ADVANCED OXIDATION PROCESS
FOR TREATMENT OF
AQUEOUS SOLUTION CONTAINING
POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

LAWRENCE LING HOE HO

CIVIL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
MAY 2013

Advanced Oxidation Process for Treatment of Aqueous Solution Containing Polycyclic Aromatic Hydrocarbons (PAHs)

by

Lawrence Ling Hoe Ho

Dissertation submitted in partial fulfillment of
the requirement of for the
Bachelor of Engineering (Hons)
(Civil Engineering)

MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Advanced Oxidation Process for Treatment of Aqueous Solution Containing Polycyclic Aromatic Hydrocarbons (PAHs)

by

Lawrence Ling Hoe Ho

A project dissertation submitted to the
Civil Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirements for the
BACHELOR OF ENGINEERING (Hons)
(CIVIL ENGINEERING)

Approved by,

____

(DR. AMIRHOSSEIN MALAKAHMAD)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

CERTIFICATION OF ORIGINALITY

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

(LAWRENCE LING HOE HO)

1

ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) is a type of persistent organic pollutant that categorized by United States Environmental Protection Agency (USEPA) as toxic, carcinogenic and mutagenic. The presence of PAHs in aquatic environment poses harmful effect to the aquatic life as well as the human beings due to the bioaccumulation in the food chain that can lead to cancer and birth defect. The advanced oxidation process- UV/H_2O_2 system had been adopted and carried out for the treatment of PAHs in the aqueous solution by many researchers. However, the optimization of the process for treatment PAHs had not yet been reported. In this study, the performance of the process was assessed by carrying out preliminary experiments and optimized by response surface methodology (RSM). The synthetic water sample was prepared by diluting the 16 PAHs standard solution mix in deionized water. The preliminary experiments were carried out to determine the range of the operational variables- H_2O_2 concentration, pH and reaction time. The maximum COD removal achieved in preliminary experiment was 71.5% under the operating condition of 1mM H_2O_2 concentration, pH of 3.5 and 90 minutes reaction time. The Design Expert Software was utilized for the optimization of the UV/H_2O_2 system by RSM based on five-level central composite design (CCD). The ranges for RSM were 1-3 mM for H_2O_2 concentration, 2-5 for pH and 30-90 minutes for reaction time. The quadratic equation fitted the model well and was found to be significant and adequate by ANOVA analysis and diagnostics plots. The optimum operating condition which achieved COD removal efficiency of 79.78% were H_2O_2 concentration of 1mM, pH of 3.5 and reaction time of 90 minutes. The experimental data and model prediction agreed well with error less than 3%. The PAHs removal efficiency was 84.28%. The study revealed that the UV/H_2O_2 process is effective for treatment of PAHs in aqueous solution and the process can be optimized by RSM.

ACKNOWLEDGEMENT

First of all, I would like to extend my sincere appreciation to my supervisor Dr. Amirhossein Malakahmad for his help, giving suggestion, guidance and encouragement to me in all the time of research and the experimental work of the study. My gratitude is also extended to my research group- Miss Sabariah (Phd Student) and my colleague, Mr Law Ming Xian for their guidance and support for the experimental works.

I wish to express my heartfelt thanks to all technicians from Civil, Chemical Engineering Department and Centralized Analytical Laboratory (CAL) especially Mr. Mohd. Khairul Anuar Jamaluddin, Ms. Yusyawati Yahya, Ms. Siti Fatimah and Mr. Hasbullah for their technical assistance and guidance.

An honourable mention also goes to the Final Year Project coordinators, Dr. Teo Wee and Ir. Idris Bin Othman for coordinating and providing relevant resources throughout the project.

My sincere appreciation also extends to my friends, colleagues and everyone who encouraged and supported me throughout the project.

Last but not least, I would like to thank my family members for their patience, support and understanding over the entire period of my studies.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

ABBREVIATION AND NOMENCLATURE

Adj. R^2	Adjusted Determination Coefficient
ANOVA	Analysis of Variance
AOPs	Advanced Oxidation Processes
AP	Adequate Precision
ATSDR	Agency for Toxic Substances and Disease Registry
CCD	Central Composite Design
COD	Chemical Oxygen Demand
CV	Coefficient of Variance
DHHS	Department of Health and Human Service
DOE	Department of Environment
GC/MS	Gas Chromatography and Mass Spectroscopy
IARC	International Agency for Research and Cancer
MCL	Maximum Contaminant Level
P	Probability of Error
PAHs	Polycyclic Aromatic Hydrocarbons
PLOF	Probability of Lack of Fit
POP	Persistent Organic Pollutants
PRESS	Predicted Residual Error Sum of Squares
R^2	Determination Coefficient
RSM	Response Surface Methodology
S.D.	Standard Deviation
SSR	Sum of Squares Due To Regression
SST	Total Sum of Squares
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The presence of persistent organic pollutants (POP) in the water and wastewater has become an emerging environmental concern recently. Polycyclic aromatic hydrocarbons (PAHs) are one of the major class of the persistent organic pollutants that consists of two or more fused aromatic (benzene) rings arranged in linear, angular and cluster order and do not contain any heteroatoms and or carry subsituents (Zakaria, Geik, Lee, & Hayet, 2005).

PAHs exist naturally but it is mainly derived from anthropogenic inputs that consists of petrogenic and pyrogenic sources. The accidential oil spills, discharge from routine tanker operations, municipal and urban runoff contributes to the petrogenic sources of PAHs. The pyrogenic PAHs are produced by incomplete combustion and prolysis of fossil fuels, organic materials, and biomass (Zakaria, Takada, Tsutsumi, Ohno, Junya Yamada, & Kumata, 2002; Zakaria et al., 2005; Qi, Liu, & Pernet-Coudrier, 2013; Zakaria & Mahat, 2006). They were found and deposited in the different medium like air, water, soil, food, plants and animals (Ledakowicz, Miller, & Olejnik, 1999).

PAHs had been detected in waste and natural waters especially the disharge of high PAHs contaminants from the creosote wood preservatives industry ((Vilhunen, Vilve, Vepsäläinen, & Sillanpää, 2010; Engwall, Pignatelloa, & Grasso, 1999; Shemer & Linden, 2007). Concentration of PAHs in surface waters varies quite widely from 0.1 to 830 ng L^{-1} (C.A., Menzie; B.B., Potocki; J., Santodonato, 1992). The occurrence, distribution and fate the polycyclic aromatic hydrocarbons (PAHs) in the estuaries and river have been reported in some studies conducted in different countries such as China and Malaysia (Qi et al., 2013; Zakaria et al., 2002; Zakaria et al., 2005). Qi et al. (2012) reported the concentration of 16 PAHs in ranged from 193 to 1790 ng/L in Wenyu River and North Canal’s surface waters, 245 to 404 ng/L in WWTP effluents and 431 to 2860 ng/L in the wastewater from the small sewers in Beijing, China. Zakaria et al. (2005) also reported the total PAHs of 1759.0 ng/g in leachate, 4781.9 ng/g in ground water, 4723.4 ng/g in landfill upstream river and 3659.4 ng/g in landfill-down-stream river at Taman Beringin and Ulu Maasop landfill site located at Kuala Lumpur, Malaysia. The Chrysene was found to have maximum concentration of 358.5 ng/g in ground water which exceeds the Maximum Contaminant Level (MCL) limit by USEPA. This indicates that the river water was polluted by the PAHs.

1.2 Problem Statement

PAHs are ranked as the 9th priority hazardous substances by the Agency for Toxic Substances and Disease Registry (ATSDR) in 2011 (ATSDR, 2011). Certain members of PAHs class like Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, Benzo(g,h,i)perylene, Indeno(1,2,3-c,d)pyrene are classified as possibly and probably toxic, carcinogenic, mutagenic and tumorigenic to human and animals by the Department of Health and Human Service (DHHS), International Agency for Research and Cancer (IARC) and United States Environmental Protection Agency (USEPA) (IARC, 1998; ATSDR, 1995; Tran, Drogui, Mercier, & Blais, 2009).

The PAHs carcinogenicity has been tested in various animals and resulted in benign and malign tumour (Jacob, 1996; ATSDR, 1995). PAHs exert their mutagenic and carcinogenic activity through biotransformation to chemically reactive intermediates- diol epoxides which bind covalently to cellular macromolecules (inter alia DNA) (WHO Regional Office for Europe, 2000). PAHs can have detrimental effects on the affected habitats' plants and animals, resulting in uptake and bioaccumulation of toxic chemical in aquatic organism and food chains that lead to cancer and birth defects in human (Samanta, Singh, & Jain, 2002).

Different approaches like volatilization, photo and chemical oxidation, absorption to soil particles, leaching, bioaccumulation and biodegradation are adopted to remove the PAHs in water (Shemer & Linden, 2007). Advanced oxidation process (AOPs) is one of the promising treatment method to oxidise the organic pollutants by producing reactive radicals.The treatment of PAHs in aqueous solution by UV/H_2O_2 system had been reported by many researchers and it is very effective. But, the process is not yet been optimized for treatment of PAHs in aqueous solution.

1.3 Objectives and Scope of Study

The objectives of this project were:

1) To access the performance of UV/H_2O_2 system for the treatment of PAHs in synthetic aqueous solution by varying one factor while keeping other factors as constant.
2) To optimize the experimental condition of the UV/H_2O_2 system for the treatment of PAHs in synthetic aqueous solution based on response surface methodology (RSM).

In this project, the reaction solution was prepared by introducing 2mL of diluted 16 PAH Accustandard PAH mix into deionized water. The UV/H_2O_2 system was employed for the treatment of synthetic solution containing PAHs to study its performance. The preliminary analysis was divided into three sets of experiments to determine the most favorable H_2O_2 concentration, pH and reaction time. The Design Expert Software 6.0.7 was used for the design of experiments for optimization of treatment process by adopting response surface methodology (RSM). The AVONA analysis was carried out to determine the interaction between the experimental variables and the responding variables and the significance of each variable. Three-dimensional plot and contour plot were obtained to study the effect of variables on the responding variables. The optimum operating condition of each variable for maximum COD removal efficiency by UV/H_2O_2 system was determined based on desirability plot. Then, extra experiments were carried out to verify the optimized model prediction. Last, the final concentration of PAHs of treated sample was determined based on the optimized operating condition by RSM.

1.4 Significance of the Project

This project is very important because the presence of recalcitrant and persistent PAHs in the wastewater's effluent and river have been reported in many studies. The PAHs pollution was detected in Malaysian waters with concentration in the range of 1700 to 4800ng/g (Zakaria et al., 2005). The PAHs pose detrimental health effect such as cancer and birth defect due to the long term accumulation in the food chain and exposure to the sources. Therefore, the UV/H_2O_2 system was adopted for treatment of synthetic aqueous solution containing PAHs and the operating variables were optimized by using RSM. The study can serve as a reference for other researchers dealing with water and wastewater with high concentration of PAHs.

1.5 The Relevancy and Feasibility of the Project within Scope and Time Frame

The project was relevant to me as a final year civil engineering student since I had been exposed to the knowledge learnt during the year of study like environmental engineering, wastewater engineering and probability and statistics. This project was feasible because all the equipment and apparatus were available in the laboratories at Universiti Teknologi PETRONAS and chemicals can be purchased locally. The project was supervised by Dr. Amirhossein and assisted by the post graduate student and lab technicians. The project was also feasible within the time and scope by progressing according to the Gantt chart scheduled.

CHAPTER 2
LITERATURE REVIEW

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic chemicals that made up of more than 100 different compounds that made up of two or more fused aromatic (benzene) ring. PAHs are lipophilic, hydrophobic, highly-stable and persistent in nature with low vapour pressure, water solubility and bio-availability (Meulenberg, Rijnaarts, Doddema, & Field, 1997; Christensen et al., 2004; Li & Chen, 2002) The vapour pressure and water solubility decrease with increasing molecular weight. While the resistant to chemical and biological degradation of PAHs increase with increasing molecular weight. (Zakaria et al., 2005).

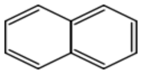
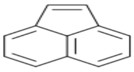
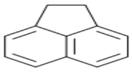
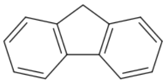
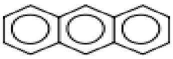
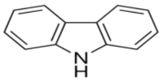
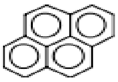
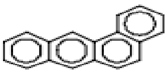
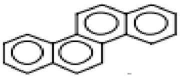
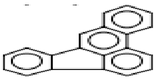
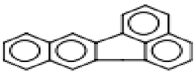
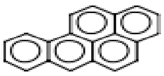
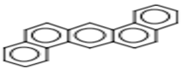
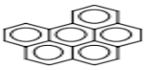
PAHs are classified into two molecular weight classes based on the physical, chemical and biological propoerties. PAHs with two and three aromatic rings such as Naphthalene ($C_{10}H_8$, M.W. 128.16) and Phenanthrene ($C_{14}H_{10,}$ M.W.178) are classified as low molecular weight PAHs. While the high molecular weight PAHs have four to seven aromatic rings such as Fluoranthene ($C_{16}H_{10}$ M.W.202) and Benzo(g,h,i)perylene ($C_{22}H_{12,}$ M.W.276) (Zakaria & Mahat, 2006). The higher molecular weight PAHs has significant acute toxicity to aquatic organisms, whereas the lower molecular weight PAHs do not (Zakaria et al., 2005).

The mximum containminant level (MCL) of the high molecular weight PAHs in water had been established by USEPA. The Safe Drinking Water Act also regulate the maximum containminant level of 0.0002 mg/L for benzo(a)pryene in the drinking water (DHHS, 2011). So far, there is not any standard established by Department of Environment (DOE) of Malaysia regarding the maximum containminant level of

PAHs in water except for Benzo(a)pryene that has maximum limit of 0.7 ppb that regulated in the National Standard for Drinking Water Quality.

The structure arrangement, molecular weights, water solubility, Log Octanol-Water Partitioning Coefficient- log (K_{ow}) and the mximum contaiminant level (MCL) of the major PAHs are summarized in the Table 2.1.

Table 2.1: Physical, chemical properties and MCL of PAHs (Bernal-Martinez, Carrere, Patureau, & Delgenes, 2007; USEPA, 2011; Gehle, MD, & MPH, 2011)

Compounds	**Structure**	**Molecular weight (gmol^{-1})**	**Water solubility at 25°C (mgl^{-1})**	**Log Octanol-Water Partitioning Coefficient Log (K_{ow})**	**MCL (pbb)**
Naphthalene		128	30	3.5	
Acenaphtylene		152	3.47	3.94	
Acenaphthene		154	4.24	3.92	
Fluorene		166	1.922	4.22	
Phenanthrene		178	1.0	4.46	
Anthracene		178	0.045	4.5	
Carbazole		167	7.48	3.59	
Fluoranthene		202	0.206	4.9	
Pyrene		202	0.132	4.88	
Benzo(a)anthracene		228	0.0094	5.63	0.1
Chrysene		228	0.0018	5.63	0.2
Benzo(b)fluoranthene		252	0.0015	6.04	0.2
Benzo(k)fluoranthene		252	0.0080	6.21	0.2
Benzo(a)pyrene		252	0.0016	6.06	0.2
Dibenzo(a,h)anthracene		278	0.0050	6.86	0.3
Benzo(g,h,i)perylene		276	0.0007	6.78	0.3
Indeno(1,2,3-c,d)pyrene		276	0.0002	6.58	0.4

2.2 Advanced Oxidation Processes (AOPs)

Among the chemical treatment process, advanced oxidation processes (AOPs) have received increased attention for treatment of wastewater containing recalcitrant organic pollutants. AOPs are based on the production of reactive radicals mostly hydroxyl radicals (OH·) that has high electro-chemical oxidant potential of 2.8V and oxidation reaction of 10^8 - 10^{10} $M^{-1}s^{-1}$ as a strong oxidant to oxidize the organic compounds. The typical AOP systems are summarized in Table 2.2. The oxidizing agents with their respective electrochemical oxidation potential are summarized in Table 2.3.

Table 2.2: Typical AOP systems (Gan H. C., 2010)

System	**With irradiation**	**Without irradiation**
Homogenous system	O_3/UV	O_3/ H_2O_2
	H_2O_2/UV	O_3/ OH^-
	H_2O_2/Fe^{2+}/UV (photo-Fenton)	H_2O_2/Fe^{2+} (Fenton)
	Electron beam	
	Ultrasound (US)	
	H_2O_2/US	
	UV/US	
Heterogeneous system	TiO_2/O_2/UV	Electro-Fenton
	TiO_2/ H_2O_2/UV	

Table 2.3: Oxidizing agents with the electrochemical oxidation potential (Metcalf & Eddy, 2004)

Oxidizing agent	**Electrochemical oxidation potential (EOP), V**	**EOP relative to chlorine, V**
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

The compounds may undergo different extent of degradation such as primary degradation (change in parent compound), acceptable degradation/defusing (change in parent compound to the extent the toxicity is reduced), ultimate degradation/ mineralization (conversion of organic carbon to inorganic carbon) and unacceptable degradation/fusing (change in parent compound resulting in increased toxicity (Metcalf & Eddy, 2004).

2.3 UV/ H_2O_2 System

Hydrogen peroxide is a strong oxidant with electro-chemical oxidant potential of 1.78 V to remove the low level of pollutants in the wastewater. But, the individual usage of H_2O_2 is not efficient for degradation of more recalcitrant and complex pollutants. In this case, the combination of UV irradiation and hydrogen peroxide is adopted for the treatment to produce the hydroxyl radicals which acts as stronger oxidizing agent. The utilization of the UV/ H_2O_2 system is found to have higher reaction rate due to the combination of two possible degradation pathways, direct photolysis and reaction with hydroxyl radicals. The UV light itself are very capable of degradation by initiating bond cleavage. The direct photolysis of hydrogen peroxide generates the hydroxyl radicals to oxidize the pollutants into products. The reaction mechanism of the two processes is shown as below:

$$A + hv \rightarrow \text{Products} \qquad (1)$$

$$H_2O_2 + hv \rightarrow 2OH\cdot \qquad (2)$$

$$A + OH\cdot \rightarrow \text{Products} \qquad (3)$$

Hydrogen peroxide can also react with hydroxyl radicals and the intermediary products formed thereby, according to the reaction mechanism described in a simplified way by Equations 7 to 11 (Alfano, Brandi, & Cassano, 2001)

$$H_2O_2 + OH\cdot \rightarrow \cdot HO_2 + H_2O \qquad (4)$$

$$H_2O_2 + \cdot HO_2 \rightarrow OH\cdot + H_2O + O_2 \qquad (5)$$

$$2OH\cdot \rightarrow H_2O_2 \qquad (6)$$

$$2\cdot HO_2 \rightarrow H_2O_2 + O_2 \qquad (7)$$

$$OH\cdot + \cdot HO_2 \rightarrow H_2O_2 + O_2 \qquad (8)$$

2.4 Factors influencing the Performance of UV/ H_2O_2 system

The operating variables are those factors that are varied during the treatment process to achieve the desired removal efficiency. In this case, the factors consist of hydrogen peroxide concentration, reaction time, wavelength of UV lamp and pH of water sample.

2.4.1 Effect of H_2O_2 concentration

The dosage of hydrogen peroxide depends of the initial concentration of pollutants in the water sample. The higher the concentration of pollutants, the higher the dosage of hydrogen peroxides. The increment of H_2O_2 concentration will produce more hydroxyl radicals to for the degradation of organic pollutants thus increase the removal efficiency. However, in the excess of hydrogen peroxide, the hydroxyl radicals tend to undergo scavenging of OH• by H_2O_2 and formation of hydroperoxyl radical as shown in Equation (7) to inhibit the degradation process. Ledakowicz et al. (1999) and Rivas et al. (2000) found out that the beneficial doses of hydrogen peroxide which maximally accelerate the degradation equal to about 0.01 M for studied PAHs (Acenaphthylene, Benzo(a)pyrene, Chrysene, Fluorene). Beltran et al. (1996) also reported the simultaneous presence of hydrogen peroxide at concentration between 10^{-3} and 10^{-2} M and 254 nm UV radiation yields significant improvements in the rate of disappearance of PAHs (Fluorene, Phenanthrene and Acenaphthene) in water.

2.4.2 Effect of UV irradiation

The low-pressure mercury vapour lamp with UV radiation of 254 nm wavelength was used for many studies oxidation of PAHs by UV/ H_2O_2 system (Beltran, Ovejero, & Rivas, 1996; Rivas, Beltrán, & Acedo, 2000; Ledakowicz et al., 1999; Vilhunen et al., 2010). According to Gan (2010), the degradation of organic pollutants in leachate was found to be the most effective under the UV irradiation of wavelength ≈ 356 nm. From the economic point of view, the UV lamp with 365 nm of wavelength is preferred for the photo-Fenton process because it is cheaper than the medium pressure mercury lamps with 254 nm of wavelength (Gan, Elmolla, & Chaudhuri, 2012).

2.4.3 Effect of pH value

The pH value influences activity of the oxidant and the substrate, the production of hydroxyl radicals and thus the oxidation efficiency of the process. Beltran et al. (1996) observed that the increase of pH from 2 to 7 leads to an increase of PAHs (fluorene, phenanthrene and acenaphthene) disappearance rate, but at higher increase of pH, up to 12 definitively reduces the oxidation rate. Neutral pH seems to be most appropriate to carry out the UV/ H_2O_2 oxidation of PAHs by different researchers (Ledakowicz et al., 1999; Shemer & Linden, 2007; Trapido, Veressinina, & Munter, 1995).

2.4.4 Relevant Research on Treatment of PAHs

Vilhumen et al. (2010) reported the UV photolysis and UV/ H_2O_2 were found to be efficient for the PAH removal in creosote contaminated groundwater. The UV_{254} and TOC removal efficiency of creosote contaminated groundwater consisting mainly of PAHs compound remained constant after 30 and 60 minutes reaction with 3mM of H_2O_2 dosage. The UV + 3mM H_2O_2 treatment successfully remove the concentration of Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenathrene, Anthracene, Fluoranthene and Pyrene to less than 0.1 *u*g/l after 60 minutes.

Rivas et al. (2000) found Acenaphthylene, 2.6 mg/l, to be readily degradable with UV/ H_2O_2 method (UV light: 254 nm, $I_0 = 3.48 \times 10^{-6}$ Einstein l^{-1} s^{-1}, L = 4.5 cm). With the treatment time less than 10 min the compound was totally decomposed with H_2O_2 dose 1 mM. The treatment was less efficient with H_2O_2 concentration of 400 mM.

Ledakowicz et al. (1999) studied the destruction of polycyclic aromatic hydrocarbons (PAHs): benzo(a)pyrene, chrysene and fluorene in aqueous solution using H_2O_2/ UV system. The optimum doses of hydrogen peroxide equal to about 0.01 M for all studied PAHs to accelerate the degradation of PAHs. The neutral and acidic condition of the solution enhances the removal of PAHs at optimal hydrogen peroxide concentration. The rate constants of the hydroxyl radicals and selected PAHs reaction were found to be $2.53x10^{10}$, $9.82x10^{9}$ and $2:77x10^{9}$ $M^{-1}s^{-1}$ for Benzo(a)pyrene, Chrysene and Fluorene, respectively.

The aqueous oxidation of three polynuclear aromatic hydrocarbons, fluorence, phenanthrene and acenaphthene was studied by Beltran et al. (1998). The Fenton's reagent was confirmed to have higher oxidation rate than other AOPs including ozone, UV radiation and hydrogen peroxide based on the experiment results obtained. The reactivity was in the following decreasing order: Phenathrene > Fluorene > Acenapthene.

Beltran et al. (1996) also reported the presence of hydrogen peroxide concentrations between 10^{-3} and 10^{-2} M and 254 nm UV radiation results in improved rate of PAH removal in water. Thus, total oxidation of the initial PAH is achieved in less than 7 min as compared to UV radiation or direct photolysis process which require 20 min. The UV/ H_2O_2 oxidation should be carried out most appropriately in neutral pH.

Trapido et al. (1995) studied the reaction kinetics of ozonation and advanced oxidation processes (AOP) of seven polycyclic aromatic hydrocarbons (PAH). Ozonation was shown to be quite effective for destruction of PAH, especially in neutral media. The reaction rates as well as the second order rate constants of PAH-ozone rection follow the series benzo(a)pyrene > pyrene > anthracene > phenanthrene > fluoranthene > benzo(ghi)perylene > fluorene.

The degradation and detoxification of wood preservatives creosote and pentachorophenol in water by the photo-Fenton reaction was studied by Engwal et. al. (1999). The study was carried out under photo-Fenton reaction, Fe^{3+}/ H_2O_2/ UV ($Fe3^{+}$=1 mM, H_2O_2=10 mM, H_2O_2/ TOC = 40:1, $1.4\times10{-}3$ M h ν min^{-1} black lamp ultraviolet light (UV) with emitting wavelength of 300nm to 400nm, pH=2.75 and 25° C). Substantial (>90%) transformation of 37 PAHs parent compounds was achieved in 5 min, except for a few 4- and 5-ring PAHs with more extensive transformation occurring thereafter. The reactivity followed the order: 2 ring PAHs> heterocyclics> phenolics> 3 ring PAHs> 4 – 5 ring PAHs.

2.5 Response Surface Methodology (RSM)

Design expert software is software for design of experiment (DOE) by Stat-Ease. It provides many powerful statistical tools like two level factorial screening studies, general factorial studies, response surface methodology (RSM), mixture design techniques and combination of process factors, mixture components and categorical factors. Besides, the program also offers rotatable 3D plots for visualization of response surface and interactive 2D contours graph.

Among the statistical tools, RSM is applied to obtain the ideal process settings for the optimum performance. RSM consists of a group of mathematical and statistical techniques used in the empirical study of the relationship between responses of interest, y and number of input variable denoted by x_1, $x_{2,}$ $_{\dots}$ x_k (I.Khuri & Mukhopapdhyay, 2010; Lin & Peterson, 2009). This method was introduced by G. E. P. Box and K. B. Wilson in 1951 (Wikipedia, 2013). The stages in the application of RSM as an optimization technique are as follows (Bezerra, Santelli, Oliveira, Villar, & Escaleira, 2008):

1) The selection of independent variables of major effects on the system through literature review and the delimitation of the experimental region, according to the objective of the study and the experience of the researcher
2) The choice of the experimental design and carrying out the experiments according to the selected experimental matrix
3) The mathematic – statistical treatment of the obtained experimental data through the fit of a polynomial function
4) The evaluation of the model's fitness
5) The verification of the necessity and possibility of performing a displacement in direction to the optimal region

6) Obtaining the optimum values for each studied variable.

RSM consists of different symmetrical experimental designs such as three-level factorial, Box – Behnken, central composite, hybrid, one-factor, Pentagonal, Hexagonal, distance-based and Doehlert designs. The central composite design most utilized for the analytical procedures development for process optimization. This design consists of the following parts:

(1) A full factorial or fractional factorial design;

(2) An additional design, often a star design in which experimental points are at a distance α from its center; and

(3) A central point.

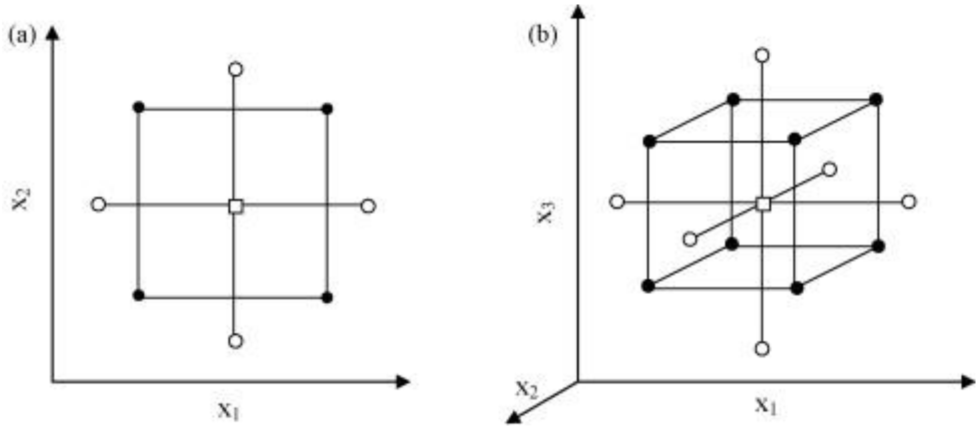


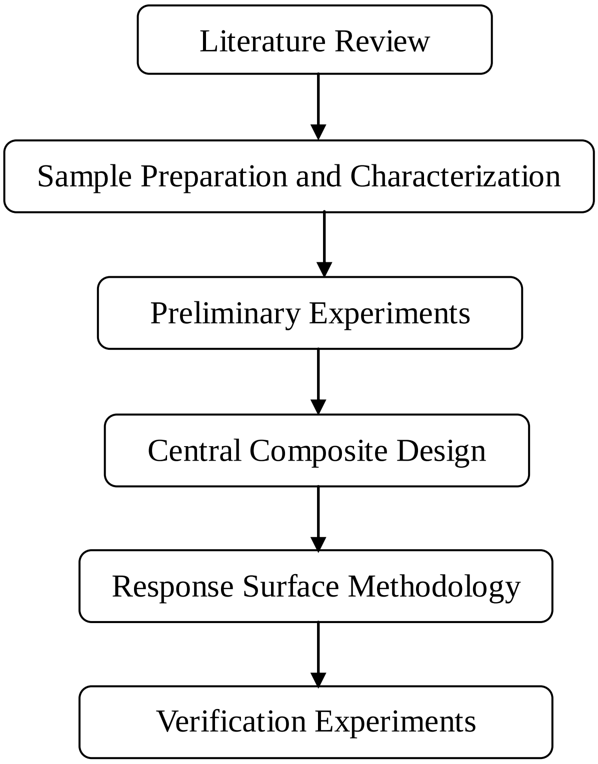
Figure 2.1: Central composite design for optimization of two and three variables (Bezerra et al., 2008)

RSM has been used to optimize the Fenton treatment of amoxicillin and cloxacilin antibiotic aqueous solution (Affam, Chaudhuri, & Kutty, 2012), photo-Fenton treatment of mature landfill leachate (Gan, Elmolla, & Chaudhuri, 2012), Cr (VI) reduction and removal by electrocoagulation (Ölmez, 2009), Fenton and electro-Fenton oxidation of biologically treated coking wastewater (Zhu, Tian, Liu, & Chen, 2011).

CHAPTER 3

METHODOLOGY

3.1 Project Activities



First, the research based study on the PAHs and the treatment method was carried out by searching the relevant journal, articles, book and website. The synthetic water solution containing PAHs was prepared and used for the treatment by dilution of the standard PAHs mix solution into the deionized water. The initial COD, TOC, pH and concentration of PAHs in the aqueous solution was determined. Three sets of preliminary experiments were carried out to determine the range of studied operational variables- H_2O_2 concentration, pH and reaction time for RSM design. Then, the Design Expert Software was used for the experimental design to optimize the UV/H_2O_2 system for efficient removal of COD in sample based on response surface methodology (RSM). The experiments were carried out based on central composite design based on the different of combination of operational variables. The relationship between response and variables and significance of operating variables were analysed. The 3D surface plot and contour was obtained to study the relationship between the variables and response. The optimum condition for the UV/H_2O_2 process was determined accordingly. Finally, the verification experiments were carried out to verify the predicted optimized model by RSM. Lastly, the PAHs concentration of the treated sample based on optimized model prediction was determined to access it removal efficiency.

3.2 Equipments, Apparatus, Chemicals and Software

3.2.1 Equipments and Apparatus

1) 1L Volumetric flask
2) 1L Pyrex reactor
3) 2 L Filter funnel
4) Separate funnel
5) Magnetic stirrer
6) UV lamp (Spectroline model; EA-160/FE, 230 V, 0.17 A, Spectronics Corporation, New York, USA) with 365nm wavelength
7) Spectrophotometer, DR2800
8) TOC analyzer
9) Gas Chromatography /Mass Spectroscopy (GC/MS), 5975C model
10) Rotary evaporator

3.2.2 Chemicals

16 PAH Accustandard PAH Mix, 2.0mg/ml, Cat Z-014G-R was purchased from AccuStandard Inc., USA. Hydrogen peroxide, H_2O_2 (30% w/w solution) and sulphuric acid, H_2SO4 (95-98%) were purchased from R&M marketing, Essex, U.K. Sodium hydroxide, NaOH (Analytical grade, 46-48%), dichloromethane, CH_2CI_2 and sodium sulphate, Na_2SO_4 were purchased from Merck, Germany. H_2SO_4 and NaOH were used for pH adjustment. H_2O_2 was used for advanced oxidation process. While CH_2CI_2 and Na_2SO_4 were used for extraction of PAHs and dehydration of the dichloromethane.

3.2.3 Software

1) Design Expert software 6.0.7

3.3 Sample Preparation and Characterization

Synthetic water sample was prepared by dissolving 2 mL of diluted PAHs standard solution mix in deionized water in 1000 mL volumetric flask. The mixing was carried out to make sure the PAHs dissolve in the water completely due to its low solubility to produce more consistent PAHs concentration in the water sample. The synthetic sample characteristics like COD, TOC, pH and the PAHs concentration were measured.

3.4 Analytical Methods

3.4.1 Measurement of pH

pH of the wastewater sample was determined using HACH pH meter (HACH platinum series pH electrode model 51910, HACH Company, USA). The pH meter was calibrated before use as to ensure the accuracy of the pH meter.

3.4.2 Measurement of Chemical Oxygen Demand, COD

The COD concentration of water sample was determined by using spectrophotometer HACH DR 2800 under Program 430. 2ml of water sample was measured and poured into a vial containing potassium dichromate. The vial was shaken with Maxi Mix II Type 37600 Mixer for few seconds. Then, the vial was inserted in the digester for heating at 150℃ for 2 hours. After that, the vial was taken out and let it cool down at room temperature. The blank was prepared by using deionized water and used to calibrate the spectrophotometer to zero reading. Then, the vial is wiped and put into the cell holder in spectrophotometer. Then, vial containing sample was inserted into it and “Read” button was pressed to know the COD concentration.

3.4.3 Measurement of Total Organic Carbon, TOC

The TOC was measured by using Total Organic Carbon Analyser. The TOC was determined by differential method where both Total Carbon (TC) and Total Inorganic Carbon (TIC) were determined by measuring them separately.

$$TOC = TC - TIC$$

3.4.4 PAHs sample extraction

The liquid-liquid extraction will be done by using the Standard Method 6410 B: 1 L volume of water sample was extracted via serial extraction with 125-, 50-, and 50-mL volumes of dichloromethane. If the emulsion cannot be broken, the extraction procedure will be continued with an additional of 60 mL volumes of dichloromethane. The water sample was shaken to ten to fifteen minutes to absorb the PAHs which present in water until formation of two layers; the solvent at the bottom layer and water at the top layer. The solvent was separated from the water using separate funnel.

The dehydration technique was done by using the Standard Method 6410 B: Anhydrous sodium sulphate was added the extracted sample to absorb any remained water in the separated organic layer for drying purpose. The anhydrous salt will change to hydrated salt. The forming of clumped hydrated form of sodium sulfate indicates the presence of water molecules in the extracted sample. The additional of salt was added until no more clumped salt formed.

The sample was concentrated by using the rotary evaporator at 35-40°C of water bath temperature with 150 rpm until the apparent volume of sample liquid reached 1 to 2 mL of dichloromethane. Then, it will be transferred into the 1.5 mL vial and stored in cool room. The samples must be analyzed by GC/MS within 40 days after the re-concentration.

3.4.5 Measurement of PAHs concentration- GC/MS Analysis

The concentration of the PAHs was determined by using GC/MS 5975C model by Agilent. GC-MS analysis was performed with Agilent 7890A GC system, direct insertion probe and pyrollzer coupled to detector- Triple Axis inert XL EI/CI MSD and mass spectrometer- Quadrupole mass analyzer. The sample was run under the PAHSIM mode for the determination of the PAHs concentration. 1 µL of sample was injected into the GC system coupled to the mass selective detector operated in scan mode (125000 amu/sec) with a mass range of 20 and 400. A 30 m x 250 µm x 0.25 µm film thickness HP-5MS cross-linked 5% phenylmethyl-silicone column was used with the following temperature program: 60 ^{o}C for 2 minutes, ramp at 10 ^{o}C/ min to 300 ^{o}C in 1 min and hold at 300 ^{o}C until 29 min run time. The injector port was 360 ^{o}C and the carrier gas was helium.

3.5 Experimental Procedure

Batch experiments were conducted using a 1L Pyrex reactor with 1L of sample. The pH of the sample was adjusted to the required value by 1N H_2SO_4 or 1N NaOH. The sample was subjected to UV irradiation by an UV lamp with emitting radiation wavelength of 365 nm placed 5 cm above the reactor. The mixing was carried out by a magnetic stirrer for complete homogeneity during the reaction. Hydrogen peroxide (H_2O_2) was added according to the dosage predefined. The time at which hydrogen peroxide added to the mixture is considered as the beginning of the experiment. Aliquots were withdrawn at the time targeted. The pH of the solution was adjusted to more than pH 10 to decompose the H_2O_2 to oxygen and water to reduce interference in the COD determination. The aliquots were filtered for COD measurement. The sample was then extracted by using dichloromethane, dehydrated by using anhydrous sodium sulphate and rotary evaporated to less than 1.5mL for determination of PAHs concentration by GC/MS.

3.6 Preliminary Experiments

The preliminary experiments were carried out to determine the optimum range for the experimental condition for UV/ H_2O_2 system for removal of PAHs in synthetic aqueous solution. First, the experiments were carried out to determine optimum range of reaction time with constant concentration of H_2O_2 and unadjusted pH. Then, the experiments were conducted based on optimum reaction time and unadjusted pH to determine the optimum range of H_2O_2 concentration. Last, the experiments were carried out to determine the optimum range of pH based on optimum reaction time and H_2O_2 concentration predetermined. All the experiments were carried out in triplicate and get the average readings. The optimum range for the operational variables was used for the RSM design.

3.7 Experiment Design and Mathematical Modeling

In this study, Design Expert Software (State-Ease Inc., version 6.0.7) was used for the statistical design of experiment and data analysis. The central composite design (CCD) and response surface methodology (RSM) was used to optimize the operating variables: H_2O_2 concentration (A), pH (B) and reaction time (C) for maximum COD removal efficiency of the sample.

The range of each operating variables were established based on the predetermined range from the preliminary experiment. The coded values for H_2O_2 dosage (A) , pH (B) and reaction time (C) was set at 5 levels: - α (minimum), -1, 0 (centre), +1and α (maximum). The design consisted of 2k factorial points augmented by 2k axial points and a center point, where k is the number of variables. Accordingly, 20 experiments (=2^k + 2k + 6, where k is the number of factors) were conducted with 14 experiments organized in a factorial design (including 4 factorial points, 3 axial points and 1 center point) and the remaining 6 involving the replication of the central point to get a good estimate of the experimental error.

After conducting the experiments, the response- COD removal efficiency was fitted by a second-order model in the form of quadratic polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i \cdot x_i + \sum_{i=1}^{k} \beta_{ii} \cdot x_i^2 + \sum_{i \leq j}^{k} \sum_{\mathrm{j}}^{\mathrm{k}} \beta_{ij} \cdot x_i \cdot x_j + \cdots + e \qquad (9)$$

where *i* and *j* are the linear and quadratic coefficients, *β* is the regression coefficient, k is the number of factors studied and optimized in the experiment and e is the random error.

The interaction between the process variables and the responses were obtained from the graphical analyses of data by analysis of variance (ANOVA). The quality of the fit polynomial model was expressed by the coefficient of determination R^2, and its significance was checked by the Fisher's F-test. Model terms were evaluated by the P-value with 95% confidence level. Three dimensional plot and their respective contour plot for the COD removal efficiency based on the two operational variables (H_2O_2 concentration, pH and reaction time) was obtained. The simultaneous interaction of the factors and the response was studied from these three dimensional plot. The optimum region was identified based on the main parameter in the desirability plot.

3.8 Verification Experiments

The optimum operating variables for the maximum COD removal efficiency based on RSM optimization was verified by carrying out verification experiments. Then, the final concentration of the PAHs in the treated sample based on optimized condition was measured to access the efficiency of the system.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthetic Sample Characteristics

The synthetic aqueous solution was prepared by diluting 2mL of standard PAHs solution mix containing 16 PAHs in 1L of deionized water. The characteristics of the synthetic solution were summarized in the table below:

Table 4.1: Sample Characteristics

Parameter	**Unit**	**Value**
pH		5.75
COD	mg/L	1026
TOC	mg/L	337.3

The total concentration of PAHs in the synthetic aqueous solution prepared was 200 ppb. The concentration of each PAHs in the synthetic aqueous solution prepared was analyzed and summarized in Table 4.2:

Table 4.2: Concentration of PAHs in synthetic aqueous solution

Compounds	**Concentration (ppb)**
Napthalene	8.85
Acenaphtylene	10.52
Acenaphthene	10.03
Fluorene	12.31
Phenanthrene	15.62
Anthracene	13.21
Carbazole	10.29
Fluoranthene	10.09
Pyrene	11.29
Benzo(a)anthracene	13.07
Chrysene	13.00
Benzo(b)fluoranthene	14.86
Benzo(k)fluoranthene	12.06
Benzo(a)pryene	6.50
Indenol(1,2,3-cd)pyrene	10.71
Dibenzo(a,h)anthracene	17.36
Benzo(g,h,i)perylene	10.23
LMW-PAHs	90.92
HMW-PAHs	109.08
TPAHs	200.00

4.2 Preliminary Experiments

The preliminary experiments were carried out to determine the optimum range of the operational variables (H_2O_2 concentration, pH and reaction time) for the RSM design. First, the experiments were carried out to determine the reaction time range by dosing 3mM of H_2O_2 and keeping the pH of the sample unadjusted at pH 5.75. The results were shown in Figure 4.1.

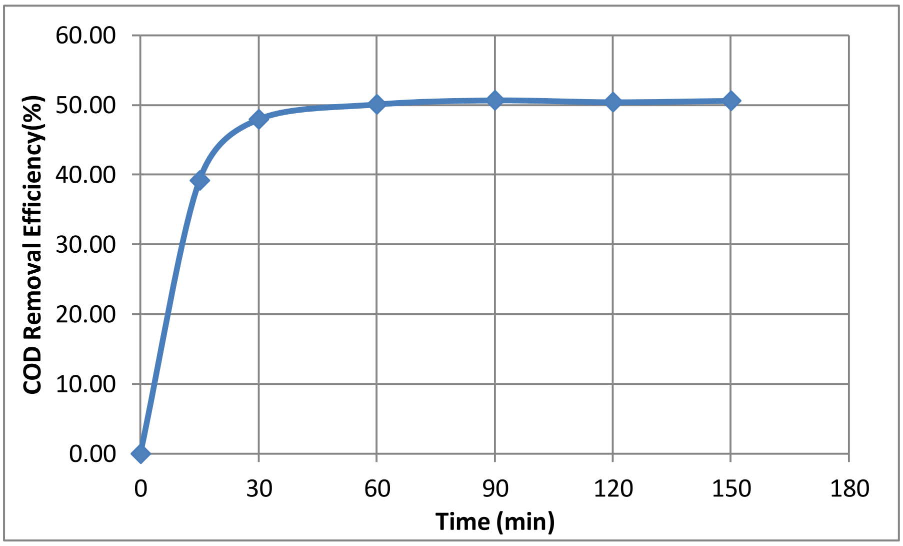


Figure 4.1: Effect of time on COD removal efficiency

As shown in Figure 4.1, at reaction time of 15, 30, 60, 90, 120 and 150, the COD removal efficiency was 39.2, 48.0, 50.1, 50.7, 50.4 and 50.6 % respectively. The COD removal efficiency achieves equilibrium after 60 minutes reaction time. This indicates that the further increase in reaction time will not increase the COD removal efficiency of the sample. The UV_{254} and TOC removal efficiency of creosote contaminated groundwater consisting mainly of PAHs compound also remained constant after 30 and 60 minutes reaction with 3mM of H_2O_2 dosage (Vilhunen et al., 2010). Thus, the reaction time range of 30-90 minute was used for the RSM design.

Next, initial H_2O_2 concentration was varied in the range of 0.5mM to 5mM to determine the range of H_2O_2 concentration. Other operating variables were fixed at reaction time of 90 minutes and unadjusted pH of the sample. The results were shown in Figure 4.2.

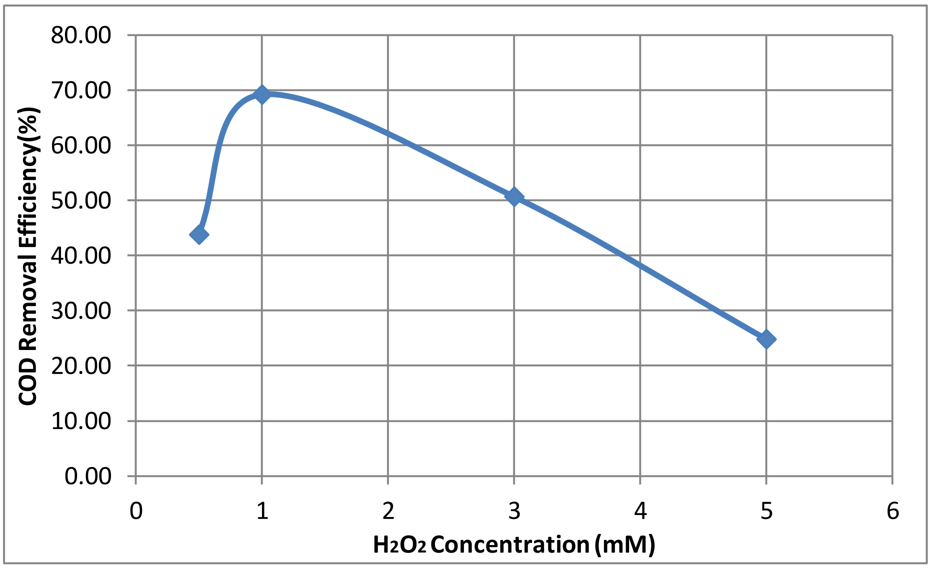


Figure 4.2: Effect of H_2O_2 concentration on COD removal efficiency

At H_2O_2 concentration of 0.5, 1, 3 and 5mM, the COD removal efficiency was found to be 43.8, 69.2, 50.7 and 24.8 % respectively. The COD removal efficiency increase with H_2O_2 concentration of 0.5 to 1 mM and decrease with further increase of H_2O_2 concentration from 1 to 5 mM. The increase of hydrogen peroxide concentration will generate more hydroxyl radical for the oxidation process to degrade the organic pollutants, thus contribute to the increment of COD removal efficiency. However, in the excess of hydrogen peroxide, the hydroxyl radicals tend to undergo scavenging of OH• by H_2O_2 and formation of hydroperoxyl radical which will lead to the decrease in COD removal efficiency. The optimum range of the H_2O_2 concentration can be used for RSM design was 1 to 3 mM. The achieved range was in agreement with those researches reported by Beltran et al. (1996) and Ledakowicz (1999).

Last, the pH of the sample was varied in the range of 2 to 8 while other operational variables were fixed at reaction time of 90 minutes and H_2O_2 concentration of 1mM. The results were shown in Figure 4.3.

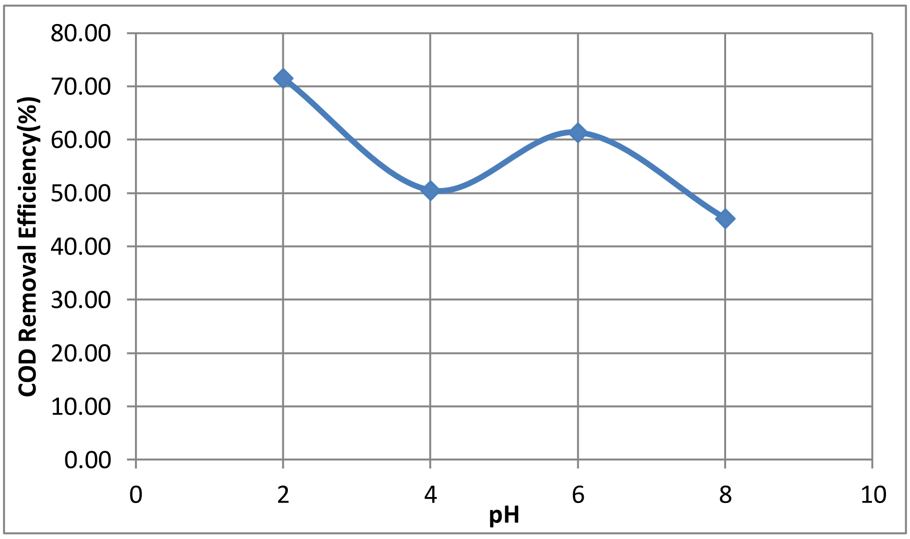


Figure 4.3: Effect of pH on COD removal efficiency

At pH of 2, 4, 6 and 8, the COD removal efficiency was 71.5, 50.5, 61.3 and 45.2 % respectively. The optimal pH for the COD removal efficiency was pH 2. The results were in a good agreement with the research reported by Beltran et al. (1996). The increment of pH from 2 to 7 increases the PAHs disappearance rate, while the increment of pH to 12 results in less disappearance rate due to the oxidation inhibition. Thus, the pH range of 2 to 5 was selected for the RSM design.

4.3 Statistical Analysis

RSM was applied to optimize the COD removal efficiency based on three operating variables (H_2O_2 concentration, pH and reaction time) of UV/ H_2O_2 system. The low and high ranges of the operating variables were chosen from the preliminary experiments. Table 4.3 shows the range and level of operating variables. The central composite design (CCD) was used to design the experimental to come out with 20 sets of experimental condition to be tested. Table 4.4 shows the experimental conditions and results of central composite design (CCD).

Table 4.3: The range and level of operating variables

Variable	Unit	Code	Range and levels				
			- α	-1	0	1	α
H_2O_2 concentration	mM	A	0.32	1	2	3	3.68
pH		B	0.98	1	3.5	5	6.02
Reaction time	min	C	0.55	30	60	90	110.45

Table 4.4 : Experimental condition and results of central composite design

Run	H_2O_2 concentration (mM)	pH	Reaction Time (min)	COD Removal Efficiency (%)
1	1 (-1)	2 (-1)	30 (-1)	47.95
2	3 (1)	2 (-1)	30 (-1)	48.68
3	1 (-1)	5 (1)	30 (-1)	61.05
4	3 (1)	5 (1)	30 (-1)	54.32
5	1 (-1)	2 (-1)	90 (1)	76.15
6	3 (1)	2 (-1)	90 (1)	76.28
7	1 (-1)	5 (1)	90 (1)	78.04
8	3 (1)	5 (1)	90 (1)	72.94
9	0.32 (-1.682)	3.5 (0)	60 (0)	71.51
10	3.68 (1.682)	3.5 (0)	60 (0)	77.73
11	2 (0)	0.98 (-1.682)	60 (0)	70.52
12	2 (0)	6.02 (1.682)	60 (0)	58.22
13	2 (0)	3.5 (0)	0.55 (-1.682)	43.37
14	2 (0)	3.5 (0)	110.45 (1.682)	88.95
15	2 (0)	3.5 (0)	60 (0)	73.42
16	2 (0)	3.5 (0)	60 (0)	74.59
17	2 (0)	3.5 (0)	60 (0)	73.29
18	2 (0)	3.5 (0)	60 (0)	73.49
19	2 (0)	3.5 (0)	60 (0)	75.47
20	2 (0)	3.5 (0)	60 (0)	74.37

The fitting of data to various models (linear, two factorial, quadratic and cubic) and their subsequent ANOVA presented that the COD removal efficiency of the sample was mostly suitably described with quadratic model. The multiple regression coefficients of a second-order polynomial model were summarized in Table 4.5. The significance of each variable was determined by F-value and P-value. The P-value suggests that the C, B^2 and C^2 are significant model term. Thus, to simplify model, the not significant terms (A, B, A^2, AB, AC and AB) were eliminated. The normalized coefficients are presented in Figure 4. The effect of the terms on the response was indicated by the normalized coefficients. The first order effects of reaction time, second order effects of pH and reaction time produce the main effect on the COD removal efficiency of the sample.

Table 4.5: Estimated regression coefficients and corresponding ANOVA results from data of central composite design experiments before elimination of insignificant model terms

	Coefficient estimate	**Sum of squares (SS)**	**Degree of freedom (DF)**	**Mean square (MS)**	**F-value**	**P-value**	
Quadratic Model	74.22	2539.97	9	282.22	13.61	0.0002	Siginificant
A	-0.037	0.019	1	0.019	9.155E-004	0.9765	Not significant
B	-0.25	0.84	1	0.84	0.041	0.8441	Not significant
C	12.31	2068.28	1	2068.28	99.71	<0.0001	Siginificant
A^2	-0.58	4.84	1	4.84	0.23	0.6393	Not significant
B^2	-4.2	254.66	1	254.66	12.28	0.0057	Siginificant
C^2	-3.57	183.75	1	183.75	8.86	0.0139	Siginificant
AB	-1.59	20.13	1	20.13	0.97	0.3478	Not significant
AC	0.13	0.13	1	0.13	6.393E-003	0.9378	Not significant
BC	-2.52	50.95	1	50.95	2.46	0.1481	Not significant

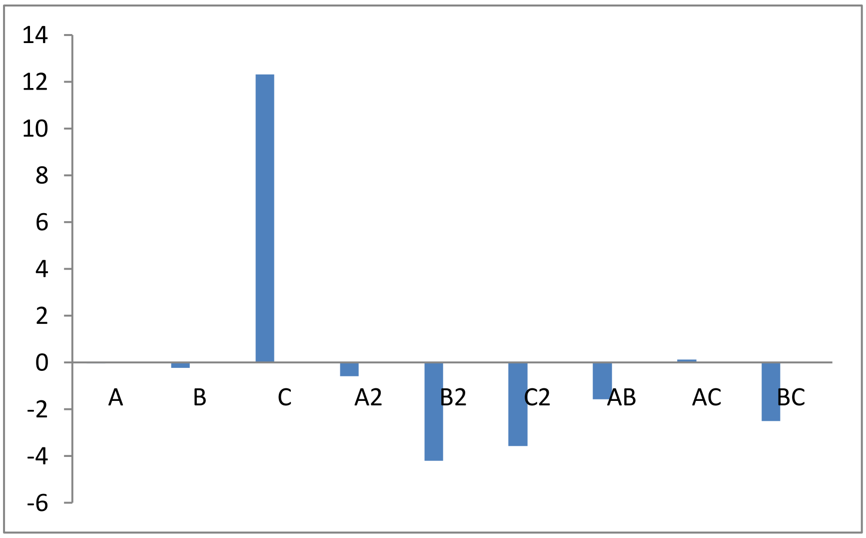


Figure 4.4: Normalized coefficient of the model

The following regression equation is the empirical model in terms of coded factors for the response before the elimination of the insignificant model.

$$Y = +\,74.22 - 0.037\,A - 0.25\,B + 12.31\,C - 0.58A^2 - 4.2B^2 - 3.57C^2 - 1.59AB + 0.13AC - 2.52\,BC \qquad (10)$$

The following regression equation is the empirical model in terms of coded factors for the response after the elimination of the insignificant model.

$$Y = +\,73.75 + 12.31\,C - 4.15B^2 - 3.51C^2 \qquad (11)$$

The adequacy and significance of results was analyzed and viewed in ANOVA analysis as shown in Table 4.6.

Table 4.6: ANOVA results for response parameter

Response	**Significant model terms**	**P**	**PLOF**	**R^2**	**Adj. R^2**	**AP**	**S.D.**	**CV**	**PRESS**
COD	C, B^2 and C^2	<0.0001	0.0005	0.8965	0.8771	21.956	4.22	6.15	579.98

P: probability of error; PLOF: probability of lack of fit; R^2: determination coefficient; Adj. R^2: adjusted determination coefficient AP: adequate precision; S.D.: standard deviation; CV: coefficient of variance; PRESS: predicted residual error sum of squares.

The quadratic model with P value (<0.0001) was significant to give less than 0.05 of probability of error.

The F-test- lack of fit (PLOF) describes the variation of data around the fitted model. If the model does not fit the model well, then this will be significant. The larger P value for lack of fit (> 0.05) show the F statistics was insignificant, indicate significant model correlation between variables and process responses. In this study, the PLOF value was 0.0005 which indicate that the model was significant.

The R^2 coefficient indicates the ratio of sum of squares due to regression (SSR) to total sum of squares (SST). It gives the proportion of the total variation in the response by the model. A high R^2 value, close to 1 is a desirable and reasonable agreement with adjusted R^2 is necessary (Ghafari, Aziz, Isa, & Zinatizadeh, 2009). R^2 should be at least 0.80 for a good fit of a model A.M. Joglekar & A.T. May (1987). The analysis gives 0.8965 and 0.8771 R^2 and adjusted R^2 value. The value is greater than 0.8 and close to 1 to ensure a satisfactory adjustment of the quadratic model to the experimental data.

Adequate precision (AP) compares the range of predicted values at the design points to the average prediction error. In this case, the AP value is 21.956 which is greater than 4 indicate adequate model discrimination and can be used to navigate design space defined by CCD (Noordina, Venkatesh, Sharif, Elting, & Abdullah, 2004).

The coefficient of variance (CV) as the ratio of estimate standard error to the mean value of the observed response defines the reproducibility of the model. A model can be considered reproducible if its CV is not greater than 10%. Low value of the coefficient of variation indicates a very high degree of precision and good deal of reliability of the experimental values (Ishak & Malakahmad, 2013). In this study, the CV is about 6.15 % indicate the model is reproducible.

The predicted residual error sum of squares (PRESS) is the ordinary residual weighted according to the diagonal elements of the hat matrix (Raissi & Farsani, 2009). In this study, the difference between the ordinary residual (3.68) and PRESS residual (579.98) is large which indicate a point where the model fits the data well.

The fit of data was interpreted by diagnostics result such as normal probability plot of residuals, outlier plot and predicted vs. actual values plot as shown in Figure 4.5 4.6 and 4.7 to verify residue analysis of the response surface design to ensure that the statistical assumptions fit the analysis data.

Figure 4.5 shows the normal probability of the residuals to very whether the standard deviation between the actual and predicted response values follow a normal distribution (Shahrezaei, Mansouri, Zinatizadeh, & Akhbari, 2012). The residues fall near to a straight line, thus there is no clear indication of non-normality of experimental results.

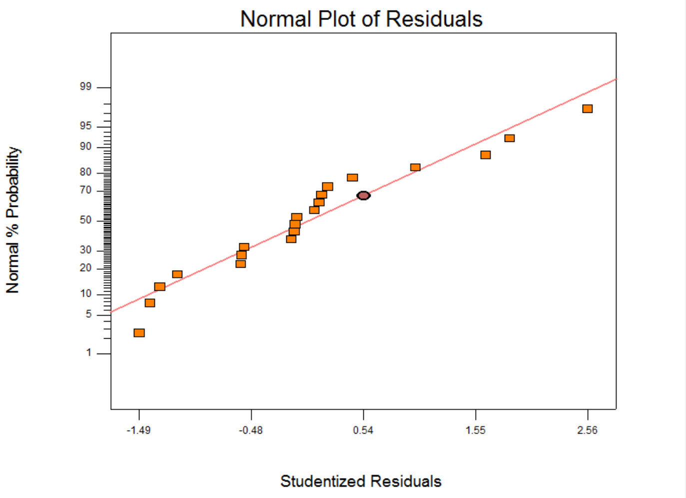


Figure 4.5: Normal probability plot of residue

The plot of residual versus predicted responses was shown in Figure 4.6. All points of experimental runs were scattered randomly within the constant range of residuals across the graph that within the horizontal lines at the point of ±1.75 with only two points lies above the +1.75 horizontal line. This implies that the proposed models are adequate and that the constant variance assumption was confirmed (Ishak & Malakahmad, 2013).

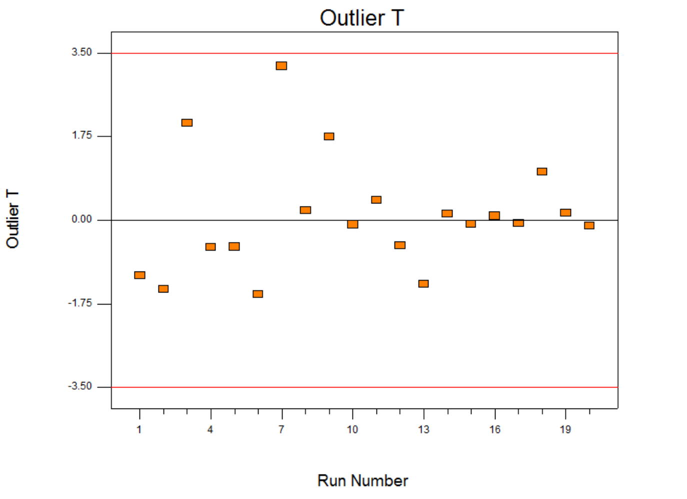


Figure 4.6: Plot of residue vs. predicted response

Figure 4.7 shows the predicted vs actual values plot for COD removal efficiency augmentation. All the responses from experimental results fitted well within an acceptable variance range when compared to the predicted values from respective empirical models.

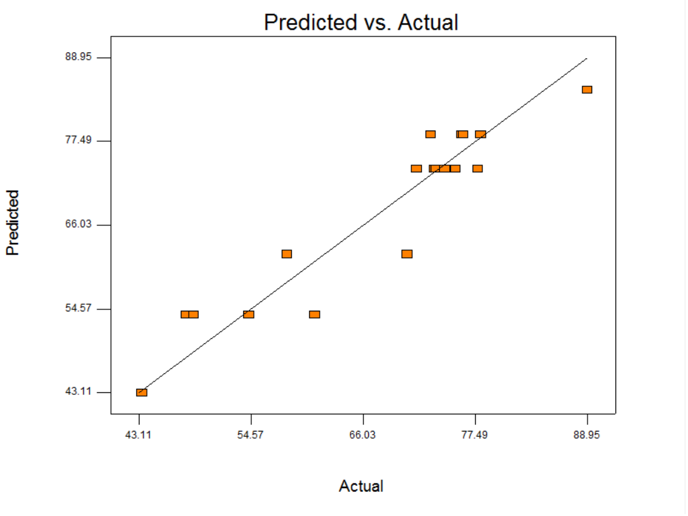


Figure 4.7: Predicted vs. actual values plot for COD removal efficiency augmentation

The three dimensional response surface plots for variables- H_2O_2 concentration (A), pH (B) and reaction time (C) was shown in Figure 4.8, 4.9 and 4.10. The plots show the interaction between each parameter to the removal of COD of the sample. As illustrated in Figure 4.8, the COD removal efficiency increase with increase of reaction time while keeping the pH of the sample at 3.5 as optimum. The H_2O_2 concentration does not contribute to the COD removal efficiency of the sample while the pH was optimum at 3.5 as illustrated in Figure 4.9. Figure 4.10 shows that the H_2O_2 concentration does not effect on the COD removal efficiency while the reaction time does.

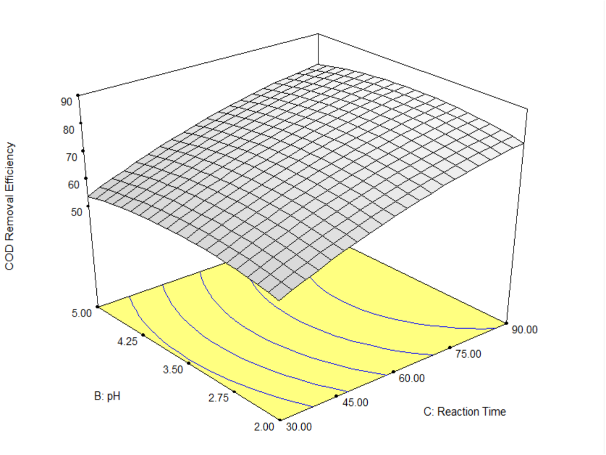


Figure 4.8: 3D plots for COD removal efficiency for pH and reaction time

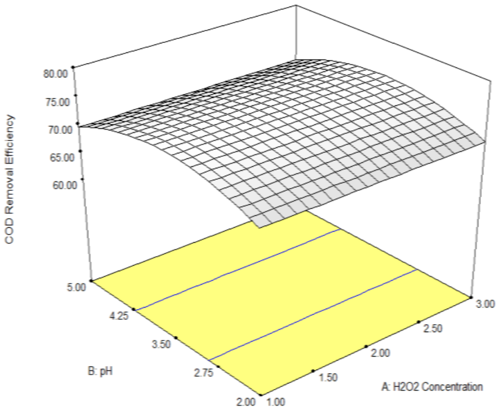


Figure 4.9: 3D plots of COD removal efficiency for pH and H_2O_2 concentration

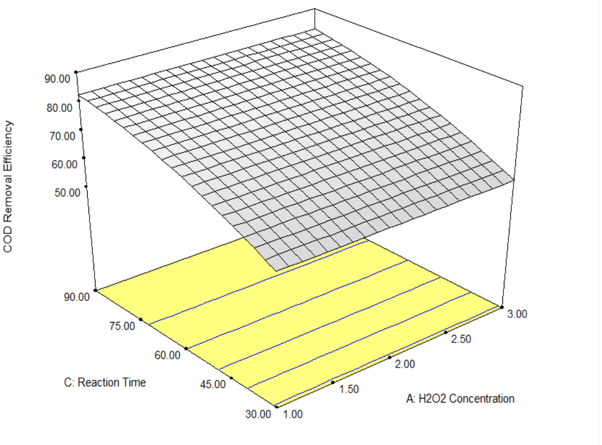


Figure 4.10: 3D plots of COD removal efficiency for reaction time and H_2O_2 concentration

4.4 Process Optimization

In the numerical optimization, the desired goal was chosen for each factor and response from the menu. The possible goals are: maximize, minimize, target, within range, none (for responses only) and set to an exact value (factors only). The goals are combined into an overall desirability function. Desirability is an objective function that ranges from zero outside of the limits to one at the goal (Raissi & Farsani, 2009). The optimization was done by setting goals for each response as shown in Table 4.7 to generate optimal condition as shown in Table 4.8.

Table 4.7: The goal set for each constraint

Constraints	**Goal**	**Lower limit**	**Upper limit**
H_2O_2 concentration	Minimize	1	3
pH	In range	2	5
Reaction time	In range	30	90/ 150
COD removal efficiency	Maximize	43.47	88.95

Table 4.8: Numerical optimization for central composite design

Solution No.	**H_2O_2 concentration**	**pH**	**Reaction time**	**COD removal efficiency**	**Desirability**
1	1.00	3.50	112.58	84.52	0.950
2	1.00	3.50	112.45	84.52	0.950
3	1.00	3.50	112.32	84.52	0.950
4	1.00	3.50	112.77	84.52	0.950
5	1.00	3.54	112.63	84.52	0.948
6	1.00	3.83	109.76	84.30	0.948
7	1.00	3.08	114.86	84.17	0.946
8	1.00	3.50	90.00	82.54	0.927
9	1.00	3.51	89.28	82.54	0.927
10	1.00	3.57	89.23	82.53	0.927
11	1.00	3.49	90.00	82.54	0.921
12	1.00	2.90	90.00	81.89	0.919
13	1.00	3.79	85.22	81.45	0.914
14	1.00	4.94	90.00	78.74	0.881

Based on the solutions generated by the Design Expert Software, the optimum condition (H_2O_2 concentration of 1mM, pH of 3.5 and reaction time of 90 minutes) predicted by RSM for the maximum COD removal efficiency (82.54%) with desirability value of 0.927 was adopted for the verification experiment. The increase in reaction time from 90 minute to 112.58 minute predicts the increment of COD removal efficiency of 1.98% with higher desirability value of 0.950. But, this solution does not offer a significant improvement in COD removal efficiency while the reaction time is prolonged to another 20 minutes.

4.5 Model Verification

In order to validate the optimum point generated by CCD, three experiment runs were carried out under the optimum condition (H_2O_2 concentration of 1mM, pH of 3.5 and reaction time of 90 minutes) to verify the results predicted by the model. The COD removal efficiency value obtained from the experiment and that estimated by the model was in agreement with less than 3% error and standard deviation of 1.95 as shown in Table 4.9.

Table 4.9: Experimental removal efficiency and model prediction

Response	**Model Prediction**	**Experimental Results**	**Error**	**Standard Deviation**
COD removal efficiency	82.54	80.41, 78.65, 80.28; Ave: 79.78	2.76	1.95

The final concentration of PAHs in the treated sample under optimized condition was shown in the Table 4.10 with its respective removal efficiency. Figure 4.11 shows the initial and final concentration of each PAHs in the sample in graphical form.

Table 4.10: Final concentration and removal efficiency of the PAHs in the treated sample

Compounds	**Before Treatment (ppb)**	**After treatment (ppb)**	**Removal Efficiency (%)**
Napthalene	8.85	0.96	89.15
Acenaphtylene	10.52	0.08	99.24
Acenaphthene	10.03	0.76	92.42
Fluorene	12.31	1.06	91.39
Phenanthrene	15.62	1.25	92.00
Anthracene	13.21	0.23	98.26
Carbazole	10.29	1.98	80.76
Fluoranthene	10.09	2.10	79.19
Pyrene	11.29	0.91	91.94
Benzo(a)anthracene	13.07	2.08	84.09
Chrysene	13.00	3.00	76.92
Benzo(b)fluoranthene	14.86	3.17	78.67
Benzo(k)fluoranthene	12.06	2.71	77.53
Benzo(a)pryene	6.50	1.80	72.31
Indenol(1,2,3-cd)pyrene	10.71	2.55	76.19
Dibenzo(a,h)anthracene	17.36	4.30	75.23
Benzo(g,h,i)perylene	10.23	2.51	75.46
LMW-PAHs	90.92	8.42	90.74
HMW-PAHs	109.08	23.03	78.89
TPAHs	200.00	31.45	84.28

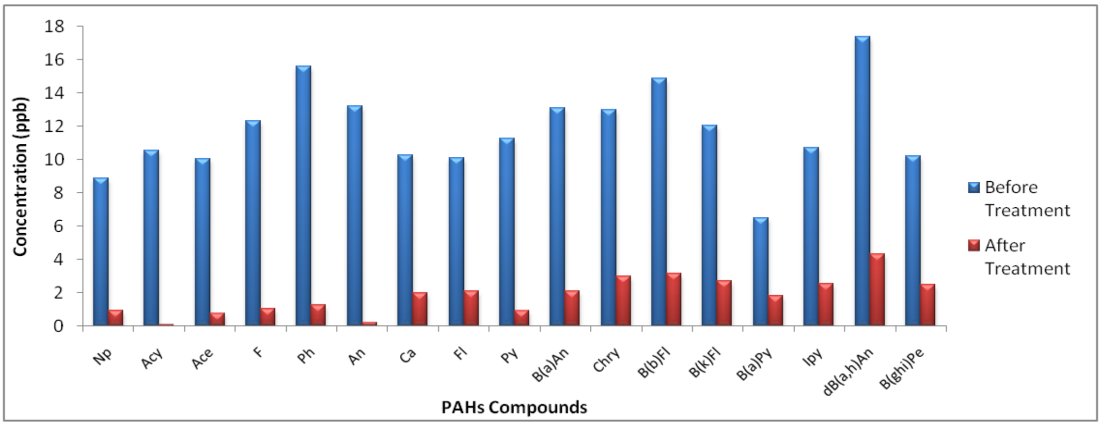


Figure 4.11: The concentration of PAHs in the sample before and after treatment

The TOC of the treated sample under the optimum operating condition was 92.13 mg/L. The total PAHs removal efficiency was 84.28%. The low molecular weighted PAHs achieved higher removal efficiency of 90.74% than the high molecular weighted PAHs which only achieved 79.89% removal efficiency. The high molecular weighted PAHs have lower removal efficiency due to its highly stable and low- bioavailability in nature. The optimum condition (H_2O_2 concentration of 1mM, pH of 3.5 and reaction time of 90 minutes) agreed well in certain extents with the studies done by other researchers even though the results cannot be compared readily due to different photoreactor design. The UV photolysis and UV/ H_2O_2 were found to be efficient for the PAH removal in creosote contaminated groundwater in which the UV + 3mM H_2O_2 treatment successfully remove the total concentration of naphthalene, acenaphthylene, acenaphthene, fluorene, phenathrene, anthracene, fluoranthene and pyrene of 711 ug/l to less than 0.1 ug/l after 60 minutes (Vilhunen et al., 2010). The simultaneous presence of hydrogen peroxide at concentration between 10^{-3} and 10^{-2} M and 254 nm UV radiation yields significant improvements in the rate of disappearance of PAHs (fluorene, phenanthrene and acenaphthene) in water. The increase of pH from 2 to 7 leads to an increase of PAHs (fluorene, phenanthrene and acenaphthene) disappearance rate, but at higher increase of pH, up to 12 definitively reduces the oxidation rate (Beltran et al., 1996).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The UV/H_2O_2 process is effective for the treatment of PAHs in aqueous solution. The performance of the system for the treatment of aqueous solution containing polycyclic aromatic hydrocarbons and the optimization of the process was reported in this study.

The main factors to affect the performance of the UV/H_2O_2 process were found to be H_2O_2 concentration, pH and reaction time. Thus, the preliminary experiments were carried out to determine the range of the studied operating variables of the system for RSM design. The maximum COD removal achieved in preliminary experiments was 71.5% under the operating condition of 1mM H_2O_2 concentration, pH of 3.5 and 90 minutes reaction time. The ranges of the variables used for RSM design were 1-3m M for H_2O_2 concentration, 2-5 for pH and 30-90 minutes for reaction time.

The process was optimized by response surface methodology (RSM) based on five-level central composite design (CCD). The experimental data fit the quadratic model predicted by RSM well. The pH and reaction time was found to produce the main effect on the COD removal efficiency of the sample. The results was found to be adequate and significant by ANOVA analysis which give $P< 0.0001$, PLOF= 0.0005, R^2= 0.8965, adjusted R^2= 0.8771, AP= 21.956, S.D. = 4.22, CV= 6.15 and PRESS= 579.98. The fit of data also analyzed by the diagnostics results generated. The three dimensional plot was produced to study the relationship of each variable to the COD removal efficiency.

Under the optimum operating condition (H_2O_2 concentration of 1mM, pH of 3.5 and reaction time of 90 minutes), the COD removal efficiency was 79.78%. The experimental removal efficiency and the model prediction were in good agreement with less than 3% error. The PAHs removal efficiency was 84.28%. The low molecular weighted PAHs achieved higher removal efficiency than high molecular weighted PAHs.

The study has revealed that RSM is a useful tool to optimize the process and the UV/H_2O_2 process is an effective treatment system for aqueous solution containing PAHs.

5.2 Recommendation

The study was carried out to study the effect of three important variables (H_2O_2 concentration, pH and reaction time) for the treatment of aqueous solution containing PAHs. The UV intensity was kept constant throughout the study and its effect to the performance of the system was not studied. Thus, it is recommended to study the optimum intensity of the UV light and the optimum wave length to improve the performance of the system.

The ferrous sulphate heptahydrate, $FeSO_4.7H_2O$ can be added to promote the catalytic decomposition of hydrogen peroxide by ferric ion to produce more hydroxyl radicals for the oxidation process. The photo-Fenton process was studied by other researchers to more effective than UV/H_2O_2 process for the removal of organic pollutants in water. However, the generation of hydroxyl radicals can be scavenged by the reaction with ferrous ion and hydrogen peroxide. Thus, the studied variables for the photo-Fenton process were H_2O_2 concentration, iron concentration, pH, UV intensity and reaction time and the process can be optimized by RSM in the same way.

REFERENCES

1. Affam, A. C., Chaudhuri, M., & Kutty, S. R. (2012). Statistical optimization of the Fenton Process for Treatment of Amoxicillin and Cloxacillin Antibiotic Aqueous Solution by Response Surface Methodology. *Proceedings 2012 International Conference on Civil, Offshore and Environmental Engineering.* Perak: Universiti Teknologi Petronas.
2. Alfano, O. M., Brandi, R. J., & Cassano, A. (2001). Degradation kinetics of 2,4-D in water employing hydrogen peroxide and UV radiation. *Chemical Engineering Journal* , 209–218.
3. ATSDR. (2011). *Detailed Data for 2011 Priority List of Hazardous Substances.* Georgia: Agency for Toxic Substances and Disease Registry.
4. ATSDR. (1995). *Toxilogical Profile For Polycyclic Aromatic Hydrocarbons.* Georgia: Agency for Toxic Substances and Disease Registry.
5. Beltran, F. J., Ovejero, G., & Rivas, J. (1996). Oxidation of Polynuclear Aromatic Hydrocarbons in Water. 3. UV Radiation Combined with Hydrogen Peroxide. *Ind. Eng. Chem. Res. 35* , 883-890.
6. Bernal-Martinez, A., Carrere, H., Patureau, D., & Delgenes, J.-P. (2007). Ozone pre-treatment as improver of PAH removal during anaerobic digestion of urban sludge. *Chemosphere 68* , 1013–1019.
7. Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta 76(5)* , 965-977.
8. C.A., Menzie; B.B., Potocki; J., Santodonato. (1992). Exposure to the carcinogenic PAHs in the environment. *Environ. Sci. Technol. 26* , 1278–1284.
9. Christensen, N., Batstone, D., He, Z., Schmidt, Angelidake, I., & J.E. (2004). Removal of Polycyclic Aromatic Hydrocarbons (PAHs) from Sewange Sludge by Anaerobic Degradati. *Water Sci. Technol. 50(9)* , 237-244.
10. DHHS. (2011). *Report on Carcinogens, Twelfth Edition.* National Toxicology Program, Department of Health and Human Service.
11. Engwall, M. A., Pignatelloa, J. J., & Grasso, D. (1999). Degradation and detoxification of the wood preservatives creosote and pentachlorophenol in water by the photo-Fenton reaction. *Water Res. 33(5)* , 1151-1158.
12. Gan, C. H., Elmolla, E. S., & Chaudhuri, M. (2012). Optimization of photo-Fenton treatment of mature landfill leachate. *Nat. Environ. Pollut. Technol. 11(1)* , 65-72.
13. Gan, H. C. (2010). A Treatment System for Landfill Leachate. Master Thesis, University Teknologi Petronas.
14. Gehle, K., MD, & MPH. (2011, July 1). *Polycyclic Aromatic*

Hydrocarbons (PAHs) Cover Page. Retrieved February 15, 2013, from Agency for Toxic Substances and Disease Registry: http://www.atsdr.cdc.gov/csem/pah/docs/pah.pdf

15. Ghafari, S., Aziz, H. A., Isa, M. H., & Zinatizadeh, A. A. (2009). Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminium chloride (PAC) and alum. *J. Hazard. Mater.* , 650-656.
16. I.Khuri, A., & Mukhopapdhyay, S. (2010, March/April). Response Surface Methodology. *Advanced Review 2* , pp. 128-149.
17. IARC. (1998, April 17). Polynuclear Aromatic Compounds, Part.1-Chemical, Environmental and Experimental Data. *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals in Humans* , pp. 95-431.
18. Ishak, S., & Malakahmad, A. (2013). Optimization of fenton process for refinery wastewater biodegradability augmentation. *Korean J. Chem. Eng.* , 1-8.
19. Jacob, J. (1996). The significance of polycylic aromatic hydrocarbons as environmental carcinogens. *Pure Appl. Chem. 68(2)* , 301-308.
20. Ledakowicz, S., Miller, J. S., & Olejnik, D. (1999). Oxidation of PAHs in water solutions by ultraviolet radiation combined with hydrogen peroxide. *Int. J. Photoenergy 1* , 1-6.
21. Li, J.-L., & Chen, B.-H. (2002). Solubilization of model polycyclic aromatic hydrocarbons by nonionic surfactants. *Chem. Eng. Sci. 57* , 2825-2835.
22. Lin, D. K., & Peterson, J. J. (2009). Statistical Inference for Response Surface Optima. In A. I. Khuri, *Response Surface Methodology and Related Topics* (pp. 65-88). London: World Scientific.
23. Metcalf, & Eddy. (2004). *Wastewater Engineering Treatment and Reuse Fourth Edition.* New York: McGraw Hill.
24. Meulenberg, R., Rijnaarts, H. H., Doddema, H. J., & Field, J. A. (1997). Partially oxidized polycyclic aromatic hydrocarbons show an increased bioavailability and biodegradability. *FEMS Microbiol. Lett. 152* , 45-49.
25. Noordina, M., Venkatesh, V., Sharif, S., Elting, S., & Abdullah, A. (2004). Application of response surface methodology in describing the performance of coated carbide tools when turning AISI 1045 steel. *J. Mater. Proc. Technol.* , 46–58.
26. Ölmez, T. (2009). The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology. *J. Hazard. Mater. 162* , 1371-1378.
27. Pignatello, J. (1992). Dark and photoassisted Fe 3+ catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.* , 944-951.
28. Qi, W., Liu, H., & Pernet-Coudrier, B. (2013). Polycyclic aromatic hydrocarbons in wastewater, WWTPs effluents and in the recipient

waters of Beijing, China. *Environ. Sci. Pollut. Res. Int.* .

29. Raissi, S., & Farsani, R. E. (2009). Statistical Process Optimization Through Multi-Response Surface Methodology. *World Academy of Science, Engineering and Technology 27* , 267-271.
30. Rivas, F. J., Beltrán, F. J., & Acedo, B. (2000). Chemical and photochemical degradation of acenaphthylene. Intermediate identification. *J. Hazard. Mater B75* , 89-98.
31. Samanta, S. K., Singh, O. V., & Jain, R. K. (2002). Polycyclic aromatic hydrocarbons:environmental pollution and bioremediation. *Trends Biotechnol. 20 (6)* , 243-239.
32. Shahrezaei, F., Mansouri, Y., Zinatizadeh, A. A., & Akhbari, A. (2012). Process modeling and kinetic evaluation of petroleum refinery wastewater treatment in a photocatalytic reactor using TiO 2 nanoparticles. *Powder Techno.* , 203-212.
33. Shemer, H., & Linden, K. G. (2007). Photolysis, oxidation and subsequent toxicity of a mixture of polycyclic aromatic hydrocarbons in natural waters. *Journal of Photochemistry and Photobiology A: Chemistry 187* , 186-195.
34. Tran, L.-H., Drogui, P., Mercier, G., & Blais, J.-F. (2009). Electrochemical degradation of polycyclic aromatic hydrocarbons in creosote solution using ruthenium oxide on titanium expanded mesh anode. *J. Hazard. Mater. 164* , 1118–1129.
35. Trapido, M., Veressinina, Y., & Munter, R. (1995). Ozonation and advanced oxidation processes of polycyclic aromatic hydrocarbons in aqueous solution- a kinetic study. *Environ. Technol. 16* , 729-740.
36. USEPA. (2010, March 31). *Domestic Wastewater and Pollution*. Retrieved 5 1, 2013, from Environmental Protection Administration: http://www.epa.gov.tw/en/epashow.aspx?list=102&path=135&guid=c4b6ad0f-13e5-4259-be98-8356037dc862&lang=en-us
37. USEPA. (2011, September 8). *United States Environmental Protection Agency.* Retrieved February 20, 2013, from Soil Screening Guidance: http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part_5.pdf
38. Vilhunen, S., Vilve, M., Vepsäläinen, M., & Sillanpää, M. (2010). Removal of organic matter from a variety of water matrices by UV photolysis and UV/H2O2 method. *J. Hazard. Mater.* , 776-782.
39. WHO Regional Office for Europe. (2000). *Air Quality Guidelines - Second Edition.* Copenhagen, Denmark: WHO Regional Office for Europe.
40. Wikipedia. (2013). *Response surface methodology*. Retrieved March 2, 2013, from Wikipedia, the free encyclopedia: http://en.wikipedia.org/wiki/Response_surface_methodology
41. Zakaria, M. P., & Mahat, A. A. (2006). Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments in the Langat Estuary. *Coastal Mar. Sci. 30(1)* , 387-395.

42. Zakaria, M. P., Geik, K. H., Lee, W. Y., & Hayet, R. (2005). Landfill leachate as a source of polycyclic aromatic hydrocarbons (PAHs) to Malaysian waters. *Coastal Mar. Sci 29(2)* , 116-123.
43. Zakaria, M. P., Takada, H., Tsutsumi, S., Ohno, K., Junya Yamada, E. K., & Kumata, H. (2002). Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) i Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs. *Environ. Sci. Technol. 36 , 36* (9), 1907-1918.
44. Zhu, X., Tian, J., Liu, R., & Chen, L. (2011). Optimization of Fenton and electro-Fenton oxidation of biologically treated coking wastewater using response surface methodology. *Sep. Purif. Technol. 81* , 444-450.

APPENDICES

Appendix 1: COD Value of Sample for Preliminary Experiments

Table A.1.1: Effect of reaction time on COD removal

Reaction time (min)	COD value (mg/L)				Removal Efficiency (%)
	1	2	3	Average	
0	530	555	380	488.33	0.00
15	335	271	330	312	36.11
30	232	279	290	267	45.32
60	280	238	250	256	47.58
90	269	217	273	253	48.19
120	265	262	236	254.33	47.92
150	245	268	247	253.33	48.12

Table A.1.2: Effect of H_2O_2 concentration on COD removal

H_2O_2 concentration (mM)	COD value (mg/L)				Removal Efficiency (%)
	1	2	3	Average	
0.5	243	361	261	288.33	40.96
1	176	138	160	158	67.65
3	269	217	273	253	48.19
5	330	459	368	385. 67	21.02

Table A.1.3: Effect of pH on COD removal

pH	COD value (mg/L)				Removal Efficiency (%)
	1	2	3	Average	
2	135	138	165	146	70.10
4	261	264	237	254	47.99
6	232	200	163	198.33	59.39
8	350	240	253	281	42.46

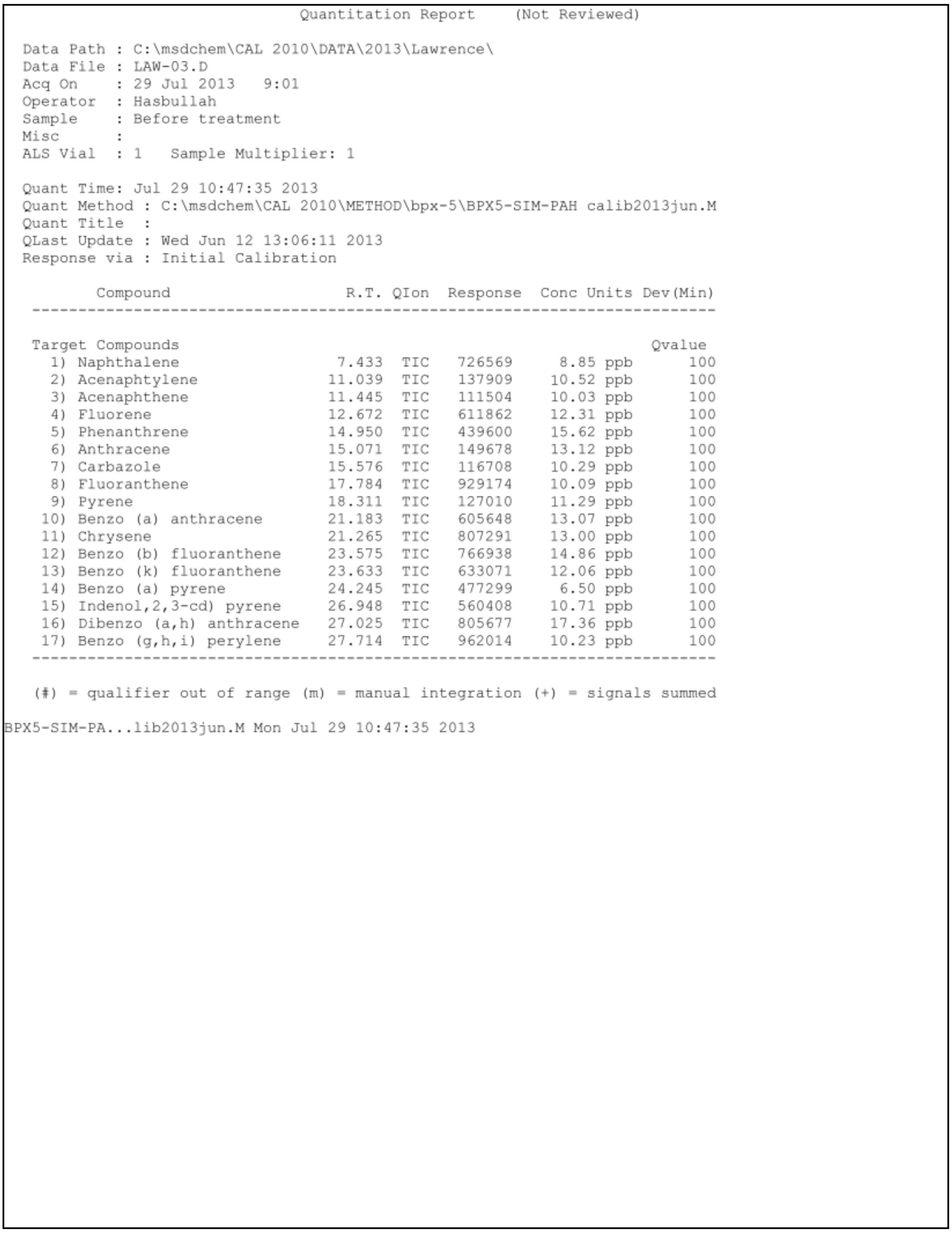
Appendix 2: COD Value of Sample for CCD

Table A.2.1: COD values and its removal efficiency for CCD

H_2O_2 concentration mM	pH	Reaction time min	COD value (mg/L)				Removal Efficiency (%)
			1	2	3	Average	
1	2	30	507	574	521	534.00	47.95
3	2	30	370	480	573	526.50	48.68
1	5	30	348	418	433	399.67	61.05
3	5	30	477	479	450	468.67	54.32
1	2	90	189	279	266	244.67	76.15
3	2	90	275	225	230	243.33	76.28
1	5	90	204	276	196	225.33	78.04
3	5	90	279	277	277	277.67	72.94
0.32	3.5	60	302	295	280	292.33	71.51
3.68	3.5	60	390	209	248	228.50	77.73
2	0.98	60	174	279	326	302.50	70.52
2	6.02	60	457	462	367	428.67	58.22
2	3.5	0.55	565	594	584	581.00	43.37
2	3.5	110.45	114	120	106	113.33	88.95
2	3.5	60	251	289	278	272.67	73.42
2	3.5	60	285	257	240	260.67	74.59
2	3.5	60	268	280	177	274.00	73.29
2	3.5	60	286	250	280	272.00	73.49
2	3.5	60	210	280	265	251.67	75.47
2	3.5	60	267	282	240	263.00	74.37

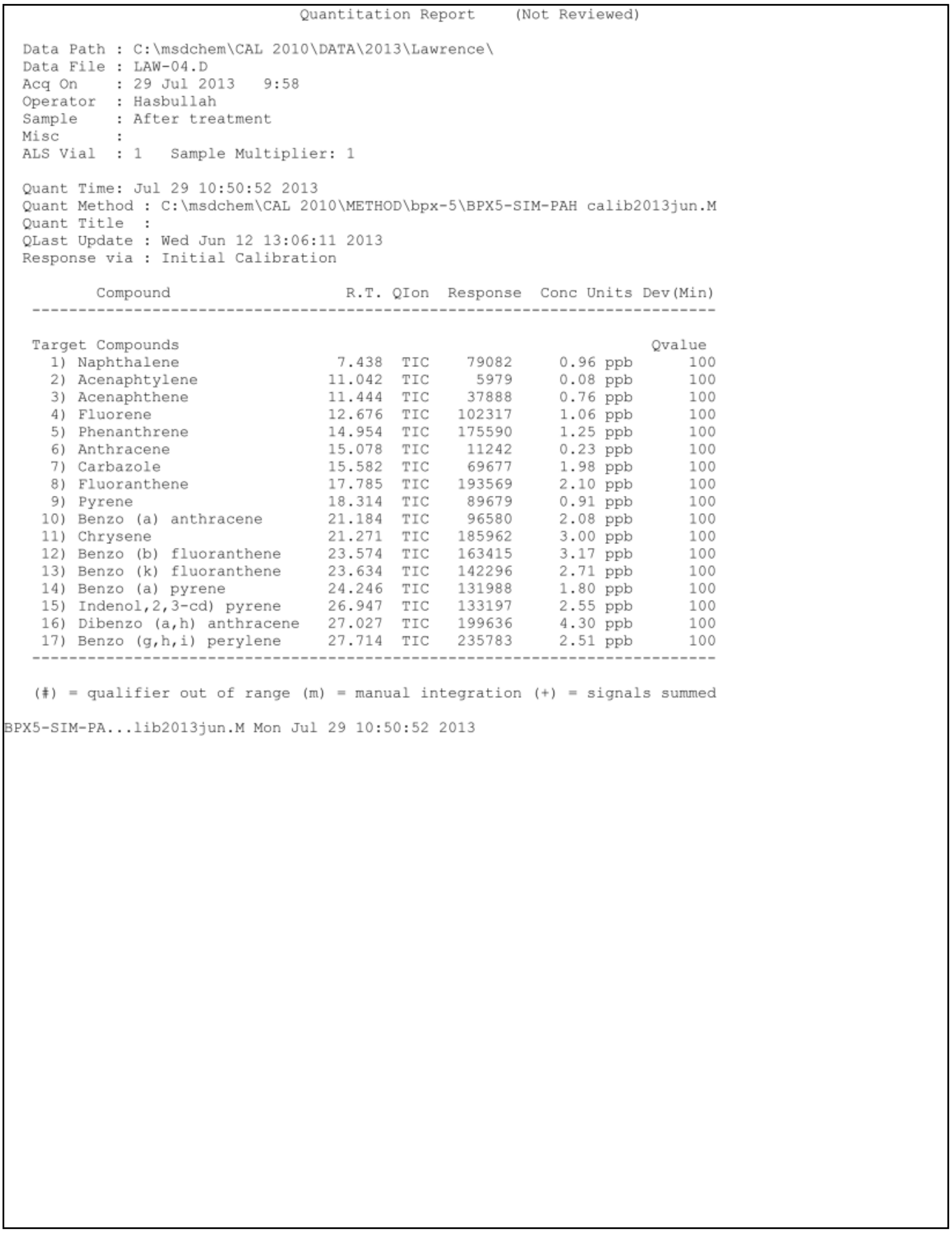
* Red colour high-lighhted result denotes inconsistent readings that are ignored for the calculation of average results

Appendix 3: The Quantitaion Report of PAHs Concentration



```
                                Quantitation Report    (Not Reviewed)

  Data Path : C:\msdchem\CAL 2010\DATA\2013\Lawrence\
  Data File : LAW-03.D
  Acq On    : 29 Jul 2013   9:01
  Operator  : Hasbullah
  Sample    : Before treatment
  Misc      :
  ALS Vial  : 1   Sample Multiplier: 1

  Quant Time: Jul 29 10:47:35 2013
  Quant Method : C:\msdchem\CAL 2010\METHOD\bpx-5\BPX5-SIM-PAH calib2013jun.M
  Quant Title  :
  QLast Update : Wed Jun 12 13:06:11 2013
  Response via : Initial Calibration

          Compound                   R.T. QIon  Response  Conc Units Dev(Min)
   ---------------------------------------------------------------------------

   Target Compounds                                                   Qvalue
     1) Naphthalene                 7.433  TIC   726569     8.85 ppb       100
     2) Acenaphtylene              11.039  TIC   137909    10.52 ppb       100
     3) Acenaphthene               11.445  TIC   111504    10.03 ppb       100
     4) Fluorene                   12.672  TIC   611862    12.31 ppb       100
     5) Phenanthrene               14.950  TIC   439600    15.62 ppb       100
     6) Anthracene                 15.071  TIC   149678    13.12 ppb       100
     7) Carbazole                  15.576  TIC   116708    10.29 ppb       100
     8) Fluoranthene               17.784  TIC   929174    10.09 ppb       100
     9) Pyrene                     18.311  TIC   127010    11.29 ppb       100
    10) Benzo (a) anthracene       21.183  TIC   605648    13.07 ppb       100
    11) Chrysene                   21.265  TIC   807291    13.00 ppb       100
    12) Benzo (b) fluoranthene     23.575  TIC   766938    14.86 ppb       100
    13) Benzo (k) fluoranthene     23.633  TIC   633071    12.06 ppb       100
    14) Benzo (a) pyrene           24.245  TIC   477299     6.50 ppb       100
    15) Indenol,2,3-cd) pyrene     26.948  TIC   560408    10.71 ppb       100
    16) Dibenzo (a,h) anthracene   27.025  TIC   805677    17.36 ppb       100
    17) Benzo (g,h,i) perylene     27.714  TIC   962014    10.23 ppb       100
   ---------------------------------------------------------------------------

   (#) = qualifier out of range (m) = manual integration (+) = signals summed

BPX5-SIM-PA...lib2013jun.M Mon Jul 29 10:47:35 2013
```

Figure A.3.1: The initial concentration of PAHs in the sample



```
                                Quantitation Report    (Not Reviewed)

  Data Path : C:\msdchem\CAL 2010\DATA\2013\Lawrence\
  Data File : LAW-04.D
  Acq On    : 29 Jul 2013   9:58
  Operator  : Hasbullah
  Sample    : After treatment
  Misc      :
  ALS Vial  : 1   Sample Multiplier: 1

  Quant Time: Jul 29 10:50:52 2013
  Quant Method : C:\msdchem\CAL 2010\METHOD\bpx-5\BPX5-SIM-PAH calib2013jun.M
  Quant Title  :
  QLast Update : Wed Jun 12 13:06:11 2013
  Response via : Initial Calibration

          Compound                   R.T. QIon  Response  Conc Units Dev(Min)
   -------------------------------------------------------------------------

   Target Compounds                                                  Qvalue
     1) Naphthalene                  7.438  TIC    79082     0.96 ppb      100
     2) Acenaphtylene               11.042  TIC     5979     0.08 ppb      100
     3) Acenaphthene                11.444  TIC    37888     0.76 ppb      100
     4) Fluorene                    12.676  TIC   102317     1.06 ppb      100
     5) Phenanthrene                14.954  TIC   175590     1.25 ppb      100
     6) Anthracene                  15.078  TIC    11242     0.23 ppb      100
     7) Carbazole                   15.582  TIC    69677     1.98 ppb      100
     8) Fluoranthene                17.785  TIC   193569     2.10 ppb      100
     9) Pyrene                      18.314  TIC    89679     0.91 ppb      100
    10) Benzo (a) anthracene        21.184  TIC    96580     2.08 ppb      100
    11) Chrysene                    21.271  TIC   185962     3.00 ppb      100
    12) Benzo (b) fluoranthene      23.574  TIC   163415     3.17 ppb      100
    13) Benzo (k) fluoranthene      23.634  TIC   142296     2.71 ppb      100
    14) Benzo (a) pyrene            24.246  TIC   131988     1.80 ppb      100
    15) Indenol,2,3-cd) pyrene      26.947  TIC   133197     2.55 ppb      100
    16) Dibenzo (a,h) anthracene    27.027  TIC   199636     4.30 ppb      100
    17) Benzo (g,h,i) perylene      27.714  TIC   235783     2.51 ppb      100
   -------------------------------------------------------------------------

   (#) = qualifier out of range (m) = manual integration (+) = signals summed

BPX5-SIM-PA...lib2013jun.M Mon Jul 29 10:50:52 2013
```

Figure A.3.2: The final concentration of PAHs in the sample

Appendix 4: Gantt Chart and Key Milestones

Table A.4.1: Gantt chart and key milestones of the project

	FYP 1														FYP 2													
	January			February				March				April			May			June				July				August		
Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Topic Selection/ Confirmation	Δ																											
Preliminary Research Study		🟩	🟩	🟩	🟩																							
Submission of Extended Proposal Defense						Δ																						
Further Research Studies						🟩	🟩	🟩																				
Proposal Defense									Δ																			
Laboratory Equipment and Experiments Familiarization										🟩																		
Water Sampling and Analysis										🟩	🟩																	
Experiment Based on RSM (1)											🟩	🟩	🟩															
Submission of Interim Draft Report													Δ															
Submission of Interim Report														Δ														
Experiment Based on RSM (2)															🟩	🟩												
1st Sub-Analysis																	🟩	🟩										
Verification Experiment																			🟩	🟩								
2nd Sub- Analysis																					🟩							
Submission of Progress Report																						Δ						
Final Report and Presentation Preparation																							🟩	🟩	🟩			
Pre-SEDEX																									Δ			
Submission of Draft Report																										Δ		
Submission of Dissertation (Soft Bound)																											Δ	
Submission of Techincal Paper																											Δ	
Oral Presentation																												Δ
Submission of Dissertation (Hard Bound)																												Δ

Δ = Key Milestone

Appendix 5: Project Photos

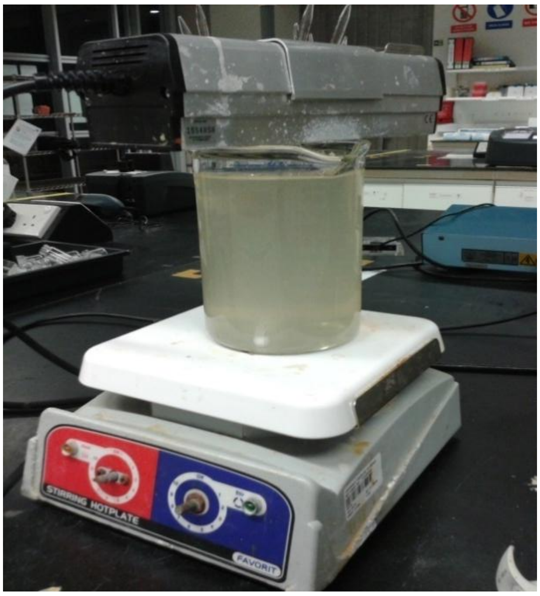


Figure A.5.1: The UV/H_2O_2 treatment process

Figure A.5.2: The liquid- liquid extraction of the sample by using filter funnel

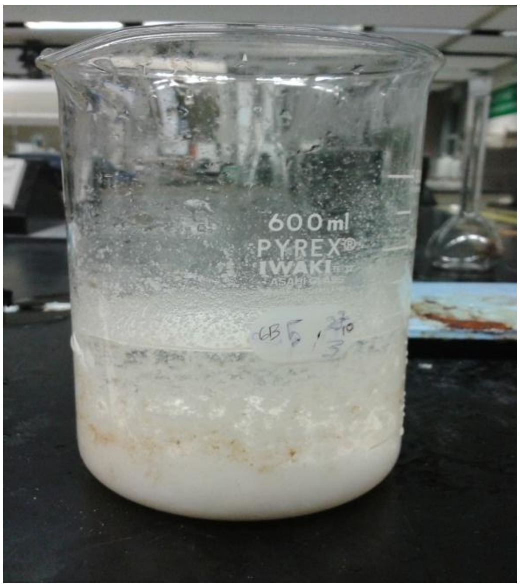


Figure A.5.3: The dehydration of sample after extraction

Figure A.5.4: The rotary evaporation of the sample

Figure A.5.5: GC/MS analysis of the sample