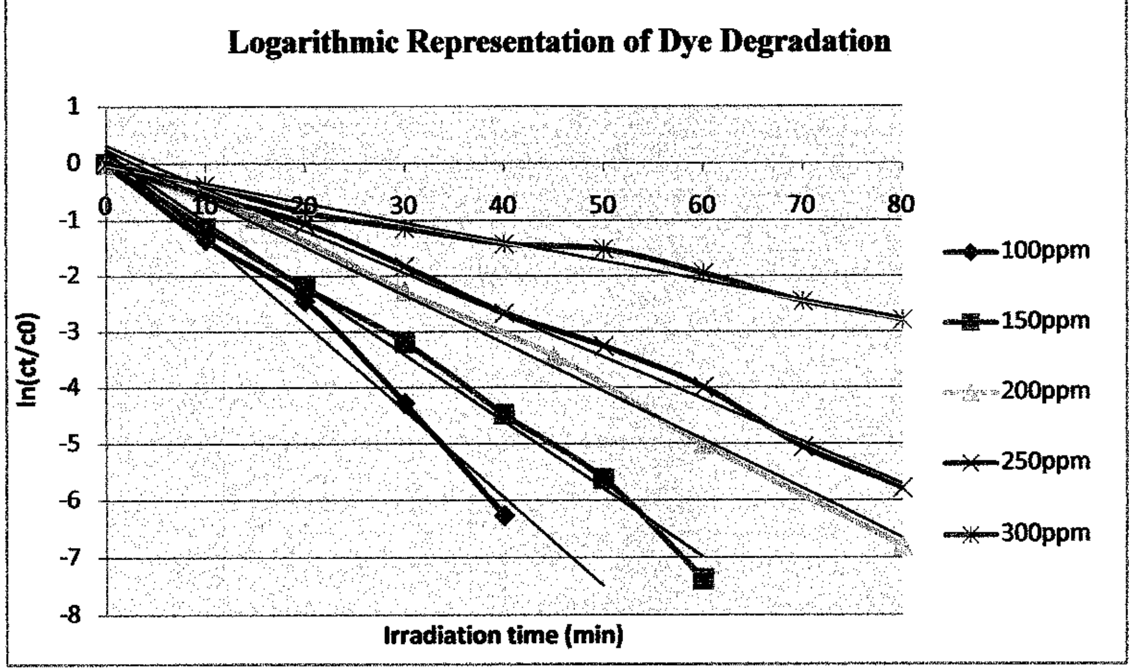


Figure 4.5: Logarithmic representation of Alizarin Yellow R Degradation with linear regression lines

4.4 Effect of Initial pH

The effect of different initial pH condition on the degradation of Alizarin Yellow R was examined by carrying out the experiments in different pH conditions (3, 5, 7, 9 and 11). The pH was varied by adding incremental amounts of either concentrated HCl or NaOH to the prepared dye solution. It is known that the pH of the solution will affect the efficiency of the UV/ H_2O_2 treatment process.

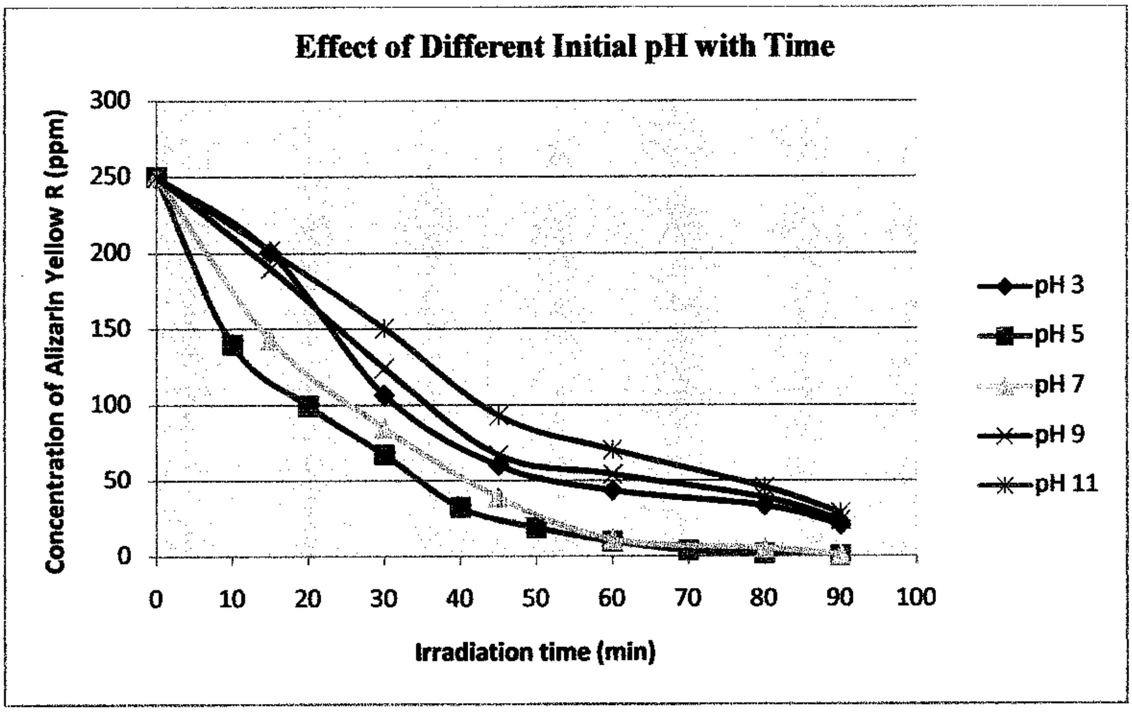


Figure 4.6: Effect of different pH with time [Initial dye concentration = 250ppm, H_2O_2 = 0.24M, Temperature = 30°C]

From Figure 4.6 we can see that during the 90 minutes of irradiation, the degradation is more efficient at medium acidic and neutral conditions and the efficiency decreases with increasing pH. This is most likely due to the fact that in alkaline condition, H_2O_2 will decompose into water and oxygen rather than hydroxyl radicals (Shu et al., 1994, Galindo et al., 1998). This causes the lower degradation rates of azo dyes at higher pH values because the concentration of OH• is reduced under these conditions.

increased the generation rate of hydroxyl radicals or directly affected the reaction rate with the dye molecule. Since the overall rate seems to be limited by the availability of hydroxyl radicals, it is likely that the higher temperature reduced the activation energy for the H_2O_2 reaction to hydroxyl radicals.

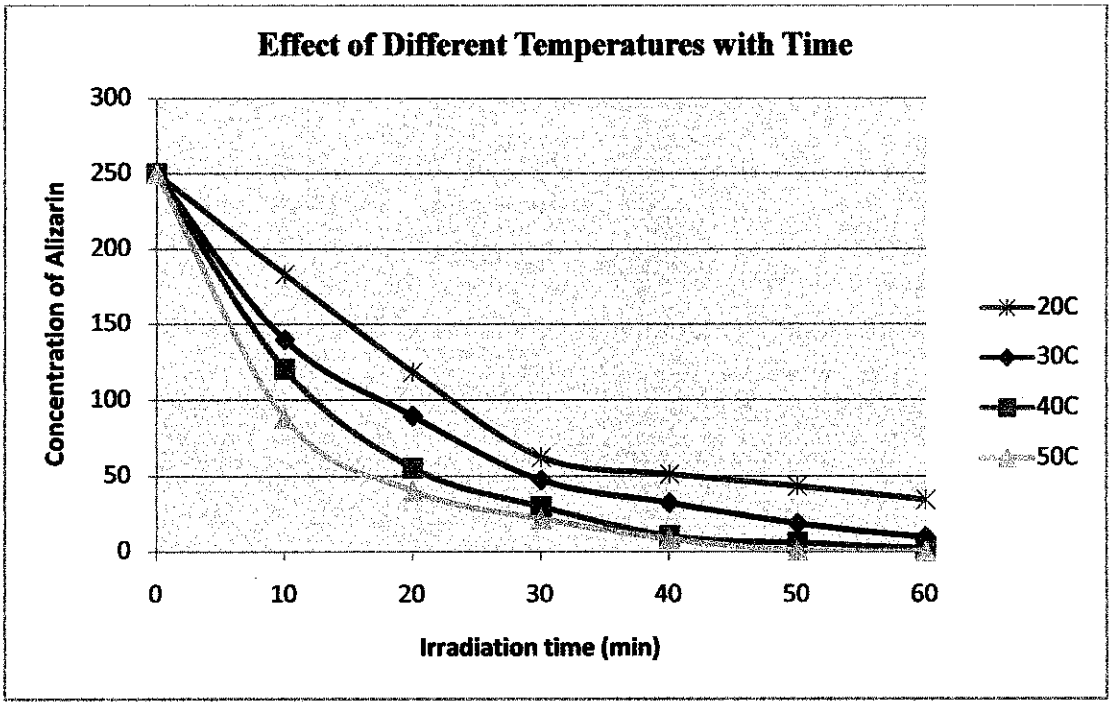


Figure 4.8: Effect of different temperature with time [Initial dye concentration = 250ppm, H_2O_2 = 0.24M, pH = 5]

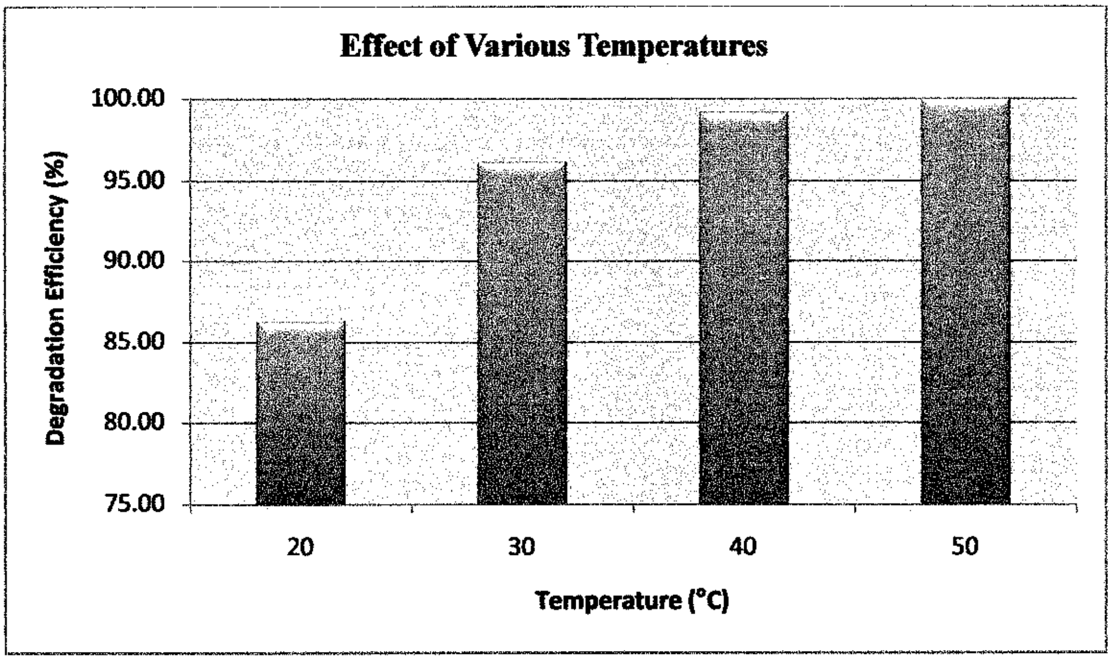


Figure 4.9: Effect of various temperatures on the percentage degradation

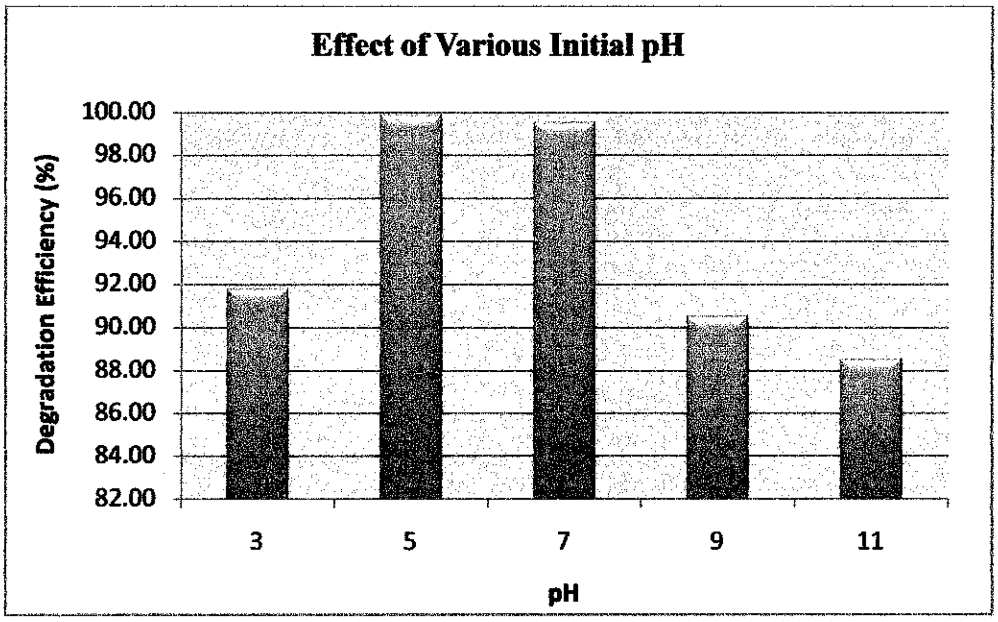


Figure 4.7 : Effect of various pH conditions on the percentage degradation

Figure 4.7 summarizes the percentage degradation of Alizarin Yellow R at various pH levels. The percentage degradation was increasingly less effective at pH values higher than 9. While acidic conditions achieve a more effective degradation, the effect of pH values in the range of 9 to 11 is still relatively limited. Typically, the final effluent from textile industries usually has normal to high pH (7-11). It would therefore be essential to ensure the most appropriate pH is used to get optimum reaction performance

4.5 Effect of Temperature

In order to investigate the effect of temperature on the degradation of dye, several experiments were conducted at temperatures between 20°C and 50°C, with H_2O_2 concentration of 0.24M, pH 5 and initial dye concentration of 250 ppm. The percentage of dye degradation increased with increasing temperature of the system as shown in Figure 4.8.

An almost complete degradation of Alizarin Yellow R was achieved in 60 minutes at 40°C, 50°C. The lowest degradation in this experiment was achieved at 20°C as incomplete degradation occurred even after 90 minutes of irradiation. Heating either

4.6 FTIR Analysis

To further examine the degradation mechanism of Alizarin Yellow R, FTIR analysis was performed using Shimadzu FTIR spectrophotometer. Figure 7 and 8 show the infrared spectrums of Alizarin Yellow R before and after degradation treatments, respectively.

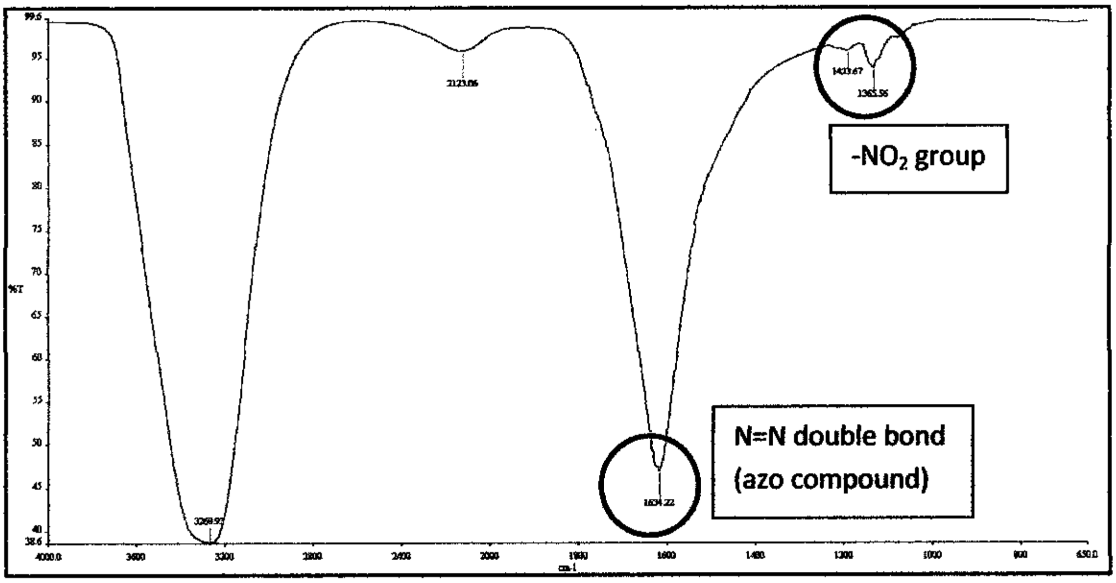


Figure 4.10:Infrared Spectrum of Alizarin Yellow R before treatment with UV/H_2O_2

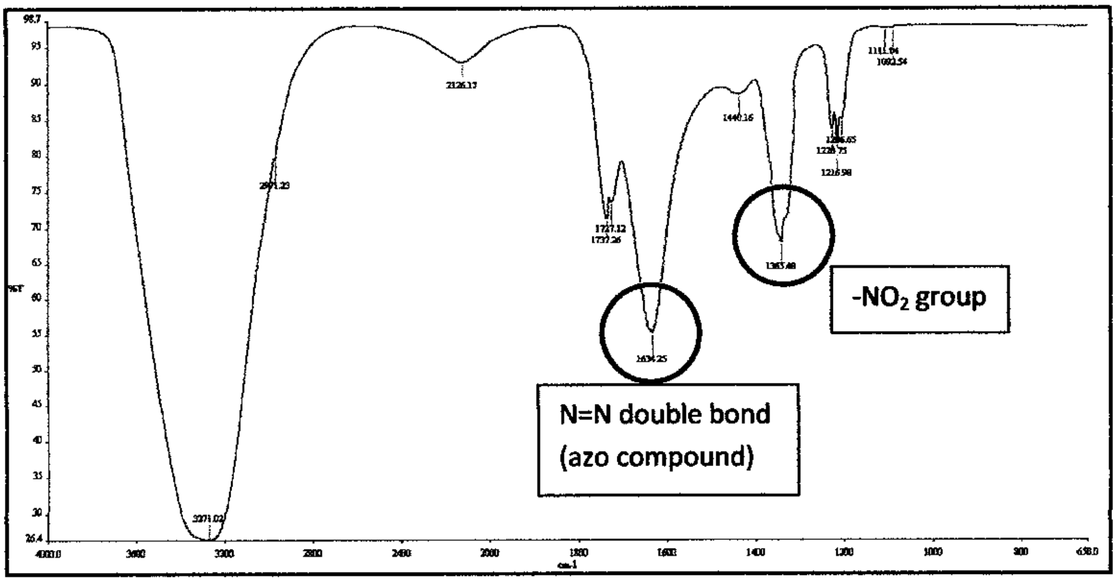


Figure 4.11: Infrared spectrum of Alizarin Yellow R after treatment with UV/H_2O_2

Comparing the intensity and position of spectral peak confirm the dissociation of –N=N– group in treated samples. Increase in the intensity of the $–NO_2$ peak at 1365cm^{-} confirms successful oxidation of azo group and its diminution leading to color removal. In this study, the amine formed as a result of reduction was further oxidized to nitro compounds. The oxidation of amine was proved in FTIR analysis as the amine band's intensity was reduced in the FTIR spectra.

4.7 Optimization

Screening of independent factor affecting the degradation percentage was carried out according to the Table 1. Range and level of factors was determined based on initial screening results which includes H_2O_2 concentration, initial pH, and temperature while other factors such as irradiation time, UV intensity and initial dye concentration was kept constant. Figure 4.12 indicates the Pareto Chart of standardized effect at p=0.05 which shows that all the three factors, initial H_2O_2 concentration, initial pH and temperature has a significant contribution on the degradation percentage.

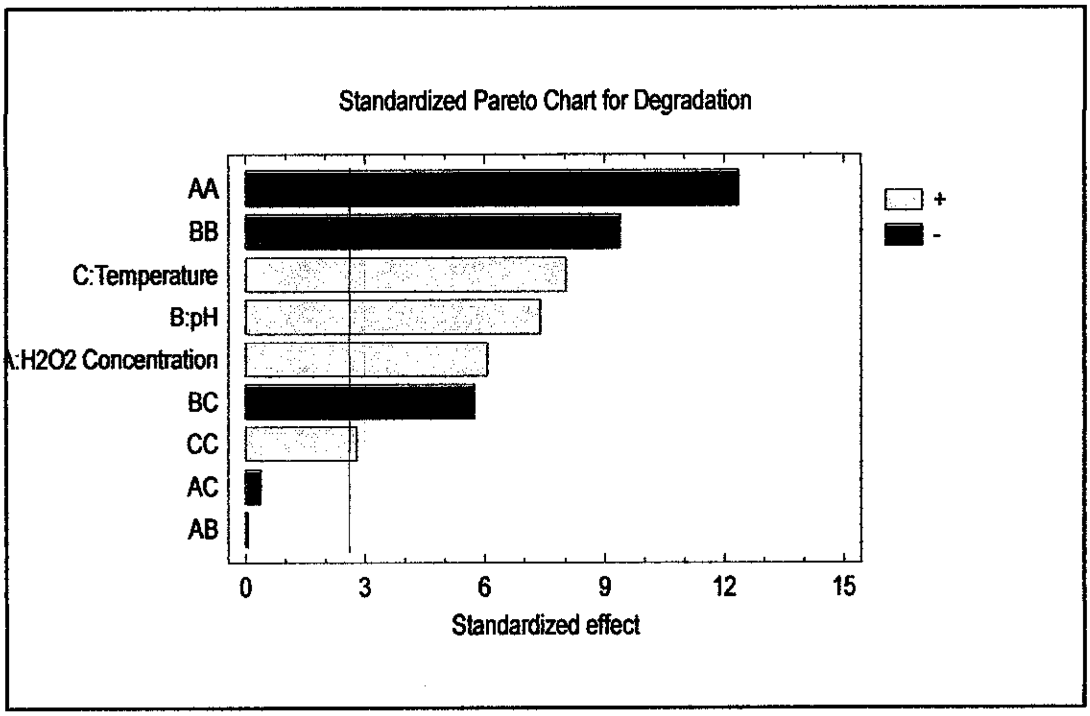


Figure 4.12: Pareto chart of the standardized effect for percentage of degradation

The optimum response and relationship between the factors and response were obtained by using response surface methodology. The quadratic regression model for the percentage of degradation is shown in Equation 12 below:

$$Y = -17.11 + 578.90X_1 + 12.34X_2 - 0.055X_3 - 1141.2X_1^2 - 0.125X_1X_2$$

$$-0.192X_1X_3 - 0.78X_2^2 - 0.09X_2X_3 + 0.009X_3^2 \qquad (14)$$

$R^2 = 0.989$

Where

$Y =$ Degradation percentage

$X_1 =$ Initial H_2O_2 concentration

$X_2 =$ initial pH

$X_3 =$ Temperature

Based on the model, the predicted value percentage degradation were calculated and compared with the observed value through the experiments. The results are summarized in Table and graph below.

Table 4.2: Comparison of degradation efficiency between predicted and observed values

Exp Num	H_2O_2 Concentration (M)	pH	Temperature (°C)	Degradation (%) experimental	Degradation (%) predicted
1	0.24	5	40	89.62	90.57
2	0.24	3	50	90.13	90.35
3	0.3	5	30	87.03	87.06
4	0.18	5	30	83.69	84.09
5	0.18	3	40	80.48	80.28
6	0.24	5	40	90.85	90.57
7	0.24	5	40	91.23	90.57
8	0.3	5	50	90.85	90.46
9	0.3	7	40	86.16	86.36
10	0.3	3	40	82.88	83.05
11	0.24	7	50	89.82	90.02
12	0.18	7	40	83.82	83.65
13	0.24	7	30	90.28	90.06
14	0.24	3	30	83.25	83.05
15	0.18	5	50	87.97	87.99

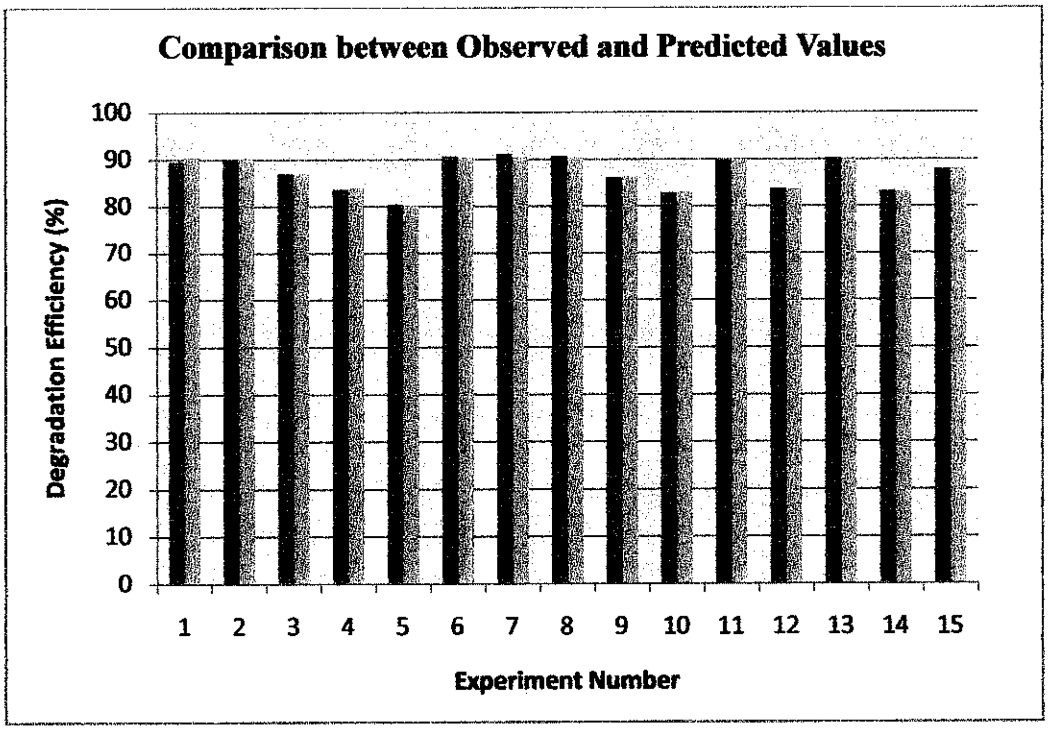


Figure 4.13: Comparison between observed and predicted values for each experiment conducted

In order to visualize the effect of factors towards the response (degradation percentage), a graphical representation known as contour plots (Figure 4.14 and 4.16) and 3D curvature of the regression model based on Equation 12 is shown in Figure below. The 3D curvature can be seen in Figure 4.15 and 4.17.

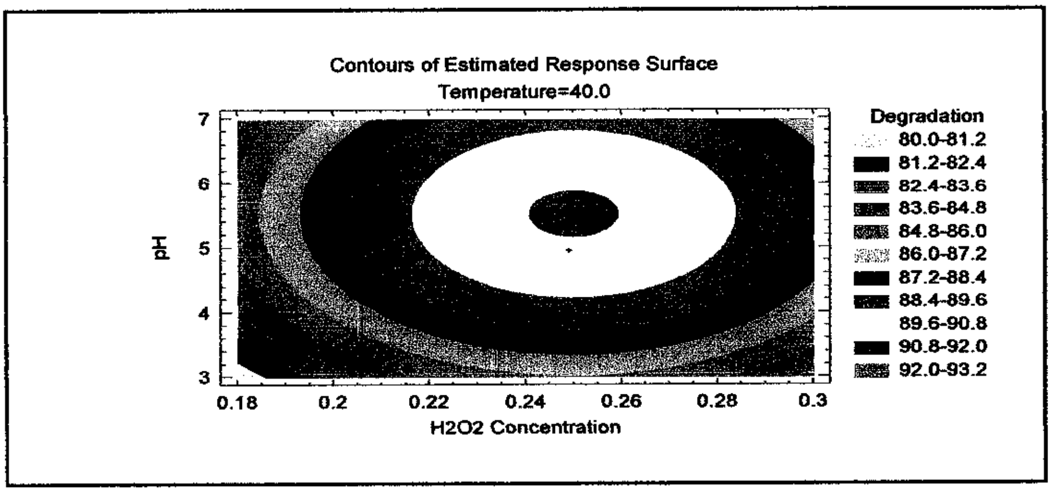


Figure 4.14: Contour plots for degradation of dye (at constant temperature)

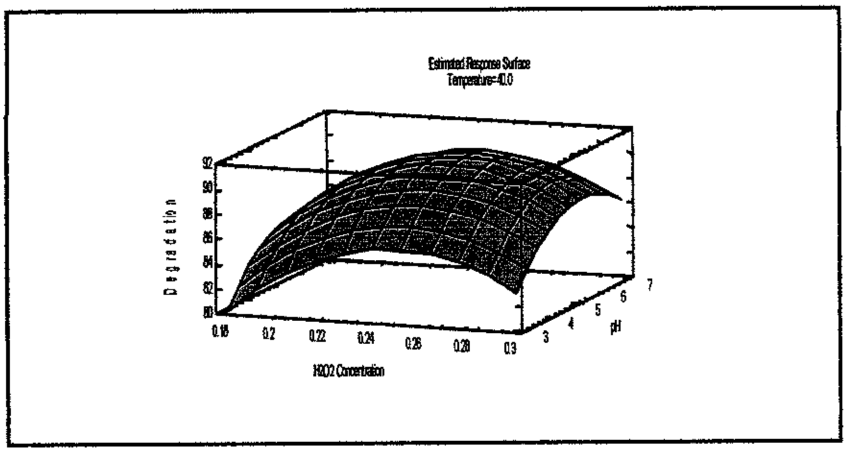


Figure 4.15: The effect of initial H_2O_2 concentration and pH on dye degradation for 250ppm initial concentration of dye (Temperature=40°C)

As demonstrated by the 3D semispherical response plot, the dye degradation percentage increased with the increase in pH until the optimum value of 4.59 and above this value the degradation efficiency decreased with the increase in pH. This is associated with the decomposition of H_2O_2 at high pH values as have been explained earlier. It can also been seen that, increasing H_2O_2 concentrations to a specific level results in an increase in degradation efficiency due to the increase in the generation of hydroxyl radicals. The decrease in degradation efficiency is related to the scavenging effect of H_2O_2 itself. (Equation 9-11). In Fig. 4.17, the effect of temperature and H_2O_2 concentration on dye degradation is shown at optimum pH 4.59 and it can be seen that dye degradation increased with increasing temperature.

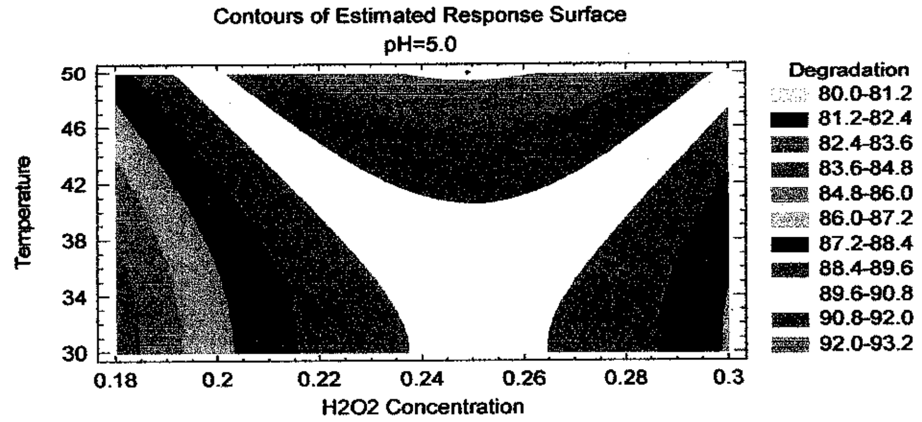


Figure 4.16: Contour plots for dye degradation (at constant pH)

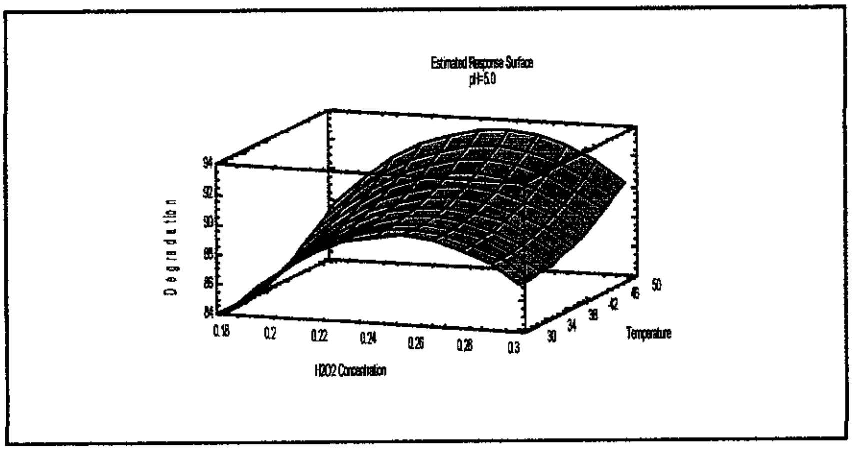


Figure 4.17: The effect of initial H_2O_2 concentration and temperature on dye degradation for 250ppm initial concentration of dye (pH=5)

The optimum conditions that obtained for oxidation are as given in Table 4.2 above. At this optimum condition, maximum value for the dye degradation was predicted to be 93.41%. In order to validate the validity of regression equation, additional two runs were carried out under the optimum conditions obtained through Box-Behnken Response Surface Methodology. The average degradation efficiency of 92.12% was achieved at the condition. The error of the model-predicted and experimental values of degradation efficiency was 1.29% which is in satisfactory agreement with the predicted value.

Table 4.3: The optimum condition for degradation of Alizarin Yellow R

Factor	Optimum Condition
H_2O_2 Concentration	0.25M
pH	4.95
Temperature	50.0

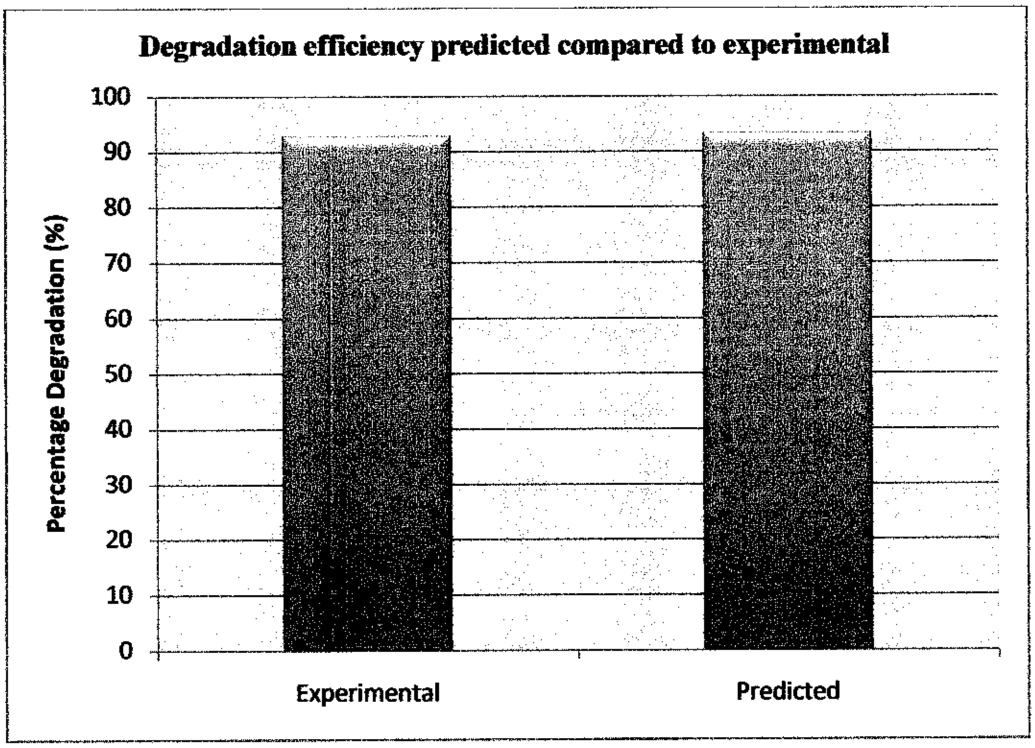


Figure 4.18: Predicted degradation efficiency compared to experimental at the optimum conditions

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this project, the experimental results show that the UV/H_2O_2 method can be efficiently utilized for the degradation of Alizarin Yellow R in a comparatively short period of time of which is 60 minutes at the optimum conditions. Various parameters particularly the initial H_2O_2 concentration, initial dye concentration, initial pH, as well as temperature strongly influence the degradation efficiency. The degradation process of Alizarin Yellow R follows first order kinetics with regards to dye concentration. Pseudo-rate constant decreases as the initial concentration of Alizarin Yellow R increases. The degradation efficiency increases with increase in initial H_2O_2 until to the optimum value of 0.24M and further increase in its concentration will reduce the degradation efficiency. The pH also had a large effect on the degradation efficiency of Alizarin Yellow R. The optimum initial pH value was around 4–6; a strong acid or alkaline environment was not beneficial to the oxidation reaction. Based on the Response Surface Methodology (RSM), the optimum condition for the oxidation of 400mL of total volume of 250ppm initial concentration of Alizarin Yellow R dye, by using the UV/H_2O_2 method was at temperature of 50°C, ph 4.59 and 0.25M of initial H_2O_2 concentration which results in degradation efficiency of 93.41%. The error of the model predicted and experimental value was found to be 1.29%. Therefore, this proves that the Box-Behnken Response Surface Methodology (RSM) was reliable to study the optimization of the degradation study of Alizarin Yellow R using UV/H_2O_2 method.

5.2 Recommendations

In general, the result indicates that the UV/H_2O_2 technology proved to have good potential for removing dyestuff from wastewater. However, further treatment might be necessary to achieve complete mineralization of the organic intermediates as FTIR analysis only indicates partial breakdown of the dye molecules. TOC (Total

Organic Carbon) removal test can be done to obtain a quantitative value for dye demineralization. Some alternatives proposed are extending the irradiation time or combining the UV/H_2O_2 method with other technologies that are able to give complete TOC removal.

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