CHAPTER 1

INTRODUCTION

1.1 Research Background

Petroleum industry can be divided into four sectors; exploration and production of crude oil and natural gas, transport, refining and marketing and distribution. The petroleum industry began in 1859 in the United States in Titusville, PA and the opening of the first refinery was two years later [1]. However, the world's first oil refinery was opened in Ploiesti, Romania [2]. The evolution of the petroleum refining process is started from a simple distillation to sophisticated and complex processes [1]. The development of electricity and the advent of the internal combustion engine significantly impacted the demand for refined products [2]. The world's total refining capacity is approximately 82 million barrels per calendar day (BPCD) [3].

In Malaysia, development of hydrocarbon industry was influenced by the Petroleum Act 1972 and the Peninsular Gas Utilization Projects (PGU). PETRONAS was established to develop Malaysia's oil and gas reserves. PETRONAS is involved in the production, processing and operation of petrochemical industries. Malaysia has reserves of hydrocarbons in the form of crude oil and gas [4]. Most of Malaysia's oil reserves are located at the Malay basin and is the third highest in the Asia-Pacific region. The total oil production in Malaysia was 716,000 barrels per day (bbl/d) in 2010 [3]. Over the years, demand for chemical products in Malaysia has been increasing due to massive infrastructure development and industrialization programs. PETRONAS operates 3 refineries with a 259,000 bbl/d total capacity; includes PETRONAS Refinery in Kerteh, Terengganu (PP (T) SB) and PETRONAS Refinery in Sg Udang, Melaka I and Melaka II. Other petroleum refineries in Malaysia are Esso Refinery in Port Dickson, Negeri Sembilan, Shell Refinery in Port Dickson, Negeri Sembilan and Shell Refinery in Lutong, Sarawak [3, 4].

Refinery processes involve the conversion of crude oil into commercial consumable products by heating and boiling the crude oil in fractioning columns. Refinery processes are divided into atmospheric distillation, vacuum distillation, naphtha hydrotreater, catalytic reformer, distillate hydrotreater, fluid catalytic converter, and dimerization and isomerization units [1, 2]. Petroleum refining operations are classified into distillation (separation of crude oil in the atmosphere and vacuum distillation columns into groups of hydrocarbon compounds based on molecular size and boiling-point ranges), conversion (decomposition, unification and reforming), treatment (desalting, hydrodesulphurization, solvent refining, sweetening, solvent extraction and dewaxing) and blending (mixing and combining hydrocarbon fractions, additives to produce finished products) [2].

In this study, untreated petroleum refinery wastewater was collected from PETRONAS Penapisan (Melaka) Sdn Bhd (PP (M) SB) and studied. The details about the operation and production of PP (M) SB are described later.

1.1.1 PETRONAS Penapisan (Melaka) Sdn Bhd (PP (M) SB)

PP (M) SB is located at Persiaran Penapisan, 76300 Sungai Udang, Melaka and began operation in 1994 as PETRONAS's second refinery after PP (T) SB. PP (M) SB produces up to 80% of Malaysia's fuel requirements approximately 220,000 bbl/d and is larger than PP (T) SB, Shell and Esso. The operation began with the PETRONAS Refinery Phase 1 (PSR-1) as a sweet hydro skimming refinery. PSR-1 is owned by PETRONAS. Then, PP (M) SB was expanded with the addition of the Second Refinery Phase 2 (PSR-2) in 1998. The function of PSR-2 is to process sour crude oil with higher sulphur content. PSR-2 is owned by the Malaysian Refining Company Sdn Bhd (MRCSB), a joint venture company between PETRONAS (53%) and ConocoPhillips (47%) [5].

The main refinery processes include crude and vacuum distillation, naphtha hydrotreater, catalytic reform, C6 isomerization, distillation hydrotreater, hydrocracker, delayed coker, hydrogen production, LPG, naphtha and kerosene treaters, and sulphur recovery. The final products are liquefied petroleum gas (LPG), petrochemical naphtha (PCN), motor gasoline (Mogas), kerosene (Jet A1), diesel, asphalt, coke and sulphur [2, 3].

The refinery is equipped with effluent treatment facilities known as the Effluent Treating System (ETS) to meet the environmental effluent regulations set by authorities. ETS is designed to treat approximately 466 m^3/h of wastewater using an activated sludge system. This treatment system can be divided into preliminary and primary, and secondary and tertiary where municipal and industrial wastewater are mixed and treated in a centralised system. The ETS process layout is shown in Figure 1.1.

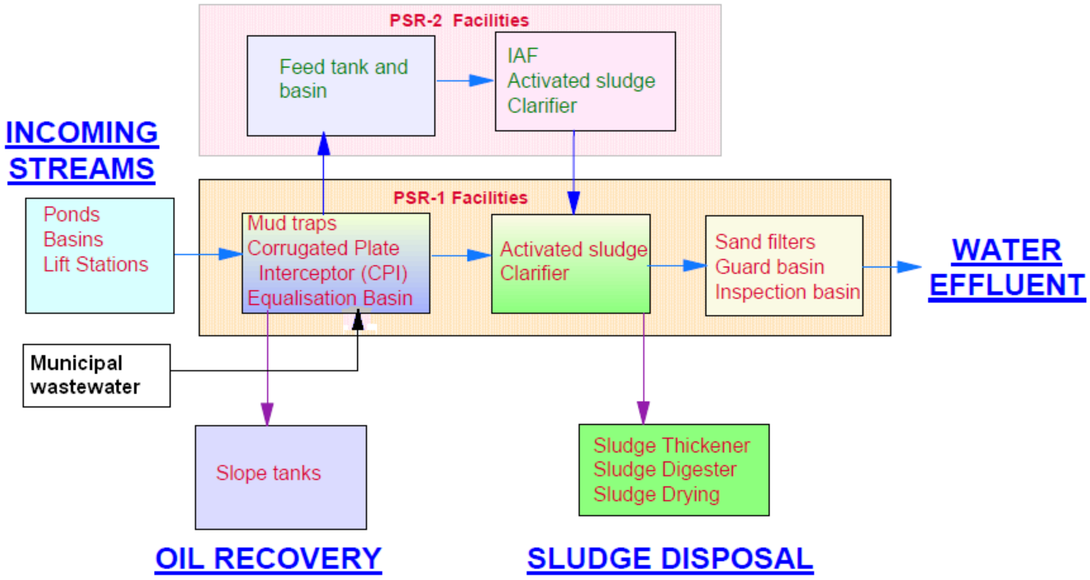


Figure 1.1: The ETS Layout

Petroleum refinery wastewater (PRW) is collected at ponds, basins and lift stations, and then sent to mud trap units for oil skimming using a Corrugated Plate Interceptor (CPI) and removal of the suspended solids as primary treatment. The process is followed by the adjustment of the pH and addition of nutrients to the wastewater. Further primary treatment is involves the air flotation pump, skimming sump and polymer preparation and, dosing unit. Then, the pretreated wastewater is sent for the secondary treatment by gravity. The secondary treatment includes the aeration tank and clarifiers. In the aeration tank, organic matter present in the wastewater is biochemically degraded into water and carbon dioxide. Meanwhile, the suspended activated sludge is separated by sedimentation in the clarifiers. The excess sludge is withdrawn and collected at the Sludge Treatment and Disposal unit. The tertiary treatment is required to filter the excess suspended solid and involves a sand filter basin and backwash water basin. The treated effluent is discharged into a guard basin and sent to the sea [6].

1.1.2 Problem Statement

Petroleum refining industries utilize large quantities of water for desalting, distillation, thermal cracking, and catalytic and treatment processes to produce liquefied petroleum gas (LPG), gasoline, jet fuel, diesel, asphalt and petrochemical feed stocks [7, 8]. The refining process generates wastewater 0.4-1.6 times the volume of the crude oil processed [9]. The discharge of this wastewater into water bodies results in environmental and human health effects due to the release of toxic contaminants such as hydrocarbons, phenol and dissolved minerals [10-12]. High exposure for long periods to these compounds can cause leukemia and tumors in multiple organs [13, 14].

Generally, PRW can be treated using physical, chemical and biological methods. However, physical and chemical methods are considered expensive due to the high price of the chemicals and equipment involved and may produce excessive amounts of sludge. Biological methods are most preferred due to their simplicity, efficiency and environmentally friendly operation [13, 15, 16].

However, PRW has relatively low biodegradability and seems to be difficult to treat by the biological system. Being low in biodegradability shows the existence of toxic compounds in the refinery wastewater [17]. Toxic compounds are able to inhibit microorganism’s growth in biological systems [18, 19]. In addition, refinery wastewater may contain recalcitrant compounds that are synthetic compounds which biodegrade slowly or are non-biodegradable [20].

1.2 Objectives

This study deals with the treatment of raw refinery wastewater using the Fenton-Sequencing Batch Reactor system. The objectives of this research are:

I. To evaluate and optimize the efficiency of the Fenton process as a pretreatment process to improve biodegradability of petroleum refinery wastewater.

II. To determine the efficiency of the Sequencing Batch Reactor in the treatment of the petroleum refinery wastewater pre-treated by Fenton process.

III. To compare the quality of the effluent from AOP-SBR to standard discharge limits.

1.3 Scope of Study

Petroleum refinery wastewater collected from PP (M) SB is low in biodegradability thus the Fenton process as a pretreatment has been implemented to improve its biodegradability. In this study, the efficiency of the Fenton process was assessed through three operating variables namely H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and reaction time (minutes). Biodegradability was expressed in terms of the BOD_5/COD ratio. After the preliminary analysis of the Fenton process, the relationship between each operating variable was assessed using the Response Surface Methodology (RSM). The fit of the data with the experimental work was represented through the ANOVA analysis in RSM. Then, the pretreated wastewater was treated using the Sequencing Batch Reactor (SBR). The performance of SBR was monitored through the effluent Chemical Oxygen Demand (COD), COD removal efficiency, Mixed Liquor Suspended Solids (MLSS), Mixed Liquor Volatile Suspended Solids (MLVSS) and Sludge Volume Index (SVI). At steady state operation, performance of SBR in treatment of pre-treated petroleum refinery wastewater was determined based on COD, BOD_5, Total Suspended Solid (TSS), colour, sulphide, phenol, ammonia nitrogen, oil and grease, and pH of the final SBR effluent.

1.4 Thesis Organization

This study contains five chapters. Chapter 1 presents the introduction, background, problem statement, objectives and scope of the study.

Chapter 2 initially explains treatment of petroleum refinery wastewater and effect of untreated petroleum refinery wastewater to environment and human health with aid of other literatures. In addition, treatment methods which have been used in the study namely Fenton method under category of advanced oxidation process (AOP) and sequencing batch reactor (SBR) as biological treatment is detailed. Response surface methodology (RSM) as the statistical model used in the study is discussed too. The chapter then covers the originality and significance of the study.

Chapter 3 focuses on the materials and methods used to conduct experiments in the study. This chapter also describes the petroleum refinery wastewater sampling and the analysis techniques to characterize the refinery wastewater samples. In addition, experimental procedures of Fenton, SBR processes and application of RSM are elaborated.

Chapter 4 highlights the results as well as discussion on the study findings. The results of experimental procedures for Fenton and SBR processes are elaborated and outcome of optimization of the oxidation method via RSM is discussed. At the end of the chapter the wastewater characteristics after treatment are compared with the standard limits instructed by Malaysian department of environment (DOE).

Chapter 5 concludes the research by confirming the findings and implication of results derived from the study. Recommendation for future research is also included in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.0 Chapter Overview

This chapter begins with the description of the petroleum refinery wastewater treatment, characteristics of petroleum refinery wastewater and its effect to environment and human health. The research works of recent and past literatures in the area of advanced oxidation process, Fenton process, response surface methodology, biological processes and sequencing batch reactor are discussed.

2.1 Petroleum Refinery Wastewater (PRW) Treatment

PRW needs to be treated before being discharged into the sea due to the existence of contaminants which are toxic to the environment and humans as well. The composition of PRW depends on the complexity of the refining process [10] but in general, the compounds in PRW include dissolved and dispersed oil, and dissolved formation minerals [21]. Oil is a mixture of hydrocarbons (benzene, toluene, ethylbenzene, xylenes, polyaromatic hydrocarbons (PAHs) and phenol). Dissolved formation minerals are inorganic compounds which include anions and cations, including heavy metals [4, 22 – 24]. Studies were reported on the characteristics of PRW as shown in Table 2.1.

Wastewater treatment can be classified into physical (screening, sedimentation, flotation, filtration and air stripping), chemical (coagulation, precipitation, oxidation and ion exchange), and biological (suspended-growth, attached-growth and hybrid systems) [17]. The typical wastewater treatment scheme for PRW, shown in Figure 2.1, consists of pretreatment, primary, secondary and tertiary treatment. The pretreatment section includes the screening process and separation tanks which are used to remove suspended solids, large solid particles and suspended substances. The primary treatment involves mechanical and physicochemical methods.

Physicochemical methods such as filtration, sedimentation or flotation are applied to reduce the heavy metal concentration. The biological treatment is applied at secondary section for removal of organic and biodegradable pollutants followed by the secondary settling in the clarifiers. Advanced treatment ensures that the quality of the effluent achieves the standard limit before being discharged into water bodies [6, 11].

Table 2.1: Characteristics of PRW

Parameter	[4]	[22]	[23]	[24]
BOD_5	570	150 - 350	150 - 350	-
COD	850 -1020	300 - 800	300 - 600	330 – 556
Phenol	98 – 128	20 - 200	-	-
Oil	12.7	3000	50	40 – 91
TSS	-	100	150	130 – 250
BTEX	23.9	1 - 100	-	-
Heavy metals	-	0.1 - 100	-	-
Chrome	-	0.2 - 10	-	-
Ammonia	5.1 - 2.1	-	10 - 30	4.1 - 33.4
pH	8.0 - 8.2	-	7 - 9	7.5 - 10.3
Turbidity	22 – 52	-	-	10.5 - 159.4

All the units are in mg/L, except turbidity (NTU) and pH.

2.2 Effect of the Untreated Petroleum Refinery Wastewater on the Environment and Human Health

Discharge of poorly treated PRW into water bodies results in environmental and human health effects due to release of hydrocarbons, phenol and dissolved minerals that are referred to as priority pollutants, 80% of which may be considered hazardous because of the presence of toxic organics and heavy metals [10-12, 25].

Studies have reported that monoaromatic hydrocarbon compounds like benzene, toluene, ethyl benzene and xylenes (BTEX) are of serious concern due to their toxicity and have also been classified as carcinogenic compounds [3, 26, 27]. High

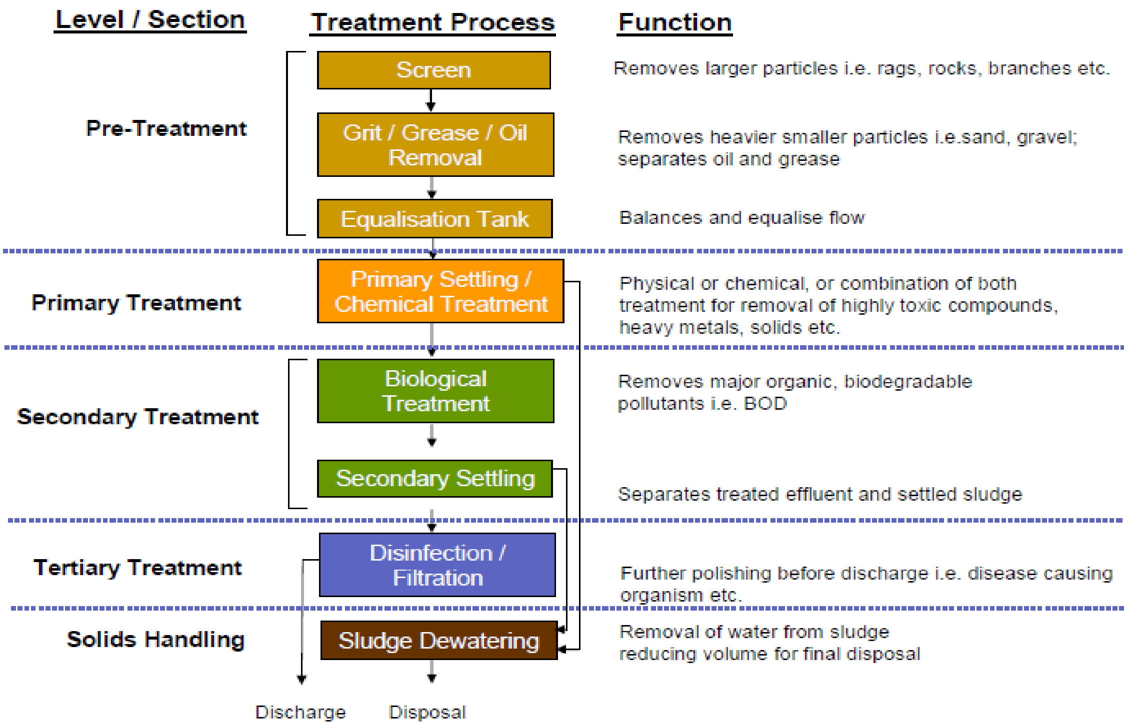


Figure 2.1: The Typical Wastewater Treatment Unit for PRW
(Source: PP (M) SB, 2010)

exposure for long periods to these compounds can cause leukemia and tumors in multiple organs due to the damage of the blood forming cells [13, 28]. Phenol and dissolved minerals, even at low concentrations, are toxic to aquatic life and lead to liver, lung, kidney and vascular system infections [14, 15]. Moreover, accumulation of nickel in the body can cause lung fibrosis, and cardiovascular and kidney diseases and also cancer [29, 30].

A study on the exposure of Nile tilapia fish to petroleum refinery effluents from the Nigerian National Petroleum Corporation showed trace metals a thousand times above the levels existing in the exposure medium; these included Pb, Zn, Cu, Mn, Cr, Ni and Cd [31]. Furthermore, a study on the impact of oil refinery effluent on aquatic environment found that refinery effluent is toxic at different concentrations to algae, invertebrates and fish. Marine species are more sensitive than freshwater species and crustaceans seem to be the most sensitive invertebrate. Moreover, the reproductive success and growth are reduced in the presence of refinery effluent [32].

Therefore, according to the Environmental Quality Act 1974, the Environmental Quality Regulations (Sewage and Industrial Effluents) 2009 and Environmental

Protection Agency (USEPA), refinery discharge has to be sufficiently treated for its quality to meet the established regulations [33, 34].

2.3 Advanced Oxidation Processes (AOPs)

AOPs are chemical oxidation processes that able to generate and use of hydroxyl free radicals (·OH) as strong oxidant [35]. AOPs were established by Glaze *et al.* [35] as oxidation processes which generate hydroxyl radicals in sufficient quantities to affect wastewater treatment. AOPs are efficient treatment methods for degrading recalcitrant materials, and inhibitory or toxic contaminants and being applied for the treatment of contaminated ground water, surface water and wastewater containing non-biodegradable organic pollutants to reduce its organic load and toxicity [35, 36]. In addition, the advantages of AOPs over conventional treatment methods are less production of chemical and biological sludge and almost complete demineralization of organics [37]. AOPs include Fenton process, photocatalysis and ozonation. The types and classification of AOPs are shown in Table 2.2 [38]. Besides, the oxidation potential of several chemical oxidizers are shown in Table 2.3.

Nowadays, different AOPs have been investigated on the removal of contaminants from wastewater like for petroleum refinery sour water [9], pharmaceutical wastewater [39, 40], and municipal treatment plants (effluent) [41].

Petroleum refinery wastewater contains substances that are toxic and resistant to biological treatment. On the other hand, the BOD_5/COD ratio of petroleum refinery wastewater is lower than 0.3 which is categorized as non biodegradable and is considered as being low in biodegradability [17]. The study reported that the ratio of more than 0.4 is considered thoroughly biodegradable [42]. Moreover, AOPs are feasible pre-treatment option prior to the biological treatment due to its efficiency in recalcitrant wastewater treatment [35].

Table 2.2: The Types and Classification of AOPs Mota *et al.,* [38]

Non-photochemical	Photochemical
Homogenous processes	
Ozonation in alkaline media (O_3/HO^-) Ozonation with hydrogen peroxide (O_3/H_2O_2) Fenton ($Fe^{2+/}$ H_2O_2) Electro-oxidation Electrohydraulic discharge-ultrasound Wet air oxidation Supercritical water oxidation	Photolysis of water in vacuum ultraviolet (VUV) UV/H_2O_2 UV/O_3 $UV/O_3/H_2O_2$ Photo-Fenton ($Fe^{2+/}$ H_2O_2/UV)
Heterogeneous processes	
Catalytic wet air oxidation	Heterogeneous photocatalysis: ZnO/UV, SnO_2/UV, TiO_2/UV, $TiO_2/$ H_2O_2/UV

Most AOPs enhance the biodegradability by reducing the COD load [17, 43-45]. AOPs generate less toxic effluents and improve biodegradability by forming intermediates similar to the metabolic pathway substances [46]. AOPs have been widely used as a pretreatment for industrial wastewater to improve biodegradability before the biological processes [47, 48].

Table 2.3: The Oxidation Potential of Several Chemical Oxidizers. Mota *et al.,* [38]

Oxidizing agent	Electrochemical oxidation potential (EOP), V
Fluorine	3.03
Hydroxyl radical	2.80
Ozone	2.07
Hydrogen peroxide	1.77
Potassium permanganate	1.67
Chlorine	1.36
Chlorine dioxide	1.50
Bromine	1.09

2.3.1 Fenton Process

The Fenton process was discovered by Henry John Horstman Fenton; it combines oxidation and coagulation reaction to reduce toxicity and COD using hydrogen peroxide and ferrous sulfate [49]. The oxidation mechanism by the Fenton process is due to the hydroxyl radical generated in an acidic solution by the catalytic decomposition of hydrogen peroxide [49].

The Fenton process includes four stages: pH adjustment, oxidation reaction, neutralization, and coagulation and precipitation. Organic substances are removed at oxidation and coagulation stages [49-52]. The Fenton reaction is shown in Eqs. (2.1-2.10) [43]. The Fenton reaction at an acidic pH leads to the production of ferric ions and hydroxyl radicals as shown in Eqs. 2.1 to 2.2:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} \bullet OH + OH^- \quad (2.1)$$

$$Fe^{3+} + H_2O_2 \leftrightarrows Fe - OOH^{2+} + H^+ \leftrightarrows \bullet H_2O + H^+ \quad (2.2)$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} or with H_2O_2 as shown in Eqs. 2.3 to 2.4:

$$\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad (2.3)$$

$$\bullet OH + H_2O_2 \rightarrow H\,O_2 \bullet + H_2O \quad (2.4)$$

Hydroxyl radicals may react with organics starting a chain reaction as shown in Eqs. 2.5 to 2.6.

$$\bullet OH + RH \rightarrow H_2O + R \bullet, \text{ RH = organic substrate} \quad (2.5)$$

$$R\bullet + O_2 \rightarrow ROO\bullet \rightarrow \text{products of degradation} \quad (2.6)$$

Ferrous ions and radicals are produced during the reactions as shown in Eqs. 2.7 to 2.10.

$$H_2O_2 + Fe^{3+} \leftrightarrows H^+ + FeOOH^{2+} \quad (2.7)$$

$$FeOOH^{2+} \rightarrow H\,O_2 \bullet + Fe^{2+} \quad (2.8)$$

$$H\,O_2 \bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \quad (2.9)$$

$$HO_2\bullet + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \quad (2.10)$$

High efficiency, simplicity in destroying the contaminants, stability to treat a wide range of substances and the non necessity for special equipment [53] are the advantages of the Fenton process. In addition, this process is cost-effective and has a short reaction time among all AOPs. This process also uses cheap and non-toxic iron and H_2O_2, where there is no mass transfer limitation due to its homogenous catalytic nature and is easy to run and controlled [54].

The Fenton process has been used for treatment of different types of wastewater including antibiotics [55], cork cooking wastewater [56] and pulp mill effluent [57]. A summary of the studies using the Fenton process is represented in Table 2.4.

Furthermore, the study on the treatment of antibiotic concentration was carried out and found that the maximum COD degradation, BOD_5/COD ratio and DOC degradation were achieved at the H_2O_2/COD molar ratio of 3, H_2O_2/Fe^{2+} molar ratio of 10 and pH 3 [55]. The increasing of the H_2O_2/COD molar ratio up to 3.5 did not improve the degradation due to the auto-decomposition of H_2O_2 to oxygen and water and the scavenging of the hydroxyl radical by H_2O_2. . Moreover, the excess H_2O_2 reacted with the ferric iron to form a hydroperoxyl radical. Then, the percentage of the COD degradation, BOD_5/COD ratio and DOC degradation increased with a decrease of the H_2O_2/Fe^{2+} molar ratios by 10. On the other hand, biodegradability increased up to 0.38 under this condition.

On the other hand, the cork cooking wastewater treatment by the Fenton process achieved the optimum result at the H_2O_2 concentration of 10g/L, Fe^{2+}/H_2O_2 1:5 and pH 3.2 with a removal efficiency of 66.4, 87.3 and 70.2% for TOC, COD and BOD_5, respectively [56]. In addition, the biodegradability was improved from 0.27 to 0.63 under this operating condition. Moreover, the results showed that an increase of the H_2O_2 concentration leads to an increase in the removal efficiency for TOC. Actually, the optimum result was achieved at the Fe^{2+}/H_2O_2 ratio 1:2 but the ratio of 1:5 was chosen in terms of economical issues since there is only a slightly difference between the TOC removal for the Fe^{2+}/H_2O_2 ratio 1:2 and 1:5 which is 69.1 and 65.4% , respectively.

Table 2.4: Summary of Studies using Fenton Process

Parameters	[55]	[56]	[57]
Type of wastewater	Antibiotics	Cork cooking	Pulp mill effluent
Operating variables	$COD/H_2O_2/Fe^{2+}$ molar ratio (1:3:0.30) at pH 3	H_2O_2 (10.6 g/L) , Fe^{2+}/ H_2O_2(1:5) at pH 3.2	H_2O_2 (50 mM) , H_2O_2/ Fe^{2+} molar ratio (20) and reaction time (30 minutes) at pH 5
Type of parameter	COD and DOC	TOC, COD and BOD_5	TOC, Color and AOX
Removal efficiency , %	81.4 and 54.3	66.4,87.3 and 70.2	88, 85 and 89%
Initial BOD_5/COD	0	0.27	-
Final BOD_5/COD	0.37	0.63	-

The study on pulp mill effluent found that the optimum removal of total organic carbon (TOC), colour and absorbable organic halogens (AOX) by the Fenton process were obtained at H_2O_2/Fe^{2+} molar ratio of 20, pH 5 and a 30 min reaction time [57]. The Fenton process showed the removal of 88, 85 and 89% for TOC, colour and AOX, respectively which is the maximum results compared to the hydrogen peroxide, UV plus hydrogen peroxide, photo-Fenton and ozonation processes.

2.4 Response Surface Methodology (RSM)

RSM is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data and has been a popular optimization method in recent years. It is applied when a response factor is influenced by several variables and was developed by Box and collaborators in the 1950s [58].

RSM consists of a group of mathematical and statistical techniques based on the fit of the empirical models to the experimental data obtained in relation to the experimental design such as a central composite design (CCD). The adequacy of the proposed model has been revealed by checking the tests provided by the analysis of variance (ANOVA) [58, 59]. Application of RSM involves several phases; they are the screening of variables, choice of the experimental design, codification of the levels of the variables, mathematical-statistical treatment of the data, evaluation of the fitted model and the determination of the optimal conditions [58]. The relationship between the response and the input is given by Eq. 2.11 [60]. The quadratic equation model for predicting the optimal variables is shown in Eq. 2.12 [58]:

$$\eta = f(x_1, x_2, ..., x_n) + \varepsilon \tag{2.11}$$

Where η is the response, f is the unknown function of response, x_1, x_2, … x_n are the independent variables, n is the number of independent variables and ε is statistical error that represent the other sources of variability not accounted for by f.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i.X_i + \sum_{i=1}^{k} \beta_{ii}.X_i^2 + \sum_{i_{i \le j}}^{k} \sum_{j}^{k} \beta_{ij}.X_i.X_j + ... + e \tag{2.12}$$

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

RSM is useful to evaluate the significance of the variables and their interactions, build models and reduce the number of experimental trials [61]. Moreover, classical methods are time consuming and large numbers of experiments are needed to explain the behavior of a system [60].

Studies were reported on the use of RSM for the optimization of petroleum refinery effluent [62], electrochemical [63], photocatalytic decolourization [64], coagulation [65] and electrocoagulation [66]. Different types of industrial wastewater were applied the RSM to optimize the Fenton process; these included olive oil mill [59], chemical laboratory [67], complex industrial [68] and petroleum refinery effluent [69] as shown in Table 2.5.

The RSM study on olive oil mill wastewater treatment includes three numerical factors which are H_2O_2/Fe^{2+}, pH and olive oil mill wastewater concentration, and four response factors COD, total phenolic (TP), colour and aromatocity removal [59]. 15 experimental runs were conducted using the range of 1.67 to 8.33 for H_2O_2/Fe^{2+}, 3 to

Table 2.5: Summary of Studies using Fenton Process and RSM

Parameters	[59]	[67]	[68]	[69]
Type of wastewater	Olive oil mill (OMW)	Chemical laboratory wastewater	Complex industrial wastewater	Petroleum refinery effluent
Type of numerical factor	H_2O_2/Fe^{2+} , pH and OMW concentration	COD/H_2O_2, H_2O_2/Fe^{2+} and pH	COD/H_2O_2 and H_2O/Fe^{2+}	H_2O_2/PRE, H_2O_2/Fe^{3+} and reaction time
Type of response factor	COD, total phenolic (TP), color and aromatocity removal	COD removal	COD removal	TOC and COD removal
Removal efficiency , %	56, 100, 33 and 32	92.3	80	70 and 98.1
Optimum condition	H_2O_2/Fe^{2+} ratio (8.33), pH (4) and OMW concentration (70%)	COD/H_2O_2 (1:9), H_2O/Fe^{2+} (4.5)and pH(4)	COD/H_2O_2 (0.58)and H_2O/Fe^{2+}(15)	H_2O_2/PRE (12), H_2O_2/Fe^{3+} (5)and reaction time (30 min)
R^2	90 - 99%	-	85%	TOC (99.84%) and COD (96.36%)

5 for pH and 40 to 100 for olive oil mill wastewater concentration, respectively. The relationship between these numerical factors was analyzed using ANOVA where the models for COD, TP, colour and aromatocity removal were significant by the F-test at the 5% confidence level (Prob>F<0.05). A high value of R^2 for COD, TP, colour and aromatocity removal of 98.8, 98.2, 99.2 and 90.2, respectively showed satisfactory adjustment of the quadratic model to the experimental data.

In addition, the coefficient for the variance was also considered reasonably reproducible since the value was not greater than 10% which was the CV for COD which was 9.68%; the TP, colour and aromatocity removal were 10.54%, 10.84% and 38.75%, respectively. The high CV for aromatocity removal showed difficulties in the aromatocity measurement but was considered acceptable based on high R^2. Moreover, the adequate precision was desirable in the range of 9 to 39 which is greater than 4. The optimum condition was H_2O_2/Fe^{2+}8.33, pH 4 and 70% of the olive oil mill wastewater concentration, respectively with R^2 of 90.2 to 99.2%. These conditions were chosen because the COD removal increased with the increasing of H_2O_2/Fe^{2+} and pH up to 8.33 and 4 respectively. A similar result was observed for TP removal. Thereafter, the aromatocity removal was increased with an increase of the olive oil mill wastewater concentration up to 70% and started to decrease at the higher concentration of 100%.

On the other hand, the optimization of the chemical laboratory wastewater treatment was studied using the COD/H_2O_2 ratio, H_2O_2/Fe^{2+} ratio and pH as numerical factors and COD removal as the response factor [67]. The experimental runs comprised of 2 stages, ie. oxidation stage and precipitation stage, thus, 28 experimental runs have been conducted. Then, this study reported that the center of the composite design was chosen based on other studies carried out by Bidga and Bishop *et.al.* where the center is at H_2O_2/Fe^{2+} 5:1 and pH 3.5, respectively. In addition, it was reported that the COD/H_2O_2 ratio was the most significant factor in the Fenton treatment of chemical laboratory wastewater followed by the H_2O_2/Fe^{2+} ratio and pH. The relationship between these numerical factors was analyzed using ANOVA where the models for the COD removal were significant by the F-test at the 5% confidence level ($Prob>F<0.05$). Then the predicted COD removal (%) versus the measured COD removal (%) was in good agreement by 94% of the data variability. It was found that, the COD removal increased to 86% by increasing the COD/H_2O_2 ratio and decreasing the H_2O_2/Fe^{2+} ratio. Meanwhile, at a constant pH between 3.5 and 4, the COD removal increased up to 92% with the increasing of the COD/H_2O_2 ratio. However, also at a similar constant pH, the COD removal increased to 91% with a decreasing in the H_2O_2/Fe^{2+} ratio which showed that H_2O_2 or Fe^{2+} is pH sensitive. Overall, the optimum conditions for the chemical laboratory wastewater treatment were found to be at the ratios of COD/H_2O_2 1:9, H_2O_2/Fe^{2+} 4.5:1 and pH 4.

The study for the complex industrial wastewater using RSM chose the COD/H_2O_2 ratio, H_2O_2/Fe^{2+} ratio and initial hydrogen peroxide concentration to be the numerical factors and the response factor was the COD removal (%) with a set of 30 experimental runs [68]. The ranges for the COD/H_2O_2 ratio, H_2O_2/Fe^{2+} ratio and initial hydrogen peroxide concentration (g/L) were set between 0.23 to 3.40, 10 to 20 and 11.62 to 85.30. ANOVA showed a high R^2 about 85% and the significance of the model was $Prob>F<0.05$. Overall, the optimum conditions for complex industrial wastewater treatment were found to be at COD/H_2O_2 ratio 0.58, H_2O_2/Fe^{2+} 15:1 ratio and initial hydrogen peroxide concentration at about 32 g/L with 80% of the COD removal.

The study on the optimization of the Fenton process for the petroleum refinery effluent (PRE) was carried out using three numerical factors which were H_2O_2/PRE, H_2O_2/Fe^{3+} and reaction time, and the response factors of the COD and TOC removal [69]. Seventeen experiments were conducted based on three-factorial central composite design. The ranges for the H_2O_2/PRE ratio, H_2O_2/Fe^{3+} ratio and reaction time were set between 2 to 12, 5 to 20 and 30 to 240 min. ANOVA showed high R^2 for COD and TOC of about 96.4% and 99.8%, respectively and the significance of the model was Prob>F<0.05. The optimum conditions for the petroleum refinery effluent were found to be at the H_2O_2/PRE ratio of 12, H_2O_2/Fe^{3+} ratio of 5, and the reaction time of 30 min by giving 98.1 % and 70% of the COD and TOC removal, respectively.

2.5 Biological Processes

Biological processes utilize microorganisms to oxidize organic matter into simple products such as CO_2, H_2O and CH_4 under aerobic, anaerobic or semi aerobic conditions [23]. The microorganisms require nutrients, carbon and energy sources for their growth. A C: N: P ratio of about 100:5:1 is considered adequate for microorganisms to grow [17, 70]. Normally, four sources of microorganisms are applied in biological treatments such as naturally-occurring microorganisms, commercial microorganisms, specific groups of microorganisms and acclimatized sewage sludge [21, 23]. The use of bacteria, fungi and other organisms for wastewater treatment is known as bioremediation. This technology is environmentally safe, cost-effective wastewater treatment and does not generate secondary waste.

A study on the biodegradation of petroleum oil by bacteria and nematode identified the *Bacillus* species as primary degrader bacteria which cooperates with nematodes for the degradation of the pollutants [71]. In a study using modified organisms known as bioaugmentation, it has been found that the activated sludge system took only 20 days to achieve COD below 80 mg/L (to give 84.2% of COD removal efficiency) and an NH_4^+-N concentration of 10 mg/L as compared to a non-bioaugmented system which needed an extra 10 days to reach a similar effluent quality [23].

Biological processes are classified into suspended-growth, attached-growth or combination (hybrid) processes. Attached-growth process has higher biomass concentrations, higher metabolic activity, greater resistance to toxicity and better biomass properties as compared to a suspended-growth process [22]. However, the sludge age for the attached-growth process is more difficult to control as compared to the suspended-growth process.

2.5.1 Suspended Growth Process

In suspended-growth processes, microorganisms are maintained in a suspension mode within the liquid in a reactor. The batch treatment using suspended biomass is the simplest operational bioreactor design. The reactor is allowed to operate with mixing under either aerobic or anaerobic conditions. One of the common suspended-growth processes is activated sludge. Typical activated sludge processes used in wastewater treatment are the plug-flow, complete mix and sequencing batch reactor (SBR) [17]. The plug-flow and complete mix activated sludge require a return activated-sludge (RAS) system and clarifiers, SBR as a modified activated sludge process operates without a clarifier.

Other suspended-growth methods are the continuous stirred tank reactor (CSTR) and membrane bioreactor. A study of CSTR carried out using the bioaugmented microbial consortium and it was found up to 95% of the COD removal and 97.5% of the total petroleum hydrocarbon (TPH) removal, respectively. It showed the efficiency of the bioaugmented bacteria like *Aeromonas punctata (Aeromonas caviae), Bacillus cereus, Ochrobactrum intermedium, Stenotrophomonas maltophilia and Rhodococcus* sp. for organic matter and TPH removal [72]. Furthermore, microorganisms, including bacteria, fungi and yeasts, predominantly aerobics, are known for their ability to degrade hydrocarbons. The aerobic degrading bacteria in an organo-polluted site belong to *Pseudomonas* sp., *Acinetobacter* sp., *Alcaligenes* sp., *Flavobacterium/Cytophaga* group, *Xanthomonas* sp., *Nocardia* sp., *Mycobacterium* sp., *Corynebacterium* sp., *Arthrobacter* sp., *Comamonas* sp., and *Bacillus* sp. [73].

A membrane bioreactor was studied and showed COD, BOD_5, SS and turbidity removal efficiency of 78-98 %, 96-99 %, 74-99 % and 99-100 %, respectively [74]. Another study using a plug-flow membrane bioreactor found 93 %, 99 % and 96 % removal for COD, BOD and TOC, respectively. It was also reported that the bacterial community was affected at a high petroleum pollutant concentration of 1000 µL/L. Bacterial population started to diverge at this dosage [75]. Table 2.6 show a summary of the above mentioned studies.

Table 2.6: Application of Suspended-Growth in Noxious Refinery Wastewater Treatment

Parameters	[73]	[74]	[75]
System	CSTR	Membrane Bioreactor	Plug Flow Membrane
BOD_5 removal (%)	-	96 - 99	99
COD removal (%)	Up to 95	78 - 98	93
Type of contaminants	TPH	-	TPH
Influent contaminants	320 mg TPH^{-1}	-	50 – 100 µL/L
Contaminants removal (%)	97.5	-	Almost 100

2.5.2 Attached Growth Process

In the attached-growth process, microorganisms are attached to an inert material like rocks, slag or plastic which makes them able to generate a biofilm [76]. The biofilm contains extracellular polymeric substances produced by microorganisms [17]. Bioreactors with adhered biofilm have advantages such as a greater concentration of biomass retained in the system with greater metabolic activities, and hence there is no requirement of the sludge to be returned to the reactor; moreover, the coexistence of anoxic and aerobic metabolic activity within the same biomass ecosystem causes a high efficiency in the pollutant removal [13].

A study on the oil refinery wastewater treatment using a fixed-film bioreactor showed the COD removal rates of 80-90 % at an 8 hr hydraulic retention time (HRT) [77]. A longer HRT is required in anaerobic systems due to the slow reaction; however, these kinds of systems have a lower operational cost as well as some energy production in the form of methane gas. A study on an anaerobic up-flow fixed-film reactor operated at $37^{\circ}C$ showed about 0.33 $m^3\ kg^{-1}\ COD\ d^{-1}$ methane production at an OLR of 6 kg COD $m^{-3}\ d^{-1}$ [78].

Fixed-film processes which are attached growth biological treatment systems can be divided into the trickling filter, fluidized bed bioreactor (FBB) and rotating biological contactor (RBC) [17, 79]. FBB involves solid particles that are denser than water which are suspended in the column by an up-flow stream of liquid [80]. The concept of FBB is similar to the trickling filter. Furthermore, it has been found that the largest COD reduction was achieved at various ratios of bed (settled) volume (V_b, L^3) to bioreactor volume (V_R, L^3), (V_b/V_R) = 0.55 and air velocities (u, LT^{-1}) = 0.029 m/s [80]. The use of a pilot internal circulating three-phase FBB (ICTFBB) was studied and it was more resistant to COD and phenol shock loading. Its operation was more stable compared to the activated sludge reactor and the average removal efficiency of COD, oil, phenol, ammonia nitrogen and phosphorus were 75.9 %, 75.3 %, 92.8 %, 40.0 %, 87.2 %, respectively [81].

The RBC reactor consists of a series of discs, on which the biofilm grows, mounted on a horizontal shaft, positioned above the liquid level and rotates at right angles to the flow of the wastewater. The discs are partially submerged and exposed both to the atmosphere where oxygen is absorbed and to the liquid phase where soluble organic matter is utilized [17]. A study on the treatment of hydrocarbon-rich wastewater using RBC showed that at the 21 hr HRT and an OLR of 27.33 g TPH/m^2d, the system was able to remove 99 % and 97 % of TPH and COD, respectively [79]. A summary of the discussed studies using the attached-growth processes are presented in Table 2.7.

Table 2.7: Application of Attached Growth Processes in Refinery Wastewater Treatment

Reference	[77]	[78]	[79]
System	Fixed-film	Anaerobic Up-flow Fixed-film	RBC
HRT (h)	8	9	21
OLR	-	6 (kg COD m^3/d)	27.33 g TPH/m^2d
COD removal	85-90 %	98 % ± 0.5	84.6-97.8 %

2.5.3 Hybrid Process

This process is a combination of the suspended and attached-growth processes in the same reactor like the combination of the activated sludge and the submerged biofilters (fixed bed biofilters). A carrier material is placed in the reactor and maintained in a suspension by aeration or mechanical mixing known as a moving bed reactor [17]. Tyagi *et al.* [82] studied the performance of the RBC-polyurethane foam (PUF) to biodegrade petroleum refinery wastewater and achieved a COD removal efficiency of up to 87 %. It was also reported on the advantageous of PUF as a structure for microorganisms to attach, grow and be protected from high external shear [82]. A study using a hybrid bioreactor system showed more than 90% of 2,4,6-trichlorophenol (TCP), COD and toxicity removal efficiencies [83]. The application of the submerged membrane bioreactor (SMBR) indicates that the removal efficiencies for COD and TOC increased by 17 and 20 %, respectively as compared to the system without a membrane [84]. A crossflow membrane bioreactor (CF-MBR) was investigated and showed about a 93% of COD removal efficiency. Moreover, the hydraulic retention time did not significantly affect the performance of this system [85].

2.5.4 Sequencing Batch Reactor (SBR)

SBR is a typical activated sludge system that is based on the fill-and-draw batch system [86]. This system is a batch operation and has been applied for industrial and municipal wastewater treatment due to its high removal efficiency of BOD, COD and suspended solids [87]. SBR offers more advantages over the conventional activated sludge system. SBR is cost effective in terms of capital and operating costs because of less civil structures, interconnecting pipes and process equipment due to the elimination of clarifiers [88]. The operation of SBR is also flexible in terms of reaction times to the concentration and the degree of the treatment required for the wastewater [88]. In addition, this system requires minimal footprint, it is easier to control the filamentous growth and settling problems, and bad settling can be recognized and corrected [86]. SBR operation requires well trained operators and the operation can be monitored automatically using computer simulation, therefore, the number of operators can be reduced.

SBR operation consists of five phases; fill (raw wastewater is added into a reactor and mixed with biomass in the reactor), react (the metabolic biological reaction (consumption of organic matter under aerobic or anaerobic conditions)), settle (aeration and mixing are stopped and the sludge is separated from the supernatant), draw (supernatant is removed) and idle (excess sludge is eliminated).

SBR has been applied in many wastewater treatments such as complex chemical wastewater (removal efficiencies of 66.4% for COD, 92.2% for BOD_5 and 7.8% for sulphate, respectively) [89], piggery wastewater (removal efficiencies of 99.8% for nitrogen and 97.8% for phosphate, respectively) [90], petroleum refinery wastewater (removal efficiencies of 88% for Hg (II) and 97.4% for Cd (II) respectively) [91], (removal efficiencies of 99% for COD, 94% for BOD_5, respectively) [92], and electroplating (removal efficiencies of 85% ±3 for COD, 79% ± 2 for BOD_5 and 97.7% ±0.7 for cyanide respectively) [93]. Summary for each study using SBR is described and shown in Table 2.8.

On the other hand, the combination of SBR and the Fenton process was also reported. A study on the textile industry wastewater treatment indicated a chemical oxidation; the Fenton process prior to the biological treatment gave the highest removal of COD (91.1%), TKN (91.6%), TP (80.6%) and colour (79.8%) [88]. Furthermore, 98% and 95% removal efficiencies of COD were achieved by using the Fenton process followed by SBR for pharmaceutical wastewater treatment [94] and swine wastewater [95], respectively. A summary for each study using the Fenton-SBR was described and is shown in Table 2.9.

2.5.5 Biological Treatment System Comparison

Activated sludge system is the common system for municipal and industrial wastewater treatment. The process is either in a continuous or semicontinuous aerobic method for biological wastewater treatment. The components of the activated sludge microorganisms are kept in suspension and aerated in the reactor, liquid-solid separation and a recycle system for returning solids removed from separation unit back to the reactor. In the conventional activated sludge process, a settleable solid is separated by gravity causing it to settle in the sedimentation tank followed by physical and chemical processes. The factors effecting this process are wastewater flow and quality, wastewater aeration time, sludge volume index (SVI), mixed liquor suspended solid (MLSS), dissolved oxygen (DO) and aeration requirements, sludge age, wastewater temperature and the concentration of the wastewater [17, 96].

Table 2.8: Summary for Studies Using SBR

Parameters	[89]	[90]	[91]	[92]	[93]
Type of wastewater	Complex chemical	Piggery	Petroleum refinery wastewater	Petroleum refinery wastewater	Electroplating
Cycle, h	24	4	8	12	1
HRT, d		0.5	15	1	
SRT, d			-	14	72±13
BOD_5 removal, %	92.2		-	99	85 ±3
COD removal, %	66.4		80	94	79 ±2
Type of contaminants	Sulphate	Nitrogen and phosphate	Hg^{2+} and Cd^{2+}	Phenol and o-cresol	cyanide
Influent contaminants	1.75 g/L	Ammonia (900 mg/L) and phosphate (90 mg/L)	9.03 ± 0.02 and 15.52 ± 0.02 (mg/L)	0.1 - 0.8 and 0.1 - 0.6 ($kg/m^3.d$)	0.022 $kgCN/m^3d$
Contaminants removal, %	7.8	99.8 and 97.8	88.3 and 97.4	-	97.7 ±0.7
Effluent TSS, mg/l			-	12	75
SVI, ml/g	50-100	-	58	80	95

Table 2.9: Summary for Studies using Fenton-SBR

Parameters	[88]	[94]	[95]
Type of wastewater	Textile	Pharmaceutical	Swine
Fenton process	Fe^{2+}/H_2O_2 (1:1) and pH 3	H_2O_2/Fe^{2+} (155) and pH 3.5	H_2O_2/Fe^{2+} (1.5) and pH 5
SBR	1 cycle	1 cycle	-
Type of contaminants	COD , TKN , TP and color	COD and BOD	COD, Total phosphorus and SS
Contaminants removal, %	COD (91.1%), TKN (91.6%), TP (80.6%) and color (79.8%)	98	98

Over the years, the activated sludge system has been improved to comply with the high-quality effluent of the wastewater treatment plants. New activated sludge technology has been developed with advanced equipment and process control. Different types of modified activated sludge are reported such as plug-flow, complete mix and sequencing batch reactor [17]. New wastewater treatment systems has been reported such as the sequencing batch reactor, continuous stirred tank reactor, fluidized bed bioreactor, rotating biological contactor, airlift bioreactor and membrane bioreactor. These systems were developed to overcome short comings of the activated sludge systems. Table 2.10 shows the advantages and disadvantages of each system.

As illustrated in Table 2.11, a comparison between each of developed processes with conventional activated sludge systems indicates that the operation of SBR, CSTR and the membrane bioreactor is considered very good based on the simplicity and flexibility of the operation. However, FBB and RBC require more complicated operations and process design as compared to the activated sludge process [97]. SBR, CSTR and FBB are more economical due to the elimination of clarifiers and less requirement equipment and civil works. However, well trained personnel are required to monitor the reactor process. The membrane and RBC obviously require a higher cost for reactor setup and maintenance [98].

SBR showed very good performance in toxicity removal as reported earlier. The membrane bioreactor also has a great potential in toxicity removal compared to the conventional activated sludge due to the use of a low sludge load and high sludge age. The high sludge age helps the bacteria to adapt with the pollutants [99]. FBB offers very good toxicity removal due to the use of small sized carrier particles that have a large specific area for bacterial growth. Stability of the bacterial growth is very important in order to achieve the optimum degradation of the organic matter. CSTR and RBC also are considered good in toxicity removal even though they have been rarely applied in recent studies.

The main problem in SBR is the possibility of the suspended solid being discharged during the draw step due to less sludge settleability [86]. However, CSTR, membrane, FBB and RBC have been characterized with good sludge settleability based on the reactor design. Bioparticles are retained in the reactor and there is less possibility of the suspended solid being discharged due to the good sludge settleability [97].

Table 2.10: Advantages and Disadvantages of Different Biological Treatment Process [100]

System	Advantages	Disadvantages
Sequencing batch reactor	• Operating flexibility and control • Minimal footprint • Eco-friendly (reduce capital cost by eliminating clarifiers)	• Higher level of maintenance • Higher level of sophistication • Potential of discharging floating sludge during decant phase
Continuous stirred tank reactor	• High-load system • Less volume and space requirement	• Longer start-up times • Require sophisticated process control
Fluidized bed bioreactor	• Treatment in low retention time due to high biomass concentration • Overcome bed clogging and the high pressure drop • Ability to operate in continuous state	• Increased reactor vessel • Pumping requirements and pressure drops • Erosion of internal components
Rotating biological contactor	• Short retention time • Low power requirements • Low sludge production	• Requirement for covering RBC units in northern climates to protect against freezing • Shaft bearings and mechanical drive units require frequent maintenance.
Airlift bioreactor	• Simple design • Well control flow and efficient mixing • Increase mass transfer	• Higher initial capital investment • Inefficient gas or liquid separation • Lower efficiency of gas compression
Membrane bioreactor	• Short hydraulic retention time • Easy to upgrade the conventional system • Low sludge production	• Membrane fouling problem • Large energy input for membrane operation • High membrane cost

Table 2.11: Comparison between Developed Methods and Conventional Activated Sludge Process* [100]

Method	Operation	Cost	Toxic removal	Sludge settleability
Sequencing Batch Reactor (SBR)	A	B	A	C
Continuously Stirred Tank Bioreactor (CSTB)	A	B	B	B
Membrane bioreactor	A	B	A	B
Fluidized Bed Bioreactor (FBB)	B	B	A	B
Rotating Biological Contactor (RBC)	B	B	B	B

*A: very good, B: good, C: normal

2.6 Originality and Significance of the Study

Petroleum refinery wastewater (PRW) can be treated either by physical, chemical or biological process. An efficient treatment method is important to provide the standard quality of effluent. Specifically, many studies on PRW treatment were reported using different types of method such as submerged ultrafiltration [101], electrochemical [102] and electrocoagulation [103]. On the other hand, some studies were reported on the application of Fenton process for PRW treatment [68, 69]. However, no study was reported on coupling of Fenton-SBR for treatment of PRW. This study focuses on Fenton process and post treatment, SBR to determine its efficiency to provide standard quality of effluent which meets the limit instructed by department of environment (DOE), Malaysia.

2.7 Summary

Discharging of improper treated PRW to water bodies results in environmental and human health effects as per described before. Thus an efficient treatment method is required to solve this problem. Due to characteristics of PRW as low in biodegradability, a pretreatment is considered useful to improve the biodegradability before post treatment by a biological process such as SBR. This study describes the definition, advantages and application of AOP, Fenton process, RSM, biological processes and SBR from various studies. Fenton process as a feasible and effective AOP have been widely applied for biodegradability improvement of recalcitrant discharges. The optimization of Fenton process using statistical models such as RSM improves the operational conditions of the treatment. Finally, SBR as an activated sludge that classified under suspended growth system of biological process were discussed.

CHAPTER 3

METHODOLOGY

3.0 Chapter Overview

This chapter explains the detail of the research methodology used in this study. Further, it explains the research instruments, sampling and experimental procedures as well as statistical analysis techniques applied for the experiment optimization in the study.

3.1 Chemicals

Hydrogen peroxide, H_2O_2 (35%, w/w solution), ferrous sulphate heptahydrate, $FeSO_4.7H_2O$ and sulphuric acid, H_2SO_4 (95-98%), were purchased from R&M Marketing, Essex, U.K. Sodium hydroxide, NaOH (Analytical grade, 46-48%) was purchased from Merck, Germany. The H_2O_2 and $FeSO_4.7H_2O$ were used for the advanced oxidation process. The H_2SO_4 and NaOH were used for pH adjustment.

3.2 Analytical Methods

Characterization of the sample was carried out by analyzing the chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solid (TSS), pH, alkalinity, turbidity, colour, ammonia nitrogen, nitrate, total phosphorus, phenols, sulphide, sulphate, total Kjeldahl nitrogen (TKN), total organic carbon (TOC), oil and grease, benzene, toluene, ethyl benzene and xylene (BTEX). The sludge was characterized through a mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solid (MLVSS) and sludge volume index (SVI) analyses. The analyses were carried out according to the Standard Method for the Examination of Water and Wastewater and HACH in triplicate [104]. The standard deviation was measured, accordingly and the calculation for the standard deviation is represented in Eq. 3.1. The measured parameters and the methods of measurement are shown in Table 3.1.

$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n}} \tag{3.1}$$

Where σ is the standard deviation, Σ is sum of, x is each value in the data set, $\bar{X}$ is the means of all the values in the data set and n is the number of value in the data set.

Table 3.1: Measured Parameters and Their Methods

Parameters	Methods	Code
COD	HACH	435(HR)
BOD_5	APHA	5210 B
TSS	APHA	2540 B
pH	Sension 4	5177560
Alkalinity	APHA	2320 A
Turbidity	Turbidimeter	2100 P
Color	Spectrophotometric –Single –wavelength method (HACH)	2120 C
Ammonia Nitrogen	Nessler method (HACH)	380 N
Nitrate	Cadmium reduction method (HACH)	355 N
Phosphorus	HACH	536
Phenol	HACH	470
Sulphate	HACH	680
Sulphide	Methylene Blue method (HACH)	690
TKN	Buchi Kjeldahl Line HACH	4500-N_{org} B
TOC	TOC Analyzer	1020 A
Oil & Grease	NIC 20A Oil Content Meter	-
BTEX	Purge and Trap Capillary-Column GCMS	6200 B
MLSS	APHA	2540 D
MLVSS	APHA	2540 E
SVI	APHA	2710 D

3.2.1 Analytical Procedures

3.2.1.1 Chemical Oxygen Demand (COD)

The COD analysis was used to measure the oxygen equivalent of the organic material in the wastewater that could be oxidized chemically using dichromate in an acid solution.

2 mL of the sample was added into the COD vials containing potassium dichromate and heated in a HACH reactor for 2 hours. The reactor was set at 150^{o}C. Initially, a blank was prepared by filling another vial with distilled water. After 2 hours, the COD vials were cooled to room temperature and the values were read using a spectrophotometer (DR 2800 HACH). The blank sample was placed in a cell holder and the 'ZERO' button was pressed. The display showed 'Zeroing…' and next '0.0 mg/L depending on the materials. The blank sample was removed and replaced by vials of the sample. The light shield was closed. The 'READ' button was pressed. The display showed 'Reading…' and then the result appeared as a concentration of the sample in mg/L.

3. 2.1.2 Biochemical Oxygen Demand, 5 days (BOD_5)

BOD_5 is the most widely used parameter for organic pollution that involves measurement of the dissolved oxygen used by a microorganism in the biochemical oxidation of organic matter.

A 5 mL sample and 2 mL seed were added into the BOD bottle and filled with aerated water. The initial dissolved oxygen (DO) was read using a DO meter (YSI 5000, Ohio, USA), then the bottle was capped and kept in an incubator (Low Temperature Incubator 815, Thermo Electron Corporation Precision) at 20^{o}C for 5 days. The blank correction was prepared by filling aerated water only into the bottle. The seed correction was prepared by filling 2 mL of the seed into the bottle and topped up with aerated water. The final DO values were read and recorded, accordingly. The minimum residual DO was at least 1.0 mg/L and the DO depletion was 2.0 mg/L after 5 days of incubation. These were considered to produce valid data because at least 2.0 mg oxygen/uptake L was needed to give a meaningful measure of the oxygen uptake and at least 1.0 mg/L must remain throughout the test to ensure that insufficient DO does not affect the rate of the oxidation of the waste constituents. The calculation for the BOD_5 analysis is shown in Eq. 3.2.

$$\mathrm{BOD}_5, \mathrm{mg/L} = \frac{(D_1 - D_2) - (S)V_S}{P} \tag{3.2}$$

Where D_1 is the DO of the diluted sample immediately after the preparation, mg/L, D_2 is the DO of the diluted sample after 5 days incubation at 20^{o}C, mg/L, S is the oxygen uptake of the seed, DO/ml seed suspension added per bottle, V_S is the volume of the seed in the respective test bottle, mL, and P is the decimal volumetric fraction of the sample used; $\frac{1}{P}$ = dilution factor.

3.2.1.3 Total Suspended Solid (TSS)

The TSS analysis is of the physical characteristic of the wastewater to determine the total solid content in the solution which was composed of floating matter, settleable matter, and colloidal matter. An empty pan with filter paper (Whatman, No.1) was weighed and filtered with 100 mL of the sample. Then, it was heated in an oven at 105 ^{o}C for 1 hour. The heated pan with the filter paper was transferred to a dessicator cabinet (Boekel Scientific, Dricycler) to balance the temperature and weight, accordingly. Calculation for TSS is shown in Eq. 3.3.

$$\mathrm{TSS, mg/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}} \tag{3.3}$$

Where A is the weight of the dried residue + pan with the filter paper in mg and B is the weight of empty pan with the filter paper in mg

3. 2.1.4 pH Measurement

The pH of the sample was measured using a pH meter (HACH Sension 4). The pH meter was calibrated by pressing ‘CAL’ , placed in a buffer solution with pH 4, 7 and

10 while pressing ‘READ’ .Then a pH probe was placed in the sample and the value was recorded when the display was stable.

3.2.1.5 Alkalinity

The alkalinity of the sample was its acid-neutralizing capacity. The alkalinity is a measure of an aggregate property of water by the presence of hydroxides, carbonates and bicarbonates of the elements such as calcium, magnesium, sodium, potassium and ammonia. The analysis was carried out by the titration method where 50 mL of the sample were added with 3 drops of phenolphthalein and titrated using 0.02N H_2SO_4 to get the phenolphthalein alkalinity. Then, 3 drops of methyl orange was added into the same sample and titrated using 0.02N H_2SO_4 to get the total alkalinity. The alkalinity value was calculated using Eqs. 3.4 and 3.5.

Phenolphthalein alkalinity (P), as mg $CaCO_3$/L

$$= \frac{(\text{mL } H_2SO_4 \text{ titrant used}) \times \text{Normality of } H_2SO_4 \times 50{,}000}{\text{mL sample}} \tag{3.4}$$

Total alkalinity (T), as mL sample mg $CaCO_3$/L

$$= \frac{(\text{Total mL } H_2SO_4 \text{ titrant used}) \times \text{Normality of } H_2SO_4 \times 50{,}000}{\text{mL sample}} \tag{3.5}$$

3.2.1.6 Turbidity

Turbidity is the physical characteristics of a sample related to suspended and colloidal matter such as clay, silt, and the finely divided organic and inorganic matter. Turbidity is an expression of the optical property that causes light to be scattered and absorbed. Turbidity was measured using the Turbidimeter (2100 P Portable Turbidimeter, HACH Company, Colo, USA). 15 mL of the sample was filled into the sample cells, capped and placed into the Turbidimeter. The ‘READ’ button was pressed. The reading was recorded in NTU.

3. 2.1.7 Colour

The term “colour” can classified into true or apparent colour. The true colour is the filtered sample as turbidity has been removed. The apparent colour is the unfiltered sample which contains colloidal or suspended matter. 10 mL of the sample were filled into the sample cells. Another sample cell was filled with distilled water. A blank sample cell was placed into a spectrophotometer (DR 2800) that was set to ‘ZERO’, removed and replaced by the cell of the prepared sample and the ‘READ’ button was pressed. The display showed ‘Reading…’ and then the concentration of the sample in Pt Co was displayed.

3.2.1.8 Ammonia Nitrogen

The ammonia nitrogen analysis is a measure of the nutrient content in wastewater in terms of nitrogen. Ammonia nitrogen present in an aqueous solution as either ammonium ions or ammonia gas, depending on the pH of the solution. 25 mL of the sample was filled into conical flasks. Another conical flask was filled with deionized water. 3 drops of the Mineral Stabilizer and the Polyvinyl Alcohol Dispersing agent were added into each conical flask and mixed well. 1.0 mL of the Nessler Reagent was added and mixed well. After a 1 minute reaction, 10 ml of the solution were poured into the sample cells. The blank sample cell was placed into a cell holder of the spectrophotometer (DR 2800) that was set to ‘ZERO’, removed and replaced by the cell of the sample. The ‘READ’ button was pressed. The display showed ‘Reading…’ and then the concentration of the sample in mg/L NH_3-N was displayed.

3.2.1.9 Nitrate

Nitrate is a measure of the nutrient content in wastewater and related to nitrification. Nitrification involves the conversion of nitrate to nitrite. This nutrient was also important for microbial growth. 10 mL of the sample and the NitraVer 5 Nitrate Reagent Powder Pillow were filled into sample cells. The sample cells were shaken vigorously for 1 minute and the reaction took taken place for 5 minutes. After the 5 minute reaction time, a blank sample cell was prepared by filling the sample only and inserting it into the cell holder of the spectrophotometer (DR 2800). The ‘ZERO’ button was pressed and the blank sample cell was removed and replaced by the cell of prepared sample. The 'READ' button was pressed. The display showed 'Reading…' and the result appeared as a concentration of the sample in mg/L NO_3-N.

3.2.1.10 Phosphorus

Phosphorus is an important nutrient for microbial growth. 5 mL of the sample and Potassium Persulfate Powder Pillow were filled into Total and Acid Hydrolysable Test Vials and shaken vigorously. Then the vials were heated using a HACH reactor at $150^{o}C$ for 30 minutes. After 30 minutes, the vials were removed from the reactor and cooled to room temperature. 2 mL of the 1.54 N Sodium Hydroxide Standard Solution was added into the vials, capped and mixed well. The vials were inserted into the cell holder of the spectrophotometer (DR 2800) while pressing 'ZERO'. The Phosver 3 Powder Pillow was added into the vials that were then shaken for 30 seconds. Then, the vials were inserted into the cell holder before pressing 'READ'. The results were displayed in mg/L PO_4^{3-}.

3.2.1.11 Phenol

300 mL of the sample, 5 ml of the Hardness reagent, Phenol Reagent Powder Pillow, Phenol 2 Reagent Powder Pillow and 30 mL of chloroform were added into a 500 ml separatory funnel and shaken for 30 seconds. The chloroform at the bottom of separatory funnel was filtered and drained into the sample cells. Another separatory funnel was filled with deionized water as a blank. A blank cell was placed into cell holder of the spectrophotometer (DR 2800). The 'ZERO' button was pressed and replaced by the prepared sample cells. The 'READ' button was pressed and the results were displayed in mg/L Phenol.

3.2.1.12 Sulphate

Sulphate ions are present in wastewater and are important for the synthesis of proteins. 10 mL of the sample and SulfaVer 4 Reagent Powder Pillow were filled into sample cells and shaken vigorously. Another sample cell was filled with 10 ml of the sample. After a 5 minute reaction time, a blank cell was placed into the cell holder of the spectrophotometer (DR 2800). The 'ZERO' button was pressed and then the blank was replaced with the prepared sample cells. The 'READ' button was pressed and the results were displayed in mg/L SO_4^{2-}.

3.2.1.13 Sulphide

High sulphide concentrations that exceed 200 mg/L will affect the biological process. A combination of sulphate and sulphide will form hydrogen sulphide and cause the corrosion of pipes. 10 mL of the sample, and 5 ml of Sulfide 1 Reagent and Sulfide 2 Reagent were added into the sample cells and mixed well. Another sample cell was filled with 10 mL of the sample. After a 5 minutes reaction time, a blank cell was placed into the cell holder of the spectrophotometer (DR 2800). The 'ZERO' button was pressed and then the blank was replaced with the prepared sample cells. The 'READ' button was pressed and the results were displayed in μg/L S^{2-}.

3.2.1.14 Total Kjeldahl Nitrogen (TKN)

The TKN analysis is a measure of the organic nitrogen and ammonia nitrogen. 20 mL of the sample and sulphuric acid were filled into the sample tube in a distiller followed by adding 10 tablets of Kjeldahl catalyst selenium. A blank was prepared by filling distilled water into a sample tube. Digestion was started at 10 rpm for 45 minutes followed by 5 rpm for 15 minutes. Then, the sample and blank cells were cooled to room temperature and transferred to a distillation unit (Buchi Kjeldahl Line, B-316, B-324, and B-339) for the distillation process. During the digestion, the organic nitrogen was converted to ammonium through the heat and acid processes. The calculation is shown in Eq. 3.6.

$$\text{TKN} = \frac{V_1 - V_2}{V_0} \times C \times 14.01 \times 1000 \qquad (3.6)$$

Where TKN is TKN in mg N/L, V_1 is the volume in ml of the acid used for the titration of the sample, V_2 is the volume in ml of the acid used for the titration of the blank, V_0 is the volume in ml of the sample, C is the molarity of the acid and 14.01is the relative atomic mass of the nitrogen.

3.2.1.15 Total Organic Carbon (TOC)

The TOC analysis is a measurement of the total amount of the organic substances in the water sample using the oxidation method’s combustion process. The sample was filled into TOC vials and placed in a chamber of the TOC Analyzer (1020A TOC Analyzer) for analysis. The results were displayed in TC (Total carbon) and TIC (Total inorganic carbon). The calculation is shown in Eq. 3.7.

$$TOC = TC - TIC \tag{3.7}$$

3.2.1.16 Oil & Grease

An Oil & grease analyzer (NIC Model Oil-20A oil content meter) was heated for 20 minutes for stabilization. 10 mL of a solvent (Tetrachloroethylene for spectroscopy Merck, 100965) was injected into the analyzer 5 times for the cleaning process. The ‘SPAN’ button was adjusted to 7.8 (refer to model) and the calibration showed ‘0.00 ppm’. 10 mL of the sample was injected and the results were shown in ppm.

3.2.1.17 BTEX

5 mL of the sample was injected to the purge and trap capillary-GCMS (Gas-Chromatography/Mass Spectrometric) (Tekmar Dohmann, 3100). ‘START’ was pressed. The sample information was saved into the system. When the system showed ‘DESORB’ and ‘READY’, the ‘START’ button was pressed again and the reaction started with preheat, bake, standby and ready for the next sample injection. The results were shown in ppm.

3.2.1.18 MLSS

The weight of the empty pan with a glass-fiber filter paper was measured using a weighing apparatus (Mettler Toledo AB204-S, Switzerland). A 5 mL sample was filtered through a glass-fiber filter paper and heated at 105°C for 1 hour. Then, it was transferred to a dessicator cabinet (Boekel Scientific, Dricycler) to balance the temperature and weight, accordingly. The calculation for MLSS is shown in Eq. 3.8

$$\text{MLSS, mg/L} = \frac{(A-B)\times 1000}{\text{sample volume, mL}} \tag{3.8}$$

Where *A* is the weight of the dried residue + pan with the glass-fiber filter paper in mg and *B* is the weight of the empty pan with the glass-fiber filter paper in mg

3.2.1.19 MLVSS

The pan with the glass-fiber filter paper (Whatman grade GF/A, 1.6µm) and residue after the MLSS analysis was heated in a furnace (P 320, Nabertherm, Germany) at 550°C for 20 minutes. Then, it was transferred to the dessicator cabinet (Boekel Scientific, Dricycler) to balance the temperature and weight, accordingly. The calculation for MLVSS is shown in Eq. 3.9.

$$\text{MLVSS, mg/L} = \frac{(A-B)\times 1000}{\text{sample volume, mL}} \tag{3.9}$$

Where *A* is the weight of the dried residue + pan with the glass-fiber filter paper before ignition in mg, and *B* is the weight of the empty pan with the glass-fiber filter paper after ignition in mg

3.2.1.20 SVI

1L sludge was filled into an I-L cylinder. The volume of the settled sludge was recorded after 30 minutes of settling. The calculation for SVI is shown in Eq. 3.10.

$$\text{SVI} = \frac{\text{settled sludge volume (mL/L)} \times 100}{\text{suspended solids (mg/L)}} \tag{3.10}$$

3.3 Petroleum Refinery Wastewater (PRW)

PRW samples were collected from a mud trap unit at the Effluent Treatment System (ETS), PP (M) SB and transported to the environmental engineering laboratory in Universiti Teknologi PETRONAS and stored in a cold room at 4^oC. The schematic diagram of ETS is shown in Figure 3.1.

The ETS system is known as a mixed treatment where wastewater from a process area (oily water and oily surface water) and domestic water are treated together. Sampling was carried out at the mud trap section before the oil skimming process. Figure 3.1 shows how the wastewater entered the mud trap section, goes to oil skimming and was mixes with domestic water at the equalization basin. The mixed wastewater then goes to the aeration basin clarifier, sand filter and guard basin. The treated wastewater is discharged into the sea after meeting the acceptable standards.

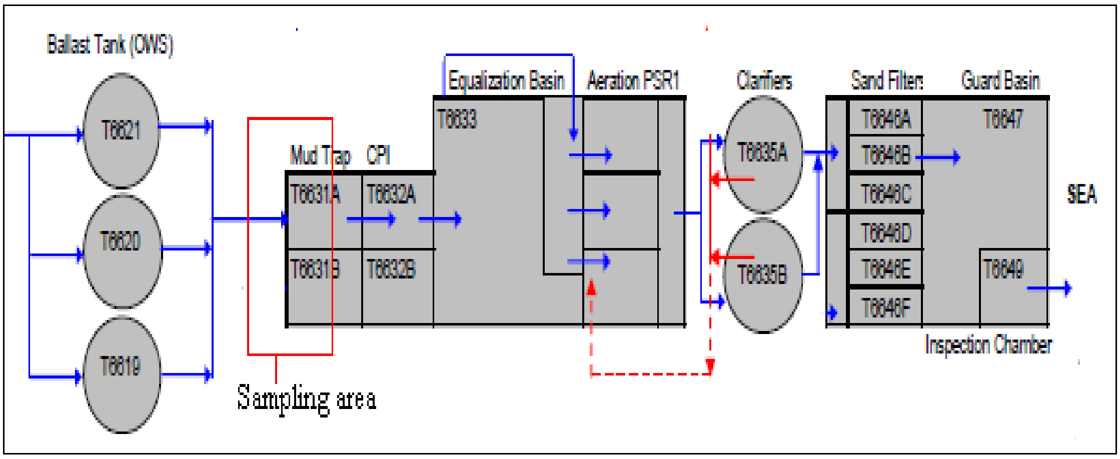


Figure 3.1: Schematic Diagram of ETS

3.4 Characteristics of Petroleum Refinery Wastewater

In this study, petroleum refinery wastewater was collected and characterized as shown in Table 3.2. It was found that BOD_5, COD, TSS, oil & grease, colour, ammonia nitrogen, phenol and sulphide concentrations exceeded the discharge limit by the DOE Standard stipulated Environmental Quality Act 1974 and the Environment Quality Regulations (Sewage and Industrial Effluents) 2009 [33]. BOD of the refinery wastewater is commonly lower than the BOD of the municipal wastewater due to the existence of organic materials that are only partially biodegradable [10]. The BOD value was higher than the acceptable level of 20 mg/L and 50 mg/L for Standard A and B, respectively. Then, COD value is also above the standard limit of 80 mg/L and 200 mg/L for Standard A and B, respectively. However, the international standard of COD for marine discharge is 150 mg/L for a complex refinery [10]. Higher COD concentrations in the refinery wastewater were due to the phenols and sulfide concentration contents [10].

The wastewater characteristics of the BOD_5/COD ratio of about 0.32 indicates low biodegradability [17] and requires a pretreatment before performing the biological treatment. Other studies reported similar BOD_5/COD ratios like for complex chemical wastewater (less than 0.3) [89] and leachate (0.39) [105]. Generally, wastewater with a BOD_5/COD ratio of about 0.5 or greater is considered to be easily treated by biological systems while it is quite difficult to deal with lower ratios [17].

The refinery wastewater showed a pH of 8.46 on average which is higher than the DOE standard. At this value, the refinery wastewater is not suitable for the microorganism’s growth in a biological system since the appropriate pH is around 6.5 to 7.5. The TSS value of about 310 mg/L indicates high total suspended solids content in the refinery wastewater which is composed of floating matter, settleable matter, and colloidal matter. Result of oil and grease analysis higher than permitted standard which is about 73 mg/L. The acceptable limits are only 1 and 10 for Standard A and B, respectively, where marine habitats such as fishes are affected at the higher oil and grease values which may be due to the decrease of the oxygen content in the surface sea water.

In terms of colour, the higher colour value is due to suspended solid materials in the wastewater that give it an undesirable colour. The colour for the collected refinery wastewater was cloudy blackish and its intensity is 3525 Pt Co. The nutrients content in the wastewater in terms of nitrogen was based on the ammonia nitrogen, nitrate and TKN analysis. Nutrients are important for the growth of microorganisms but lead to eutrophication if in excess. The international standard of TKN for refinery wastewater varies from 10 to 100 mg/L; thus, the results are in the suitable range [10]. However, ammonia nitrogen is 43 mg/L that is higher than the Malaysia standard discharge limit.

Table 3.2: Petroleum Refinery Wastewater Characteristics

Parameter	Range	Average
COD	744 - 1673	1209
BOD_5	405 - 648	527
BOD_5/COD	0.24 - 0.39	0.32
pH	7.50 - 9.41	8.46
Turbidity	402 - 419	411
Colour	3400 - 3650	3525
Nitrate	3.30 - 4.90	4.10
TSS	280 - 340	310
Alkalinity	133 - 138	136
Ammonia nitrogen	40 - 45	43
Oil and grease	48 - 97	73
Phosphorus	1.67 - 1.73	1.70
TOC	184 - 217	201
Phenol	1.16 - 1.44	1.30
Sulphide	14 - 17	16
Sulphate	40 - 50	45
TKN	82 - 95	89
Benzene	33.31 - 34.36	33.85
Toluene	38.58 - 41.08	39.83
Ethylbenzene	1.80 - 1.90	1.85
Xylene	30.03 - 33.04	31.54

All the units shown in Table 3.1 are in mg/L, except turbidity (NTU), color (Pt Co) and pH.

The phenol level was about 1.3 mg/L and also exceeded the discharge limit and needed to be removed because they are harmful and form other harmful products. Phenols are usually in high concentration in the spent caustic streams [10].

Sulphur compounds are measured based on sulphide and sulphate analyses. Refinery wastewater contains sulphur due to the presence of hydrogen sulphide, mercaptans and disulphides in the crude oil [10]. Both analyses showed higher than the discharge limit with values of 16 mg/L and 45 mg/L for sulphide and sulphate, respectively; however, the sulphate ion is important for synthesis of proteins.

The turbidity value of 411 NTU expresses the concentration of light being scattered and absorbed due to suspended and colloidal matter such as clay, silt, and finely divided organic and inorganic matter in the refinery wastewater. Thus, the maximum limit of phosphorus in a wastewater treatment plant is between 0.3 to 0.5 mg/L and considered to be limiting the nutrients in water bodies. However, the phosphorus level in the refinery wastewater was in excess for the biological process at about 1.7 mg/ L and may lead to eutrophication over the years.

The TOC analysis is a measurement of the total amount of organic substances in a water sample and the value was around 201 mg/L. Petroleum hydrocarbons in the refinery wastewater were determined based on Benzene, Toluene, Ethyl benzene and Xylene. The International standard limit is 5 ppm, thus, it shows that the refinery wastewater is higher in the BTEX concentration. High BTEX levels may lead to health problems as this compound acts as a carcinogenic agent.

Overall, the petroleum refinery wastewater needs to be treated before being discharged into the sea according to the standard limit.

3.5 Experimental Procedures

3.5.1 Fenton Process

The Fenton process was applied in this study to improve the biodegradability of PRW. The optimization of the Fenton process was conducted using the Response Surface Methodology (RSM). Preliminary analyses were conducted to determine the range of the operating variables to be used in RSM.

Experiments were conducted using a jar test apparatus (VELP-Scientifica, Model JLT6, Italy) with a reaction volume of 500 mL. The sample was filtered through filter paper (Whatman No.1) and set to pH 3 using H_2SO_4. $FeSO_4.7H_2O$ and H_2O_2 (35%, w/w solution) were added into the solution to initiate the Fenton process. Fenton process was initiated by adding H_2O_2 into the solution. The mixture was continuously mixed at 100 rpm. After the reaction time, the pH was increased to 10 using NaOH to promote the coagulation and the precipitation reaction that occurred due to the decomposition of H_2O_2 and the deactivation of a ferrous catalyst with the formation of ferric hydroxo complexes. The solution was settled overnight and filtered to remove excess flocculates and to reduce the interferences in COD determinations. The pH of the solution was decreased to the range of 6.5 to 7.5, that suitable for biological systems. COD and BOD_5 analyses were carried out, respectively, to check the biodegradability improvement in the samples.

3.5.1.1 Preliminary Analysis

The preliminary analysis was divided into three sets of experiments to determine the ranges for the reaction time, H_2O_2/COD and H_2O_2/Fe^{2+}. The first experiment was carried out by varying the reaction time (minutes) within 20, 40, 60, 80,100 and 120 minutes. Other operating conditions were fixed at H_2O_2/COD 2:1 and H_2O_2/Fe^{2+} 5:1.

Further experiments were carried out by varying the H_2O_2/COD molar ratios within 2, 4, 6, 8, 10 and 12. Other operating conditions were fixed at H_2O_2/Fe^{2+} 5:1 and 60 minutes of reaction time.

Then, experiments were carried out by varying the H_2O_2/Fe^{2+} molar ratios within 5, 10, 15, 20, 25 and 30. The operating conditions were fixed at 60 minutes of reaction time and H_2O_2/COD 2:1. Results were analyzed based on biodegradability in terms of the BOD_5/COD ratio.

3.5.2 Statistical Analysis

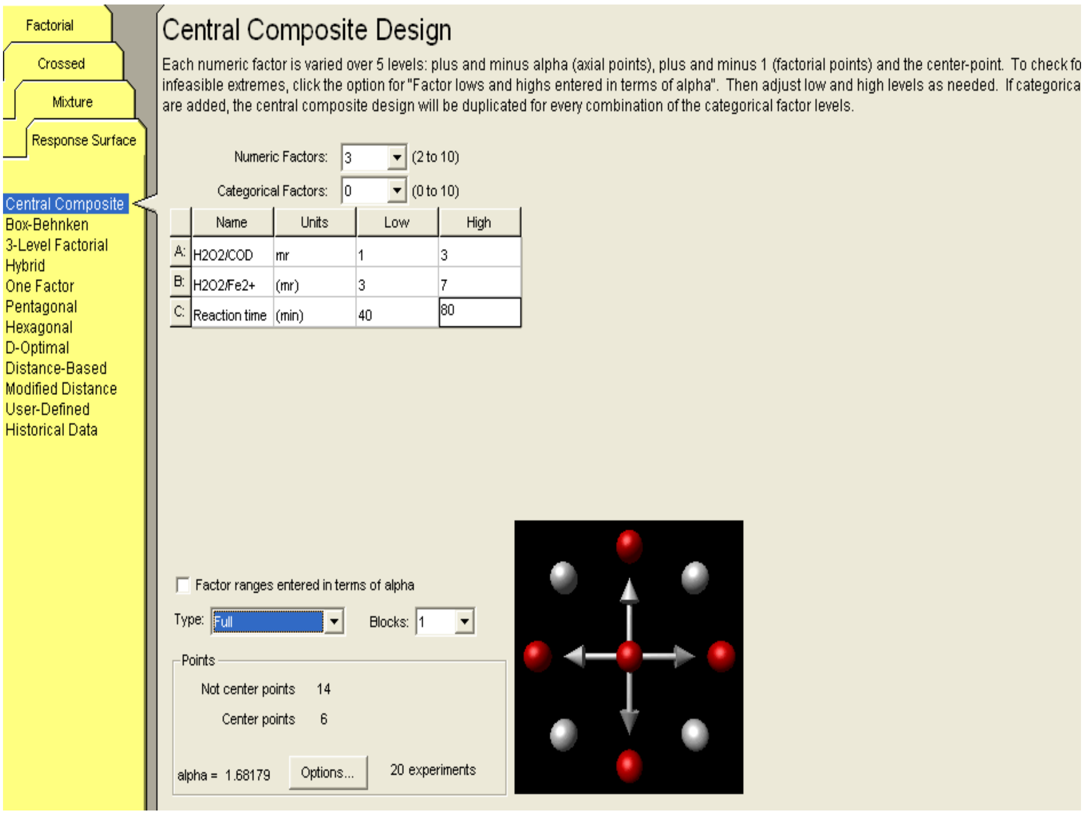
Based on the results achieved from the preliminary analysis, the Design Expert Software (version 6.0) was used for the statistical design of experiments and data analysis. In RSM, the CCD was applied to optimize the operating variables which were H_2O_2/COD (molar ratio), H_2O_2/Fe^{2+} (molar ratio) and reaction time (minutes). The experimental runs were designed based on the preliminary analyses as were discussed previously. The ranges chosen were H_2O_2/COD molar ratio 1- 3, H_2O_2/Fe^{2+} molar ratio 3-7 and reaction time 40-80 minutes, as shown in Table 3.3, since the optimum biodegradability was achieved within these ranges.

Table 3.3: Experimental Ranges of Operating Variables for RSM Analysis

Operating conditions	Values (range)			References
	-1	0	1	
H_2O_2/COD	1	2	3	[69]
H_2O_2/Fe^{2+}	3	5	7	[22, 58, 66, 69]
Reaction time	40	60	80	[22, 69]

3.5.2.1 Program Setup

The program was setup by choosing CCD under the response surface tab followed by keying in the details of the numerical factors (operating variables) including the name units, and the low and high ranges as shown in Figures 3.2 and 3.3. Automatically, the software showed the number of experiments and the 'Alpha' (α) value. The α-value at 1.68179 in coded units is the axial distance from the center point and the design rotatable. The same procedure was applied for keying in of the response factor. Then, the design layout of the experimental runs was automatically designed as shown in Table 3.4.



Central Composite Design

Each numeric factor is varied over 5 levels: plus and minus alpha (axial points), plus and minus 1 (factorial points) and the center-point. To check fo infeasible extremes, click the option for "Factor lows and highs entered in terms of alpha". Then adjust low and high levels as needed. If categorica are added, the central composite design will be duplicated for every combination of the categorical factor levels.

Numeric Factors: 3 (2 to 10)

Categorical Factors: 0 (0 to 10)

	Name	Units	Low	High
A:	H2O2/COD	mr	1	3
B:	H2O2/Fe2+	(mr)	3	7
C:	Reaction time	(min)	40	80

☐ Factor ranges entered in terms of alpha

Type: Full Blocks: 1

Points

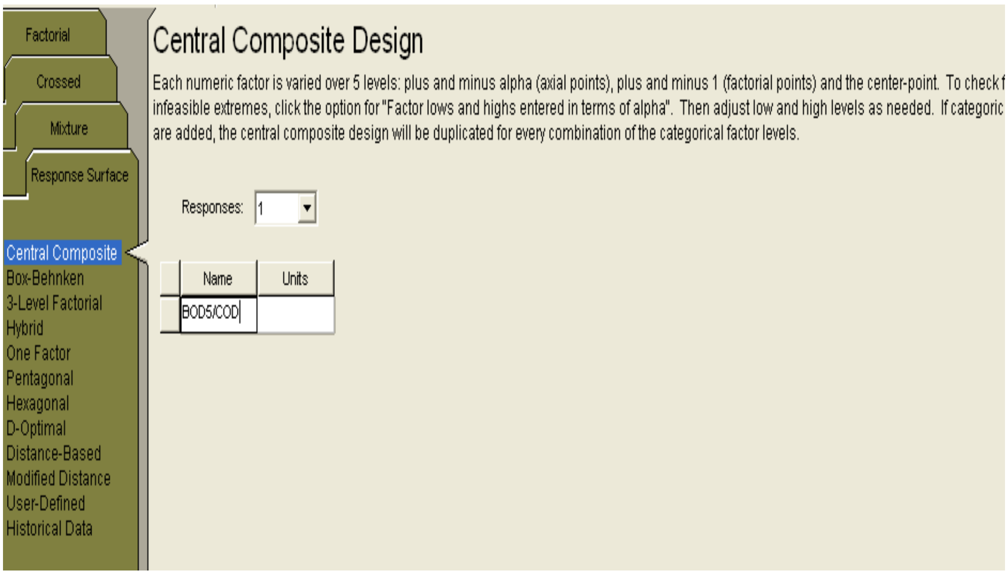
Not center points 14

Center points 6

alpha = 1.68179

20 experiments

Figure 3.2: Setup of Numerical Factors in RSM Design



Central Composite Design

Each numeric factor is varied over 5 levels: plus and minus alpha (axial points), plus and minus 1 (factorial points) and the center-point. To check f
infeasible extremes, click the option for "Factor lows and highs entered in terms of alpha". Then adjust low and high levels as needed. If categoric
are added, the central composite design will be duplicated for every combination of the categorical factor levels.

Responses: 1

	Name	Units
	BOD5/COD	

Figure 3.3: Setup of Responses in RSM Design

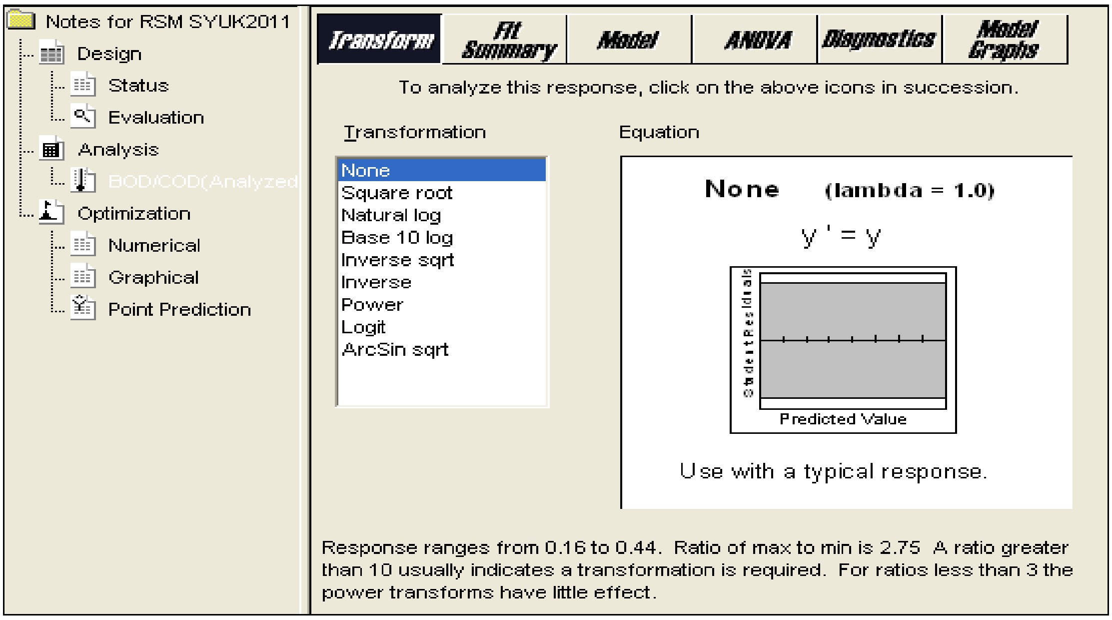
Table 3.4: The Design Layout of the Experimental runs

Run	H_2O_2/COD	H_2O_2/Fe^{2+}	Reaction time
1	1.0 (-1)	3(-1)	40(-1)
2	3.0 (1)	3(-1)	40(-1)
3	1.0(-1)	7(1)	40(-1)
4	2.0(0)	5(0)	60(0)
5	3.0(1)	7(1)	40(-1)
6	1.0(-1)	3(-1)	80(1)
7	2.0(0)	5(0)	60(0)
8	3.0(1)	3(-1)	80(1)
9	1.0(-1)	7(1)	80(1)
10	1.0(1)	7(1)	80(1)
11	2.0(0)	5(0)	60(0)
12	0.3(-1.682)	5(0)	60(0)
13	3.7(1.682)	5(0)	60(0)
14	2.0(0)	2(-1.682)	60(0)
15	2.0(0)	5(0)	60(0)
16	2.0(0)	8(1.682)	60(0)
17	2.0(0)	5(0)	26(-1.682)
18	2.0(0)	5(0)	60(0)
19	2.0(0)	5(0)	94(1.682)
20	2.0(0)	5(0)	60(0)

3.5.2.2 Data Analysis

After the experimental run was completed, the data were filled and shown, accordingly, in response factor column. Then, the data were analyzed by clicking the ‘Conversion’ tab. Under ‘Conversion’, there were different data analysis tabs including ‘Transform’, “Sequential Model Sum of Squares’, ‘Lack of Fit Tests’, ‘Model Summary Statistics’ ‘Model Result’, ‘ANOVA’, ‘Diagnostic’ and ‘Model graph’. As shown in Figure 3.4, ‘Transform’ was set at ‘none’ as the ratio was less than 3.

Next, Figure 3.5 shows the “Sequential Model Sum of Squares’ summary. It shows how the terms of the increasing complexity contribute to the total model. The model hierarchy was automatically set to quadratic and not aliased. Next, the data were analyzed through the ‘Lack of Fit Tests’ table as shown in Figure 3.6 to compare the residual error to the ‘pure error’ from the replicated design points. Then, the ‘Model Summary Statistics’, as represented in Figure 3.7, shows the details of the model. In this case, the chosen model was the quadratic based on the low standard deviation, high R^2 and low ‘PRESS’. Overall, the program was automatically selected by underlining the significant model as ‘Suggested’. Consequently, the selection of the model is shown in ‘Model Result’ table (Figure 3.8).



To analyze this response, click on the above icons in succession.

Transformation: None

Equation

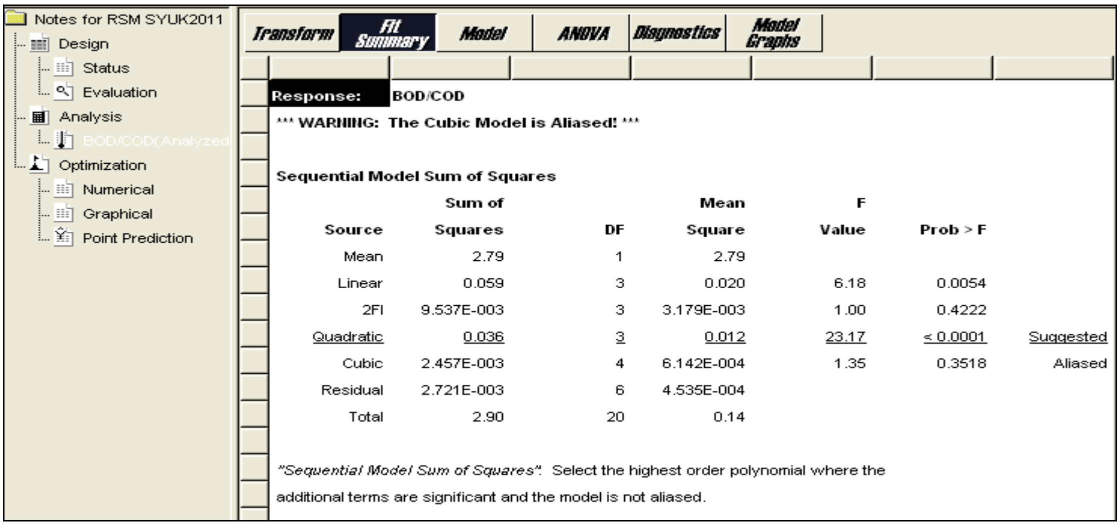
None (lambda = 1.0)

y ' = y

Use with a typical response.

Response ranges from 0.16 to 0.44. Ratio of max to min is 2.75 A ratio greater than 10 usually indicates a transformation is required. For ratios less than 3 the power transforms have little effect.

Figure 3.4: Begin Analysis of Conversion



Response: BOD/COD

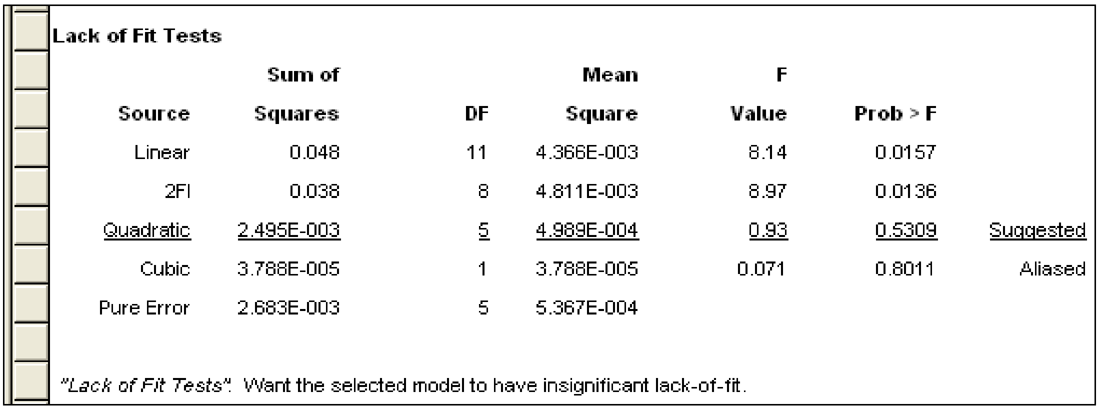
*** **WARNING: The Cubic Model is Aliased!** ***

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	2.79	1	2.79			
Linear	0.059	3	0.020	6.18	0.0054	
2FI	9.537E-003	3	3.179E-003	1.00	0.4222	
Quadratic	0.036	3	0.012	23.17	< 0.0001	Suggested
Cubic	2.457E-003	4	6.142E-004	1.35	0.3518	Aliased
Residual	2.721E-003	6	4.535E-004			
Total	2.90	20	0.14			

"Sequential Model Sum of Squares": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Figure 3.5: Fit Summary Table: Sequential Model Sum of Squares

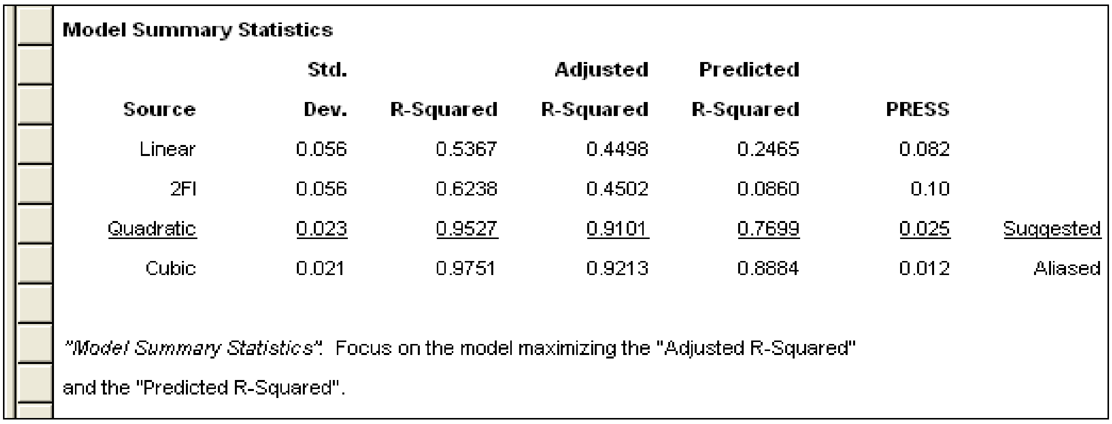


Lack of Fit Tests

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Linear	0.048	11	4.366E-003	8.14	0.0157	
2FI	0.038	8	4.811E-003	8.97	0.0136	
Quadratic	2.495E-003	5	4.989E-004	0.93	0.5309	Suggested
Cubic	3.788E-005	1	3.788E-005	0.071	0.8011	Aliased
Pure Error	2.683E-003	5	5.367E-004			

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit.

Figure 3.6: Fit Summary Table: Lack of Fit Tests



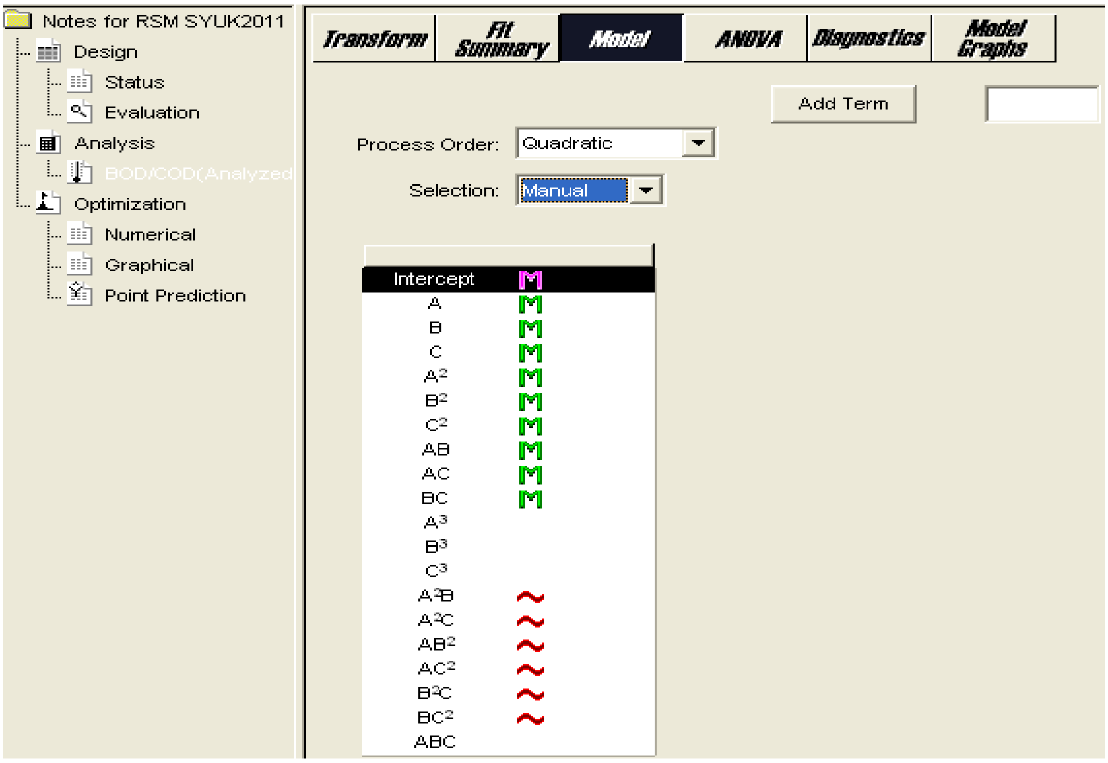
Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.056	0.5367	0.4498	0.2465	0.082	
2FI	0.056	0.6238	0.4502	0.0860	0.10	
Quadratic	0.023	0.9527	0.9101	0.7699	0.025	Suggested
Cubic	0.021	0.9751	0.9213	0.8884	0.012	Aliased

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

Figure 3.7: Fit Summary Table: Model Summary Statistics

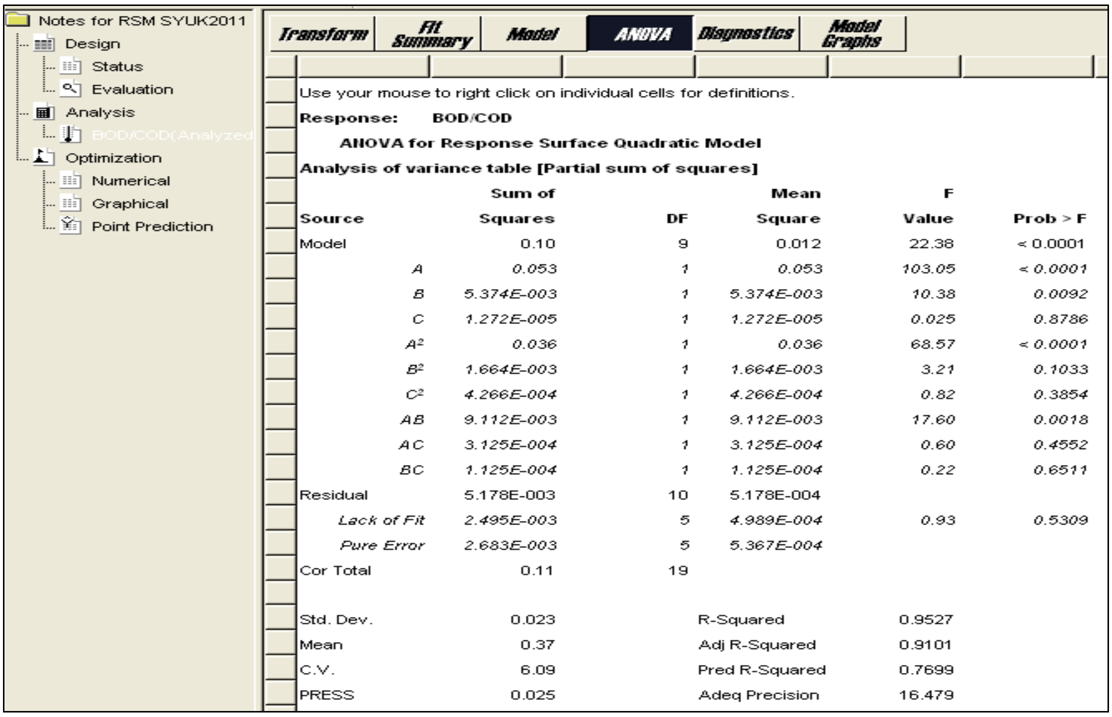
The data were then analyzed by 'ANOVA' where it showed the adequacy of the model (Figure 3.9). The model was considered significant by *Prob>F* is less than 0.05. Next, figures 3.10 and 3.11 show the coefficient of the associated confidence intervals for each term in the model and the final model equation, respectively. The analyzing of the data was continued by clicking the 'Diagnostic' tab where it showed the normal probability plot as in Figure 3.12. Then, the 'Model graph' tab was chosen to reveal the plot of the graph either in (a) contour, (b) 3D or (c) perturbation. The different plotted graphs are shown in Figure 3.13.



Process Order: Quadratic

Selection: Manual

Figure 3.8: Model Results



Use your mouse to right click on individual cells for definitions.

Response: **BOD/COD**

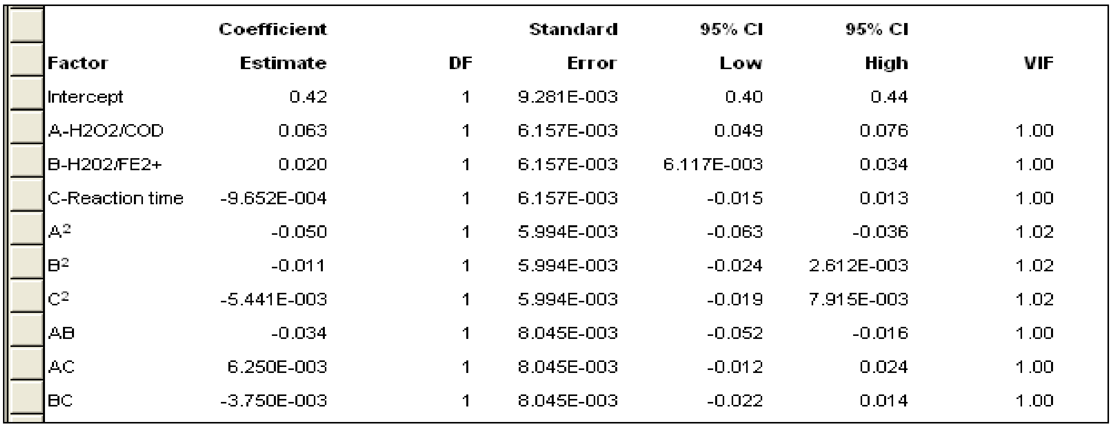
ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
Model	0.10	9	0.012	22.38	< 0.0001
A	*0.053*	*1*	*0.053*	*103.05*	*< 0.0001*
B	*5.374E-003*	*1*	*5.374E-003*	*10.38*	*0.0092*
C	*1.272E-005*	*1*	*1.272E-005*	*0.025*	*0.8786*
A²	*0.036*	*1*	*0.036*	*68.57*	*< 0.0001*
B²	*1.664E-003*	*1*	*1.664E-003*	*3.21*	*0.1033*
C²	*4.266E-004*	*1*	*4.266E-004*	*0.82*	*0.3854*
AB	*9.112E-003*	*1*	*9.112E-003*	*17.60*	*0.0018*
AC	*3.125E-004*	*1*	*3.125E-004*	*0.60*	*0.4552*
BC	*1.125E-004*	*1*	*1.125E-004*	*0.22*	*0.6511*
Residual	5.178E-003	10	5.178E-004		
Lack of Fit	*2.495E-003*	*5*	*4.989E-004*	*0.93*	*0.5309*
Pure Error	*2.683E-003*	*5*	*5.367E-004*		
Cor Total	0.11	19			

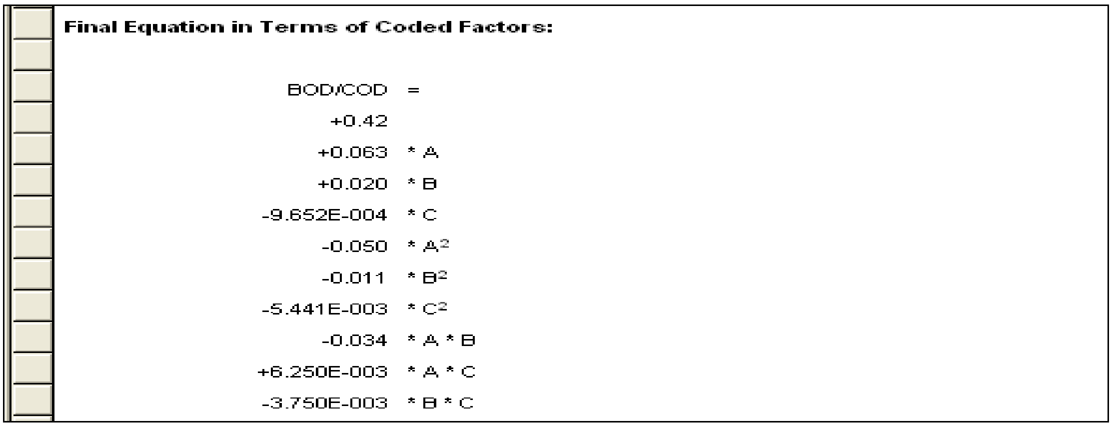
Std. Dev.	0.023	R-Squared	0.9527
Mean	0.37	Adj R-Squared	0.9101
C.V.	6.09	Pred R-Squared	0.7699
PRESS	0.025	Adeq Precision	16.479

Figure 3.9: Statistics for Selected Model ANOVA Table



Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.42	1	9.281E-003	0.40	0.44	
A-H2O2/COD	0.063	1	6.157E-003	0.049	0.076	1.00
B-H202/FE2+	0.020	1	6.157E-003	6.117E-003	0.034	1.00
C-Reaction time	-9.652E-004	1	6.157E-003	-0.015	0.013	1.00
A^2	-0.050	1	5.994E-003	-0.063	-0.036	1.02
B^2	-0.011	1	5.994E-003	-0.024	2.612E-003	1.02
C^2	-5.441E-003	1	5.994E-003	-0.019	7.915E-003	1.02
AB	-0.034	1	8.045E-003	-0.052	-0.016	1.00
AC	6.250E-003	1	8.045E-003	-0.012	0.024	1.00
BC	-3.750E-003	1	8.045E-003	-0.022	0.014	1.00

Figure 3.10: Coefficients for the Quadratic model



Final Equation in Terms of Coded Factors:

```
        BOD/COD   =
          +0.42
         +0.063   * A
         +0.020   * B
    -9.652E-004   * C
         -0.050   * A^2
         -0.011   * B^2
    -5.441E-003   * C^2
         -0.034   * A * B
    +6.250E-003   * A * C
    -3.750E-003   * B * C
```

Figure 3.11: Final Equation for Conversion Response Coded

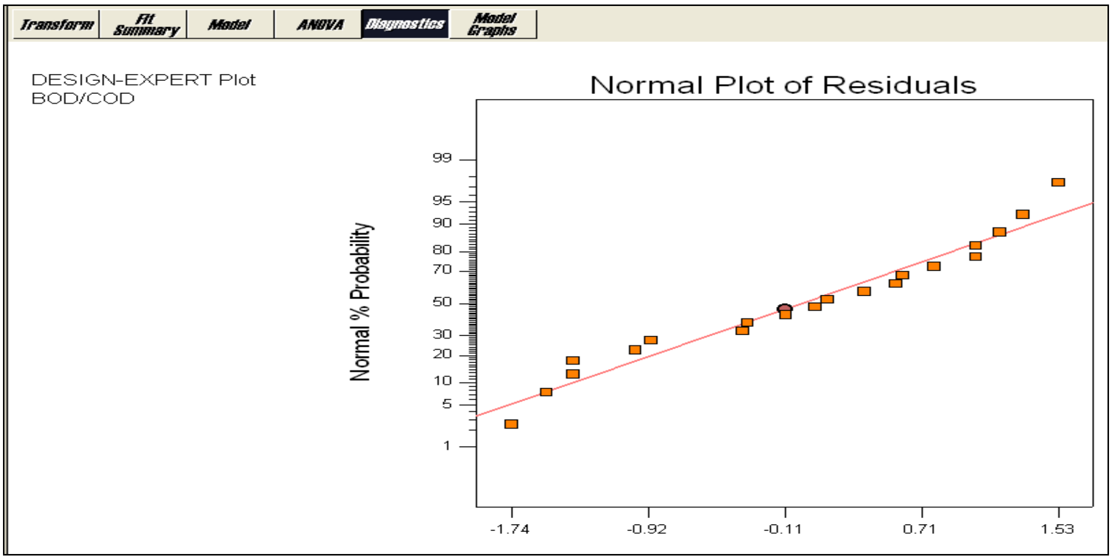


Figure 3.12: Normal Probability Plot of the Residuals

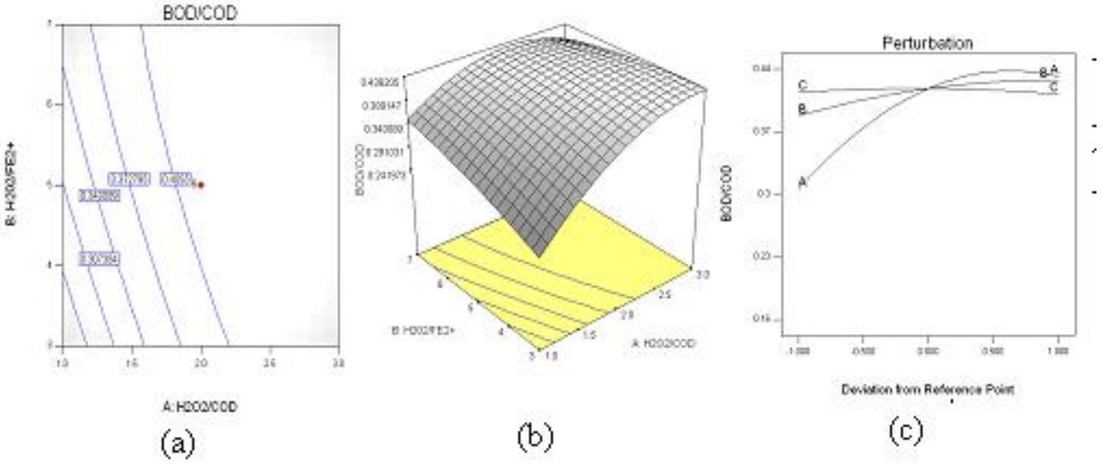
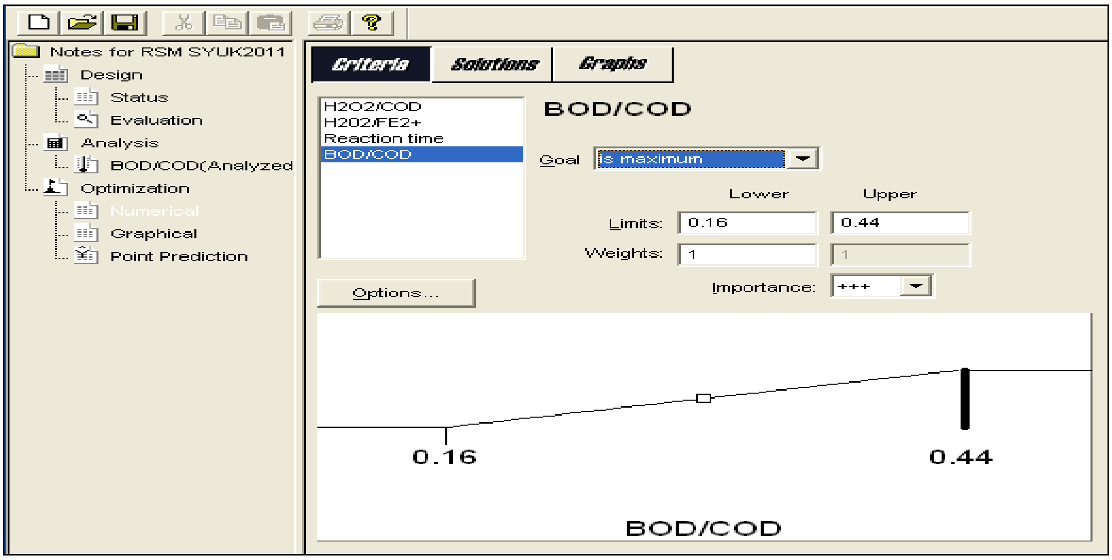


Figure 3.13: Model Graphs

3.5.2.3 Data Optimization

The optimization of the data was started by clicking the ‘Numerical’ tab. It was divided into ‘Criteria’, ‘Solutions’ and ‘Graphs’. All the numerical factors and the response factor were set at ‘is in range’ and ‘is maximum’ accordingly, to determine the maximum response factor as shown in Figure 3.14. Then, optimization was started by clicking the ‘Solutions’ tab. From the Solutions table, the maximum biodegradability was found to be at H_2O_2/COD 2.8, H_2O_2/Fe^{2+} 4 and the reaction time was 71 minutes through the underlined and selected label (Figure 3.15).



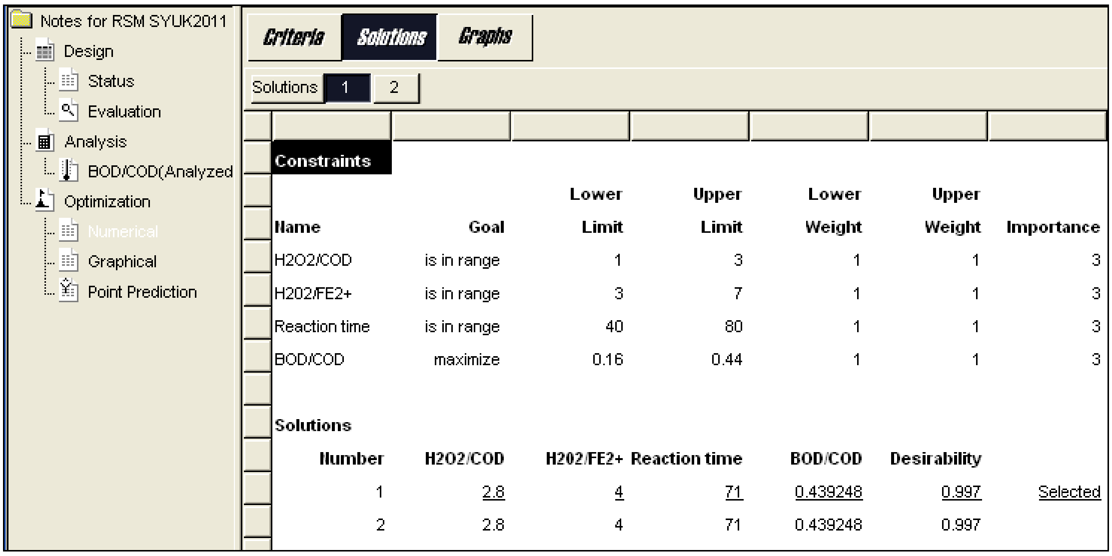
BOD/COD

Goal: is maximum

	Lower	Upper
Limits:	0.16	0.44
Weights:	1	1

Importance: +++

Figure 3.14: Setting Numeric Optimization Criteria



Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
H2O2/COD	is in range	1	3	1	1	3
H202/FE2+	is in range	3	7	1	1	3
Reaction time	is in range	40	80	1	1	3
BOD/COD	maximize	0.16	0.44	1	1	3

Solutions

Number	H2O2/COD	H202/FE2+	Reaction time	BOD/COD	Desirability	
1	2.8	4	71	0.439248	0.997	Selected
2	2.8	4	71	0.439248	0.997	

Figure 3.15: Numerical Optimization Report on Solutions

3.5.2.4 Confirmation of Data

Experiments were conducted using a jar test apparatus (VELP-Scientifica, Model JLT6, Italy) with a solution volume of 500 mL. The sample was filtered through filter paper (Whatman No.1) and set to pH 3 using $H_2SO_{4.}$ $FeSO_4.7H_2O$ and H_2O_2 (35%, w/w solution) were added into the solution, accordingly, at the molar ratio of 2 and 5, respectively. The solution was continuously mixed at 100 rpm. After 60 min, the pH was increased to 10 using NaOH. The solution was settled overnight and filtered to remove excess flocculates. The pH of the solution was decreased to the range of 6.5 to 7.5, which is suitable for biological systems. COD and BOD_5 analyses were carried out, respectively, to check the biodegradability improvement in the samples. Thereafter, the sample was prepared based on confirmation test as to be used further in SBR

3.5.3 Sequencing Batch Reactor (SBR)

A preliminary analysis was carried out to determine the volume of biomass to be seeded in SBR. Five beakers with a volume of 1 L were prepared by varying the F/M ratio to 0.05, 0.1, 0.15, 0.2 and 0.25. 800 mL of the sample and sludge were filled into beakers and aerated continuously for 3 d. The performance of system was assessed by measuring the COD of effluent and its removal efficiency throughout the experiment. The calculation of the F/M ratio is shown in Eqs. 3.11-3.12.

$$Q = V_{in} \cdot N_{cycle} \tag{3.11}$$

$$F/M = \frac{Q \cdot COD_{in}}{V \cdot MLVSS} \tag{3.12}$$

Where Q is the flow rate of the influent feed per cycle (L), V_{in} is the influent feed volume per cycle (L/cycle), N_{cycle} is the number of cycles per day, V is the volume of SBR (L) and $MLVSS$ is the sludge concentration in the reactor (mg/L).

3.5.3.1 SBR Configuration and Operation

A cylindrical reactor with a total working volume of 5 L and exchange volume of 1 L was used. The Fenton treated PRW was filled and drawn using feeding pumps (Astro 300, China) and a draw pump (Orange HT210, China), respectively. The SBR operation cycles were controlled by programmable timers (HWD-EE01, China). Air was supplied from the bottom of SBR using an air compressor (IKE 2525, China). The diagram of SBR is shown in Figure 3.16.

SBR was operated in 3 cycles/day under a batch sequence system: fill, react, settle, draw and idle. The cycle was started by filling a 1 L sample into the reactor under the fill phase. During the reaction phase, the reactor was aerated for 6 hours and then allowed to settle for 1 hour and 50 minutes. 1 L of supernatant was withdrawn and the reactor was filled up to 5 L with 1 L of the pretreated sample for the new cycle. In this experiment, the idle phase was applied to ensure the system was under the appropriate conditions for the next cycle and sludge wasting. The operating parameters of the SBR system are shown in Table 3.5.

The performance of the SBR was monitored through COD, MLSS, MLVSS and SVI analyses. The steady state phase was achieved when the effluent COD reached constant values and the MLVSS concentration gradually increased.

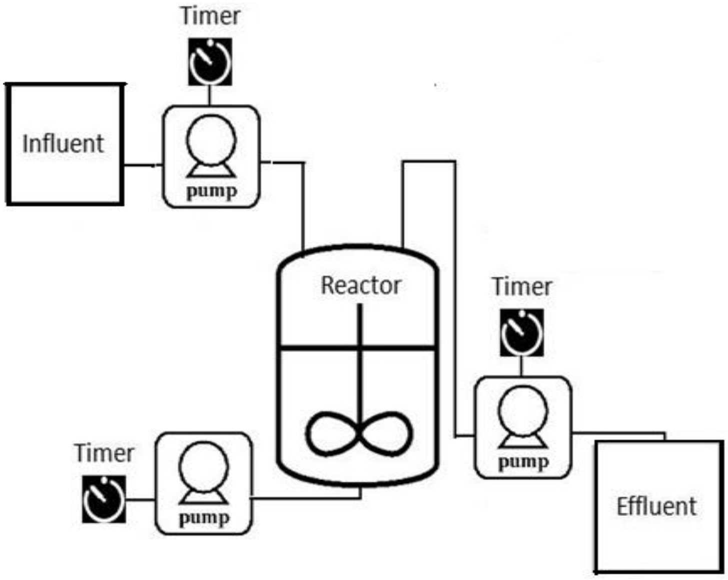


Figure 3.17: The diagram of SBR

Table 3.5: Operating Conditions of SBR

Operation parameter	Value
Total volume (L)	5
Influent flow rate (L/d)	3
Cycle	3
Cycle length (h)	8
Feed volume per cycle (L)	1
Each step of the cycle (min)	
Fill	2
React	360
Settle	210
Draw and Idle	8

3.6 Summary

The characteristics of petroleum refinery wastewater were initially determined. The samples were taken from PP (M) SB and analyzed for COD, BOD_5, TSS, pH, alkalinity, turbidity, colour, ammonia nitrogen, nitrate, phosphorus, phenol, sulphate, sulphide, TKN, TOC, oil and grease and BTEX. Then, Fenton process was applied to improve the biodegradability of the sample. To determine the range of the operating variables to be used in RSM, the preliminary analyses of Fenton process were carried out. Then, optimization of Fenton process using RSM was carried out and data were analyzed based on ‘Fit Summary’, ‘Model Result’, ‘ANOVA’, ‘Diagnostic’ and ‘Model’ graph. Finally, the readily biodegradable solution was treated by post treatment, SBR. Preliminary analyses of SBR were conducted to determine the suitable F/M ratio to be used in operation of SBR. To assess the performance of SBR, experiments were done includes COD, MLSS, MLVSS and SVI analyses.

CHAPTER 4

RESULTS AND DISCUSSION

4.0 Chapter Overview

This chapter contains the results of experimental works for preliminary analysis of Fenton process, optimization of Fenton process by RSM, performance of SBR and comparison of SBR effluent to Malaysian standard limits set by department of environment (DOE). The achieved results in the study were also being discussed and compared with other researches.

4.1 Preliminary Analysis of the Fenton Process

4.1.1 Effect of the Reaction Time

The effect of reaction time on the Fenton process was tested to determine an experimental condition for further research. The reaction time for the Fenton process was varied in the range of 20-120 min, at a constant initial COD of 1667 mg/L (52 mM). Other operating conditions were fixed at the H_2O_2/COD molar ratio of 2 and the H_2O_2/Fe^{2+} molar ratio of 5. As shown in Figure 4.1, it was found that at a reaction time of 20, 40, 60, 80, 100 and 120 min, the BOD_5/COD ratios were 0.40, 0.42, 0.44, 0.43, 0.41 and 0.39, the COD removal efficiencies were 73, 79, 79, 75, 69 and 73% and the BOD removal efficiencies were 72, 77, 77, 72, 68 and 72%, respectively. In terms of the maximum biodegradability, the optimal reaction time was 60 minutes with 0.44 BOD_5/COD, and 79 and 77% COD and BOD removal efficiencies, respectively.

The oxidising of the organic materials by the Fenton process can be divided into three types of degradation: a primary degradation, a structural change in the parent compound where biodegradability might be improved; acceptable degradation, degradation to the extent that toxicity is reduced; ultimate degradation, complete to carbon dioxide, water and other inorganics [106, 107]. As shown in Figure 4.1, the result demonstrated that the organic materials were rapidly degraded by the Fenton process. It seems like most of the organic materials accomplished the optimum biodegradability within 60 minutes and achieved the primary degradation. Then, the biodegradability decreased after this reaction time. At the same reaction time, COD and BOD removal also increased up to 79 and 77% to show that the acceptable degradation was achieved. On the other hand, COD and BOD removal efficiency plots showed the same trend where their efficiency slightly increased at 40 to 60 minutes and decreased at 80 and 100 and again increased at 120 min.

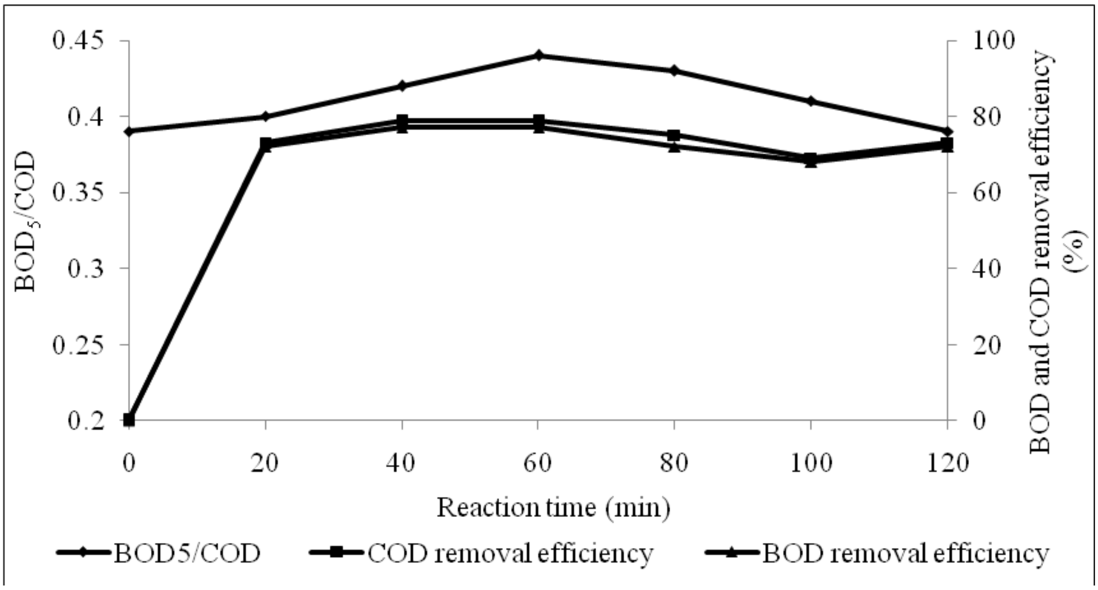


Figure 4.1: Effect of Reaction Time (Min) on BOD_5/COD, COD Removal Efficiency and BOD Removal Efficiency at fixed H_2O_2/COD (2) and H_2O_2/Fe^{2+} (5)

In general, the reaction time for the Fenton process was carried out between 20 to 120 minutes and most of the experimental works have reported on the maximum reaction time within 60 minutes [19]. A similar reaction time was also reported for treatment of the petroleum refinery sourwater (55% of the dissolved organic content (DOC) removed) [9] and the coking wastewater (44-50% and 95% of the COD and the total phenol removed, respectively) [108]. However, a different reaction time was applied for the heavily polluted fermentation waste broth (10-30 minutes) [54], antibiotic solution (10- 60 minutes) [55], textile wastewater (30 minutes) [88], treatment of high-strength semiconductor wastewater (1.5 h) [109], and acrylic fiber manufacturing wastewater (0.5 - 4.0 h) [110].

Overall, the optimum biodegradability was achieved at the reaction time of 60 minutes and at a constant H_2O_2/COD molar ratio of 2 and H_2O_2/Fe^{2+} molar ratio of 5 to give 0.44 BOD_5/COD with 79 and 77% COD and BOD, removal efficiencies, respectively.

4.1.2 Effect of the H_2O_2/COD Molar Ratio

The initial H_2O_2 concentration was varied in the range of 104-625 mM at a constant initial COD of 1667 mg/L (52 mM). Other operating conditions were fixed at a reaction time of 60 minutes and the H_2O_2/Fe^{2+} molar ratio of 5. It was found that at the H_2O_2/COD molar ratios of 2, 4, 6, 8, 10 and 12, the BOD_5/COD ratios were 0.44, 0.40, 0.37, 0.30, 0.34 and 0.39. The COD removal efficiencies were found to be 79, 82, 82, 88, 90 and 90% and the BOD removal efficiencies were 77, 82, 83, 90, 91 and 90% respectively as represented in Figure 4.2. The results indicated that in terms of maximum biodegradability, the optimal H_2O_2/COD molar ratio was 2.

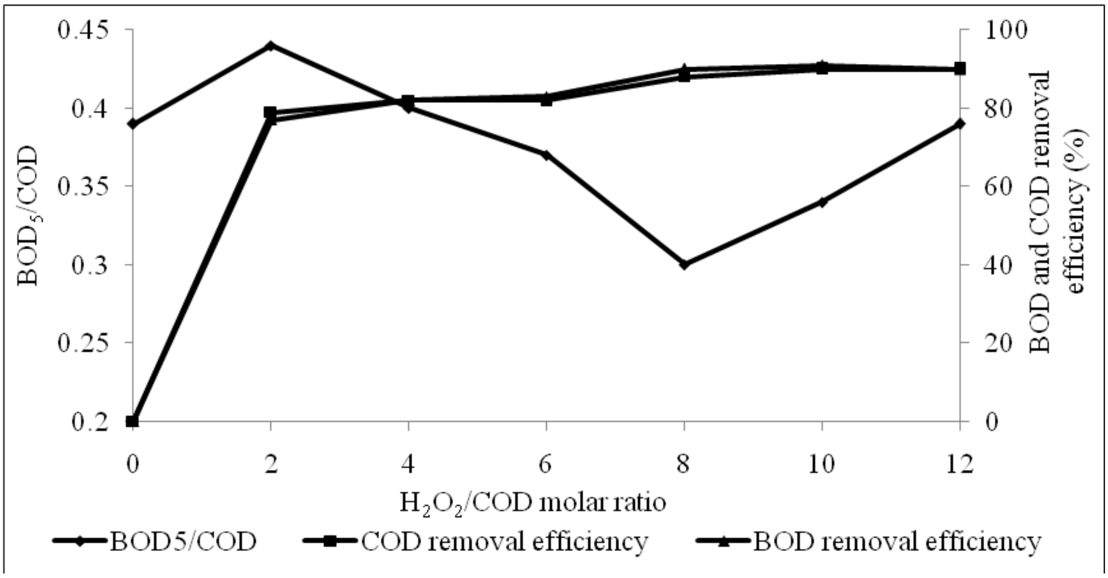


Figure 4.2: Effect of H_2O_2/COD (Molar Ratio) on BOD_5/COD, COD Removal Efficiency and BOD Removal Efficiency at fixed H_2O_2/Fe^{2+} (5) and Reaction Time (60 min)

Generally, increasing the H_2O_2 concentration will generate more hydroxyl radicals for better organic degradation [50]. However, at certain limits, the complete organic removal could not be achieved even with a higher than stoichiometric quantity of H_2O_2/COD; thus, this lead to a decrease of the removal efficiency. In this study, the COD and BOD removal kept increasing until the H_2O_2/COD molar ratio was 12. The biodegradability declined after the H_2O_2/COD molar ratio of 2 which could be due to the auto decomposition of the H_2O_2 to the oxygen and water, and the scavenging of OH• by H_2O_2. The excess H_2O_2 also reacts with the ferric ions to form hydroperoxyl radicals as stated in Eqs. 4.1 to 4.3 [55].

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{4.1}$$

$$H_2O_2 + \bullet OH \rightarrow HO_2\bullet + H_2O \tag{4.2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \tag{4.3}$$

4.1.3 Effect of the H_2O_2/Fe^{2+} Molar Ratio

The H_2O_2/Fe^{2+} concentration was varied in the range of 3-21 mM at a constant initial COD 1667 mg/L (52 mM). Other operating conditions were fixed at a reaction time of 60 minutes and the H_2O_2/COD molar ratio of 2. The reaction time and the H_2O_2/COD molar ratio were selected since these were the optimum values of biodegradability as described previously. It was found that at the H_2O_2/Fe^{2+} molar ratios 5, 10, 15, 20, 25 and 30, the BOD_5/COD ratios were 0.44, 0.33, 0.30, 0.31, 0.21 and 0.33 as represented in Figure 4.3.

The best COD removal efficiency was found to be 79 at the H_2O_2/Fe^{2+} molar ratio of 5. In terms of the optimum biodegradability, the optimal H_2O_2/Fe^{2+} molar ratio was 5. It was found that, biodegradability declined with an increase of the H_2O_2/Fe^{2+} molar ratio. However, COD and BOD removal efficiency increased at the H_2O_2/Fe^{2+} molar ratio of 5 and considered steadily constant until it reached the molar ratio of 30.

Peroxidase dose and iron concentration (Fe^{2+}) are important factors in the Fenton reaction [111]. The Fe^{2+} concentration is important for the reaction of the kinetics while the peroxide dose is for better degradation efficiency [111, 112]. In this experiment, an increase in the H_2O_2/ Fe^{2+} molar ratio means less concentration of the Fe^{2+} which causes a lower value of the biodegradability. A lower H_2O_2/ Fe^{2+} molar ratio causes a high removal of the target compound and formation of early intermediates [55]. In addition, it was found that a higher dose of Fe^{2+} is better for COD removal which may generate more hydroxyl radicals for the degradation process [67]. As represented in Eqs.4.4 to 4.6, excessive formation of Fe^{2+} competes with the organic carbon for the hydroxyl radicals when a high Fe^{3+} concentration is used [36].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH\bullet \tag{4.4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \tag{4.5}$$

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^- \tag{4.6}$$

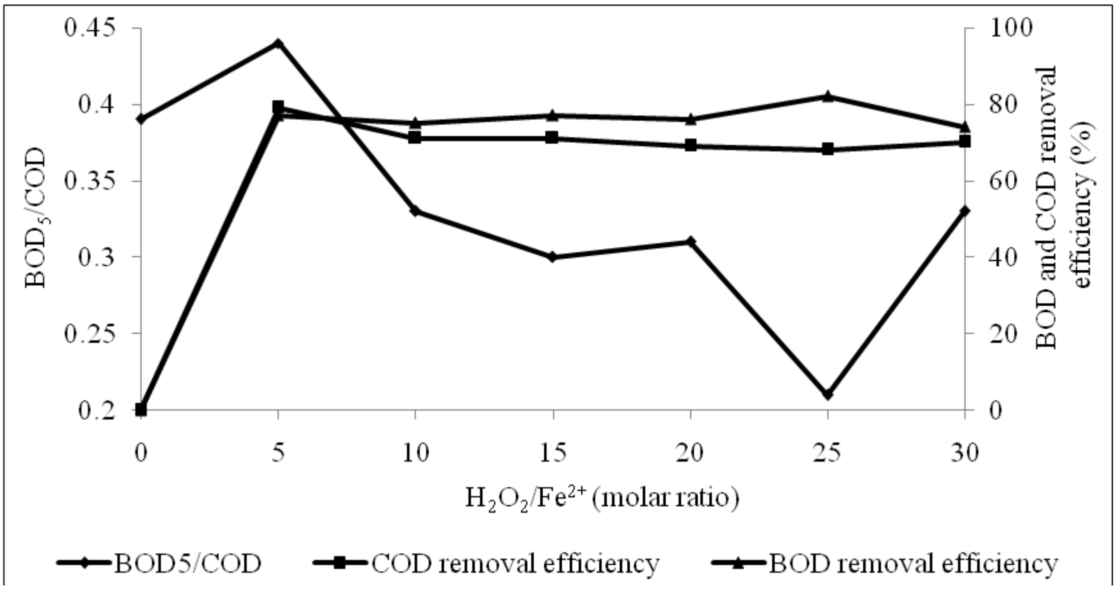


Figure 4.3: Effect of H_2O_2/Fe^{2+} (Molar Ratio) (A) BOD_5/COD, (B) COD Removal Efficiency (%) and (C) BOD Removal Efficiency (%) at fixed H_2O_2/COD (2) and Reaction Time (60 min)

Likewise, this optimal H_2O_2/Fe^{2+} molar ratio was found to be similar as reported by Benatti (2006) [67]. However, a higher optimum H_2O_2/Fe^{2+} molar ratio was reported for the antibiotics solution (10) [55], cresol destruction (6.5) [112], chlorophenol (10) [113], 2, 4-Dichlorophenol oxidation (11) [114], and aliphatics (40) [115].

Overall, the maximum biodegradability of 0.44 was achieved at the H_2O_2/COD molar ratio 2, H_2O_2/ Fe^{2+} molar ratio of 5 and reaction time of 60 minutes.

4.2 Response Surface Methodology (RSM)

4.2.1 Data Analysis: ANOVA

In RSM, the adequacy and significance of the results were analyzed and viewed in ANOVA. The ANOVA results for experimental run are summarized in Table 4.1. It was found that the quadratic model was significant enough to give less than 0.05 of the probability of error (*P*). Moreover, the model was fit with the data based on the insignificance of the Lack of Fit result at a value of 0.93. Besides, that *A* was the most significant factor followed by *B*, A^2 and *AB*. In addition, the high R^2 and adj. R^2 (0.95 and 0.91) show satisfactory adjustment of the quadratic model to the experimental data and high values close to 1 show better estimation of the regression equation to fit the sample data [116, 117].

Table 4.1: ANOVA Results for Response Parameters

Response	SD	R^2	Adj.R^2	AP	CV	PRESS	*P*-value	*F*-value
BOD_5/COD	0.023	0.95	0.91	16.479	6.09	0.025	<0.0001	0.93

SD: standard deviation, R^2: determination coefficient, Adj. R^2: adjusted R^2, AP: adequate precision, CV: coefficient of variation, PRESS: predicted residual error sum of squares, *P*: Probability of error, *F*: Lack of fit

On the other hand, Adequate Precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination and can be used to navigate the design space defined by the CCD [116, 118, 119]. In this study, the AP value was found to be 16.479 which was greater than 4 and considered a satisfactory result. The coefficient of the variance (CV) as the ratio of the estimate standard error to the mean value of the observed response defined the reproducibility of the model. A model can be considered reproducible if its CV is not greater than 10% [120]. In this study, the model was reproducible since the CV was about 6.09 %; low values of the CV (9.6-67.6) indicated the good precision and reliability of the experiments [121].

A second order model, typical for the response surface in terms of the coded variables *Xi*, was reduced to the form of Eq. (4.7) based on the experimental results describing the BOD_5/COD by the Fenton process. In order to simplify the model not significant terms (C, B^2, C^2, AC and BC) were eliminated. Coefficients of the model terms are listed in Table 4.2 and normalized coefficients are presented in Figure 4.4. Normalized coefficients indicate effects of the terms on the response. The first-order effects of H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios and second-order effects of H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios produce the main effect on biodegradability improvement of refinery wastewater.

The final equation in terms of the coded factors is presented in Eq. 4.7

$$Y = +0.42 + 0.063A + 0.020B - 0.050A^2 - 0.034AB \tag{4.7}$$

Table 4.2: Estimated regression coefficients and corresponding to ANOVA results from the 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	0.42	0.1	9	0.012	22.38	< 0.0001	Significant
A	0.063	0.053	1	0.053	103.5	< 0.0001	Significant
B	0.020	5.374E-003	1	5.374E -003	10.38	0.0092	Significant
C	-0.004	1.272E-005	1	1.272E -005	0.025	0.8786	Not significant
A^2	-0.050	0.036	1	0.036	68.57	< 0.0001	Significant
B^2	-0.011	1.664E-003	1	1.664E -003	3.21	0.1033	Not significant
C^2	-0.003	4.266E-004	1	4.266E -004	0.82	0.3854	Not significant
AB	-0.034	9.112E-003	1	9.112E -003	17.60	0.0018	Significant
AC	-0.003	3.125E-004	1	3.125E -004	0.60	0.4552	Not significant
BC	-0.003	1.125E-004	1	1.125E -004	0.22	0.6511	Not significant

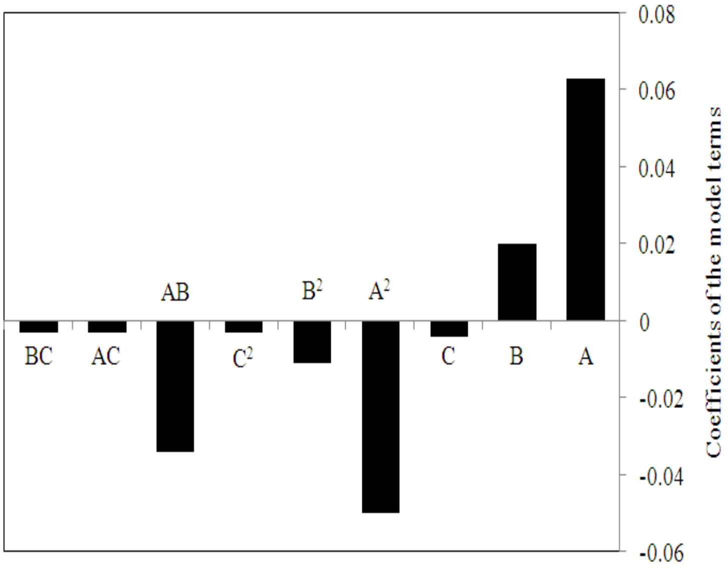


Figure 4.4: Normalized Coefficient of the Model

4.2.2 Data Analysis: Diagnostic

A diagnostic result interprets the fit of the data based on graphs such as a normal probability plot of the residuals and the outlier plot. If the residual plot is approximately a straight line, the normality assumption is considered satisfied [116]. In this study, the residuals were normally distributed as to show that the normality assumption was satisfied as shown in Figure 4.5. Besides that, the outlier plot showed a satisfactory result as all the points fall within the lines as represented in Figure 4.6. All points of experimental runs were scattered randomly within the constant range of residuals across the graph, i.e. within the horizontal lines at the point of ±1.75. This implies that the proposed models are adequate and that the constant variance assumption was confirmed. This plot indicates an adequate agreement between the real data and the data from the model [117]. Responses from experimental results also fitted well within an acceptable variance range when compared to the predicted values from respective empirical models as shown in Figure 4.7.

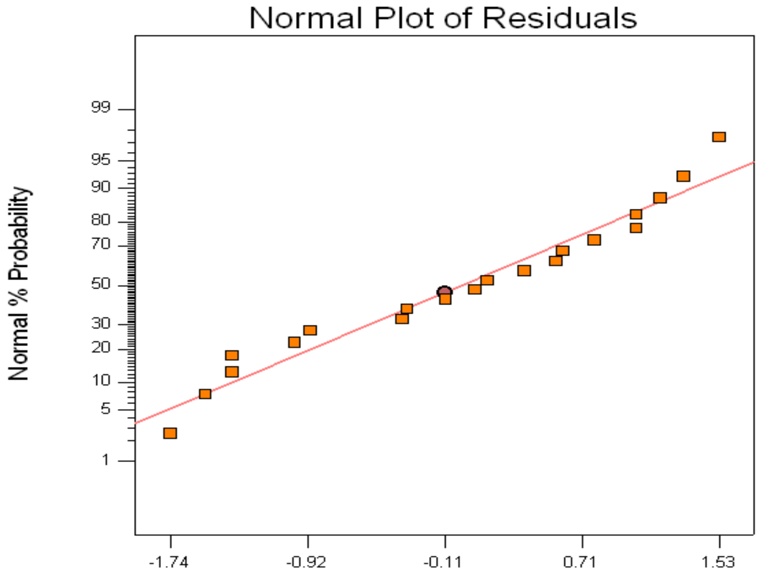


Figure 4.5: Normal Probability Plot of Residuals Graph

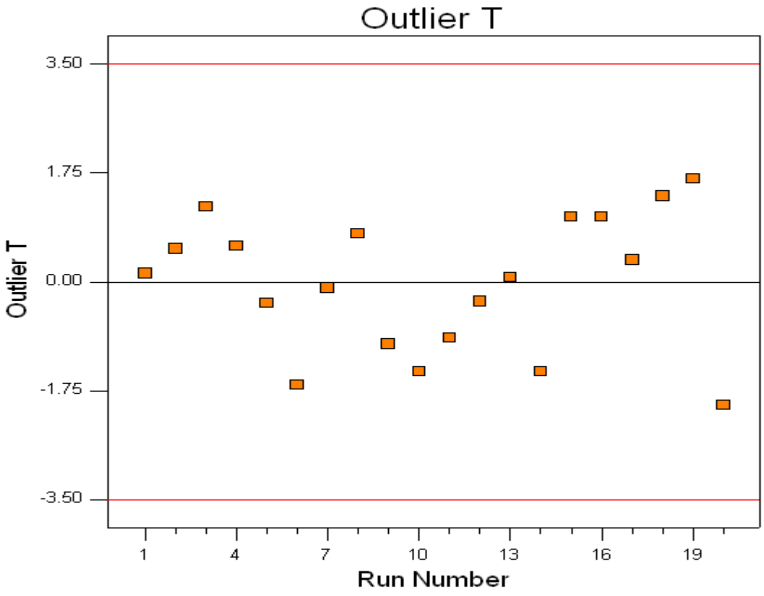


Figure 4.6: Plot of Residual vs. Predicted Response

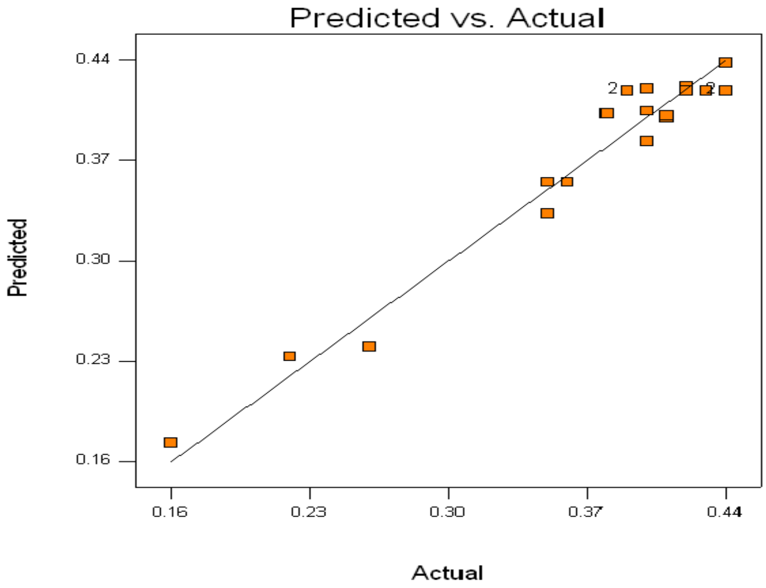


Figure 4.7: Predicted vs. Actual Values Plot

4.2.3 Data Analysis: Model Graph

The three-dimensional response surface plots for the variables of the H_2O_2/COD molar ratio (*A*), H_2O_2/Fe^{2+} molar ratio (*B*) and reaction time minutes (*C*) on BOD_5/COD improvement are shown in Figures 4.8-4.10. In general, these plots show the interaction between each operating parameters.

As shown in Figure 4.8, it was found that, BOD_5/COD is improved with increase of H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio. The addition of the hydroxyl radical to organic compounds found in refinery wastewater results in the production of a radical organic compound that can be oxidized further by ferrous iron to produce stable oxidized end product. Hydroxyl radical attack on the product is more rapid than on the parents compounds [122] and as long as the organic carbon was removed rapidly after degradation of petroleum hydrocarbons at the early stage of reaction, the longer duration does not produce any significant effect on biodegradation augmentation. It may be explained by the fact that the half-life of the hydroxyl free radicals is short and extension of reaction time does not improve degradation. This phenomenon can be observed in Figure 4.9 and Figure 4.10. The relationship between H_2O_2/COD molar ratio and reaction time in Figure 4.9 indicates BOD_5/COD is improved only with increase of H_2O_2/COD molar ratio. The best result is obtained at H_2O_2/COD molar ratio of 2. A further increase in oxidant concentration does not improve the biodegradability. The observed fact can be explained by considering the oxidation of organic substances by hydrogen peroxide in the presence of Fe(II), according to Welling [123] when the [H_2O_2] is much higher than [Fe^{2+}] the share of following competing reactions increases and may reduce the available hydroxyl radicals:

$$HO\bullet + H_2O_2 \rightarrow H_2O + HO\bullet_2 \qquad (4.8)$$

$$2HO\bullet \rightarrow H_2O_2 \qquad (4.9)$$

The 3-D plot of H_2O_2/Fe^{2+} molar ratio and reaction time (Figure 4.10) indicates that increase of Fe (II) improves the biodegradability. But an optimum balance between [organic substances] and [Fe^{2+}] is vital to avoid any decrease in hydroxyl radical generation. It is better to maintain the lower value of the ratio of the catalyst to the concentration of the organic substances [50, 57].

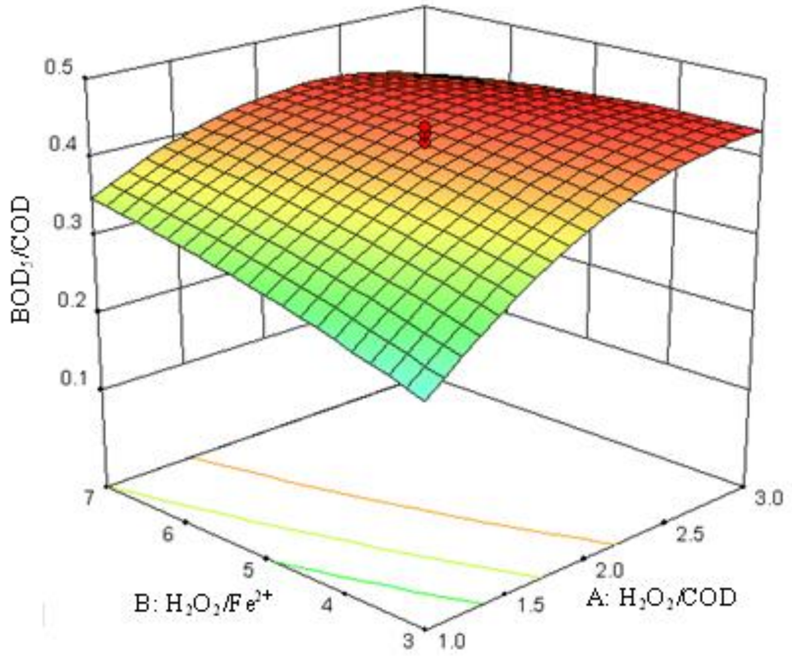


Figure 4.8: 3D Plot of H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio

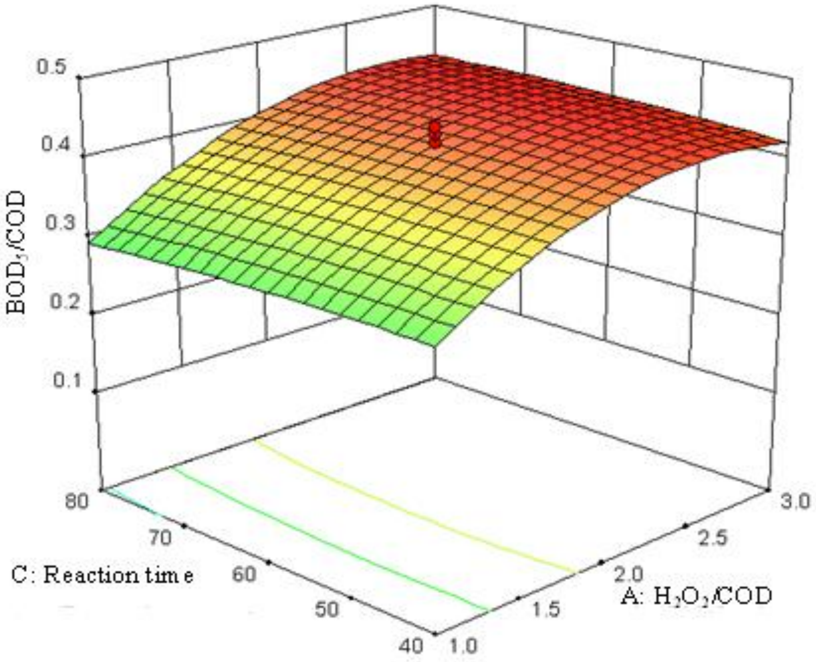


Figure 4.9: 3D Plot of H_2O_2/COD molar ratio and Reaction Time

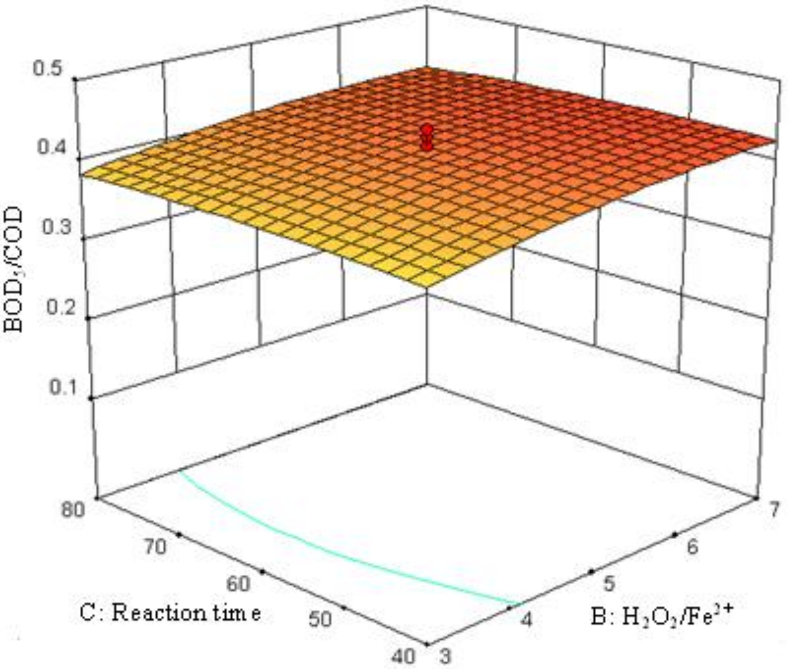


Figure 4.10: 3D Plot of H_2O_2/Fe^{2+} molar ratio and Reaction Time

4.2.4 Optimization

Overall, based on RSM, the optimum operating variables were found to be at the H_2O_2/COD 2.8 molar ratio, H_2O_2/Fe^{2+} 4 molar ratio and reaction time of 71 min to give BOD_5/COD 0.44.

4.2.5 Data Confirmation

Results from the RSM and preliminary analyses were compared and it was found that both values gave similar results of BOD_5/COD which was 0.44. Table 4.3 shows the calculation for the chemical usage for the preliminary and RSM results. As the concern in terms of economical approach is to reduce the chemical usage and the duration of the process, the preliminary results were shown to be more appropriate and feasible values, and therefore they have been selected to be applied in SBR. At this value, the reaction time has been reduced and the usage of H_2O_2 and $FeSO_4.7H_2O$ has been reduced by 29% and 43%, respectively as compared to the result from RSM.

Table 4.3: Calculation for Chemical Usage for Preliminary and RSM Results

Operating variable	H_2O_2/COD^a	H_2O_2/Fe^{2+a}	Reaction time^b	H_2O_2 usage (mL)	$FeSO_4.7H_2O$ usage (g/L)
Preliminary	2	5	60	10.32	29.41
RSM	2.8	4	71	14.45	51.47

Initial COD: 1700
H_2O_2 : 350 w/w
[a] molar ratio
[b] minutes

4.3 Application of the Sequencing Batch Reactor (SBR) for the Post-Treatment of the Fenton Treated Refinery Wastewater

4.3.1 Preliminary Analysis of F/M

The F/M ratio or sludge loading rate is the most useful loading parameter that influences the ability of the sludge to settle and compact [124, 125]. The typical F/M ratio for SBR is from 0.09 to 0.23 F/M kg COD/kg MLVSS.d [17]. However, the F/M ratio should be determined individually since the values can vary in each treatment plant [126]. Therefore, five different samples with different F/M ratios were set for three days and analyzed. The results are shown in Figure 4.11. It was found that the F/M ratio of 0.1 was the suitable which resulted in 67% of the COD removal efficiency. The F/M ratio of 0.1 showed the lowest effluent COD concentration as compared to the other ratios. A similar ratio was reported by Sirianuntapiboon (2007) [127]. On the other hand, the F/M ratio of 0.1 showed the highest COD removal efficiency with the lowest COD concentration within the experiments.

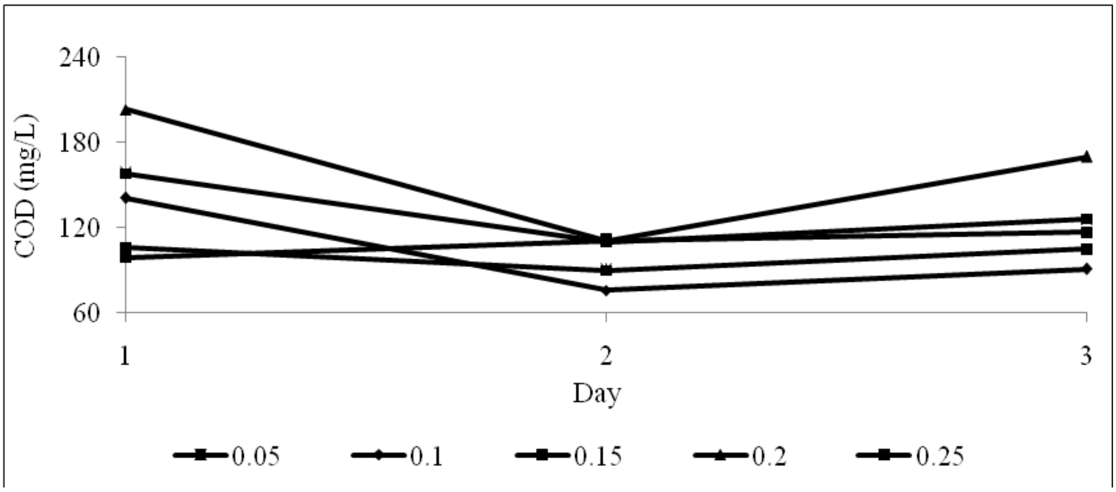


Figure 4.11: COD Concentration of Preliminary Analysis

4.3.2 Reactor Performance

After the preliminary analysis, the SBR system was run for 49 days at room temperature. The COD concentration, MLSS and MLVSS were measured to monitor the SBR performance. The results of the COD influent, COD effluent and its removal efficiency are shown in Figures 4.12 and 4.13. It was found that the COD effluent ranged from 306 to 115 mg/L to give 21 - 70 % of COD removal efficiencies at the COD influent ranged of 104 - 386 mg/L during the 49 days of the experiment.

The COD removal efficiency was increased from day 1 to day 3 and started to fluctuate until day 26. The real petroleum refinery wastewater from PP (M) SB was collected and added into the reactor. Therefore, the characteristics may have varied for each sampling. A fluctuation occurred due to the addition of the new pretreated sample with a lower COD value and different characteristics thus, may affect the microorganism’s activity. The COD effluent and removal efficiency from day 12 to 26 showed different characteristics which was due to the addition of the new pretreated sample with a low COD value into the reactor. After day 27 until day 49, the COD removal efficiency showed nearly constant values. The steady values around 58- 69% of the COD removal efficiency indicated the adaptation of the microorganism in SBR [17, 128].

An acclimation period is necessary to expose the microbial community to the potentially inhibitory or toxic organic compounds present in the wastewater [88, 129]. Likewise, the bacteria that have prior exposure and adaptation to petroleum hydrocarbons exhibit higher biodegradation rates [130]. A similar trend for the COD removal efficiency was also reported and demonstrated that bioaugmentation is a powerful tool to shorten the adaptation time of the biological system and resistance to shock loading [23].

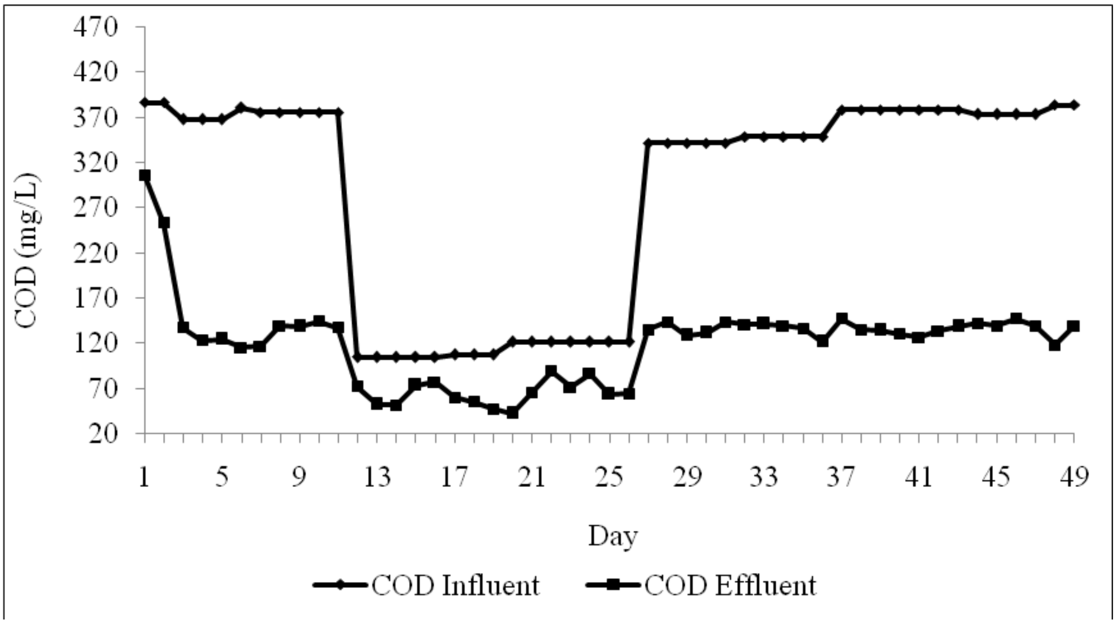


Figure 4.12: COD Influent versus COD Effluent

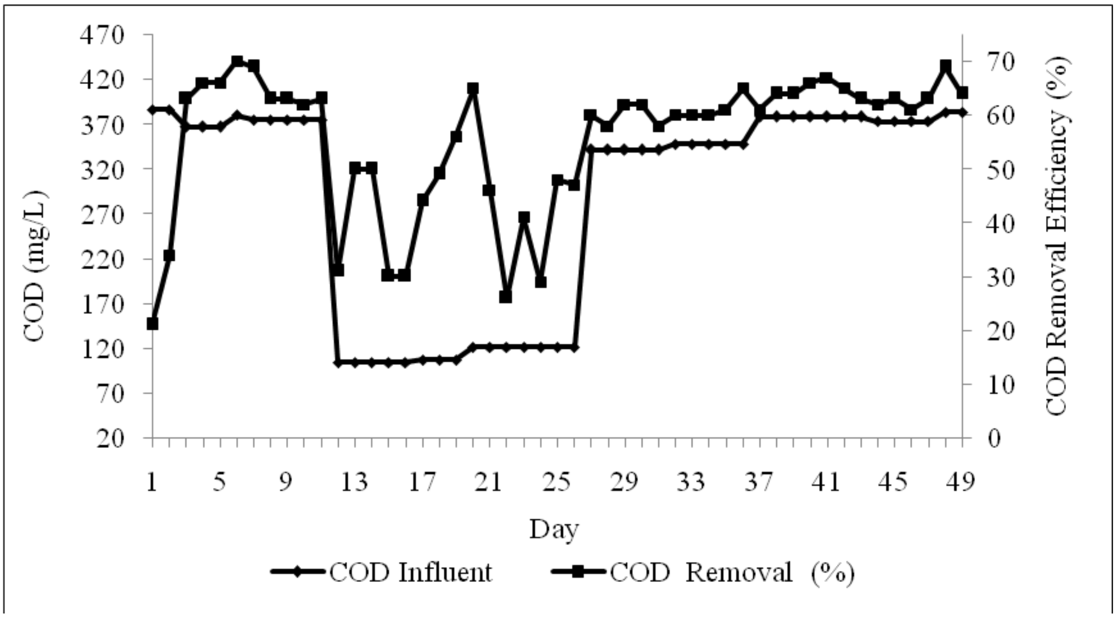


Figure 4.13: COD Influent versus COD Removal Efficiency (%)

MLSS and MLVSS showed similar trends as compared to COD within this experiment (Figure 4.14). Generally, MLSS and MLVSS are analyzed to measure the microorganisms' concentration in the system. MLSS indicates the presence of volatile and inert solids in the sludge. MLVSS closely approximates the biologically active portion of the solid in the sludge and an adequate MLVSS concentration has to be maintained to ensure a sufficient biomass concentration for biological reactions [17]. The typical MLSS concentration for activated sludge is in the range of 3000-6000 mg/L. In this study, the MLSS concentration was at 5907 mg/L at the beginning to provide sufficient biomass in the system.

During the experiment, initially the MLSS and MLVSS concentrations declined from 5907 to 1620 mg/L and 5137 to 1373 mg/L respectively. Application of the real petroleum refinery wastewater in this study was a challenge in the treatment system. The collected wastewater normally has different characteristics in every sampling in terms of the contamination rate. The contamination rate was based on the values of COD, BOD, oil and grease etc. High values for these parameters showed that the wastewater was highly polluted and may have contained non biodegradable compounds. In addition, such compounds would have the ability to kill the microorganisms due to their toxicity, thus affect the organic matter degradation. The activity and the biological performance in the SBR might have been affecting by the toxic compounds and could have lead to the constant drop in the bacterial count at the early treatment stage [131-133].

Thereafter, MLSS and MLVSS concentrations demonstrated a steady rise from 1745 to 4060 mg/L and 1737 to 3767 mg/L, respectively. The steady rise in the MLVSS concentration reflected the active growth of the bacteria which indicates the successful adaptation of the bacteria to the wastewater which was due to formation of new cells by the bacteria using organic matters [130]. The MLVSS: MLSS ratio in this study was found to be 0.81-0.97. The volatile fraction (MLVSS: MLSS ratio) coincides with the typical values between 0.80-0.85 [17, 88].

The correlation of the MLVSS and the COD removal efficiency is presented in Figure 4.15. The microorganisms' concentrations kept decreasing while the COD removal efficiency increased in the first few days of the experiment. This may have been due to various reasons such as the presence of resistant microorganisms in the refinery sludge as well as the microorganism biosorption phenomena. After day 12, the microorganisms could adapt with the real wastewater and started reproduction with continues improvement in the MLVSS concentrations. In addition, the activities of the microorganisms removed some portions of the pollution loads as a result of the biosorption [88]. Biosorption expresses the transport of organic matter from the wastewater to the activated sludge followed by the retention within the flocs. It is usually caused by the electrostatic or hydrophobic interactions according to the nature of the organic matter [134, 135]. Biosorption of the soluble and colloidal matter of the wastewater and activated sludge can reach a steady state after 20 to 40 min. of mixing.

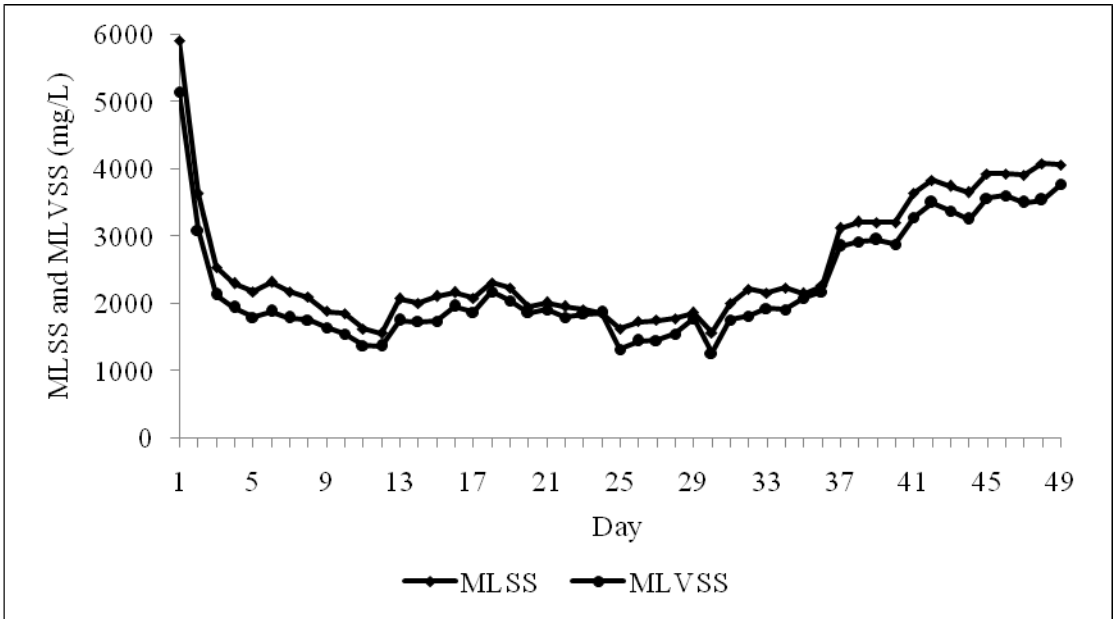


Figure 4.14: Concentration of MLSS and MLVSS.

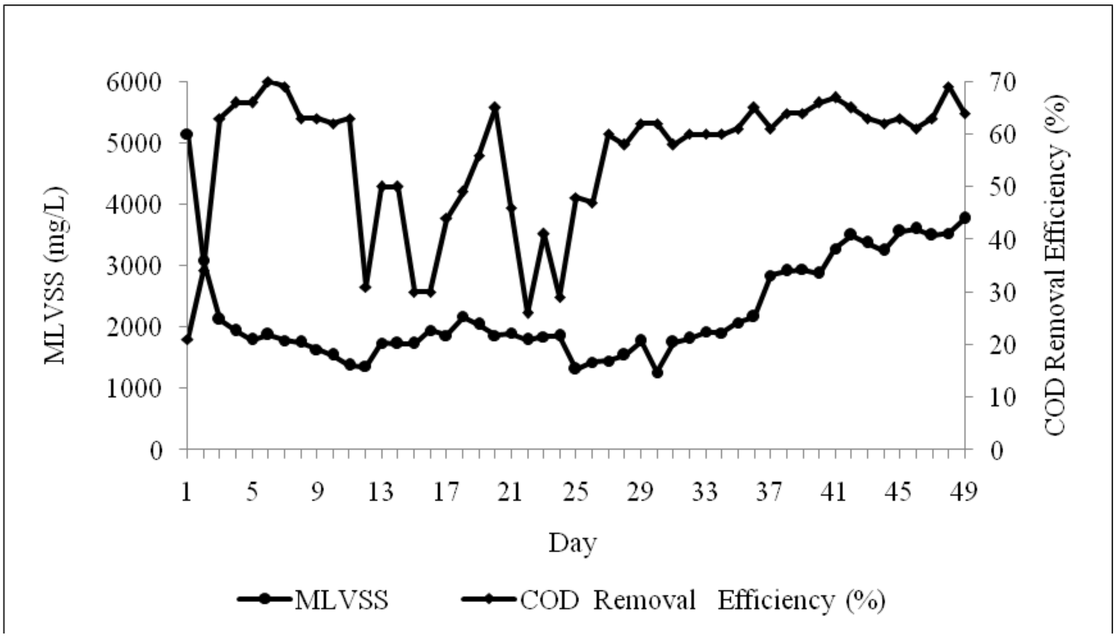


Figure 4.15: MLVSS versus COD Removal Efficiency (%)

SVI is a process parameter and was measured daily to assess the stability of the sludge in the aerobic suspended growth system. SVI values below 80 were considered excellent, while SVI between 80 - 150 showed a moderate condition. Practically, SVI values more than 150 specified a poor sludge quality [97]. As shown in Figure 4.16, the SVI values from 31- 63 were observed in this study which indicated excellent settling properties. Moreover, the lower SVI number showed faster solid settling [124]. In the SBR system, good sludge settling was an important process parameter in order to avoid sludge being withdrawn during the draw step [125].

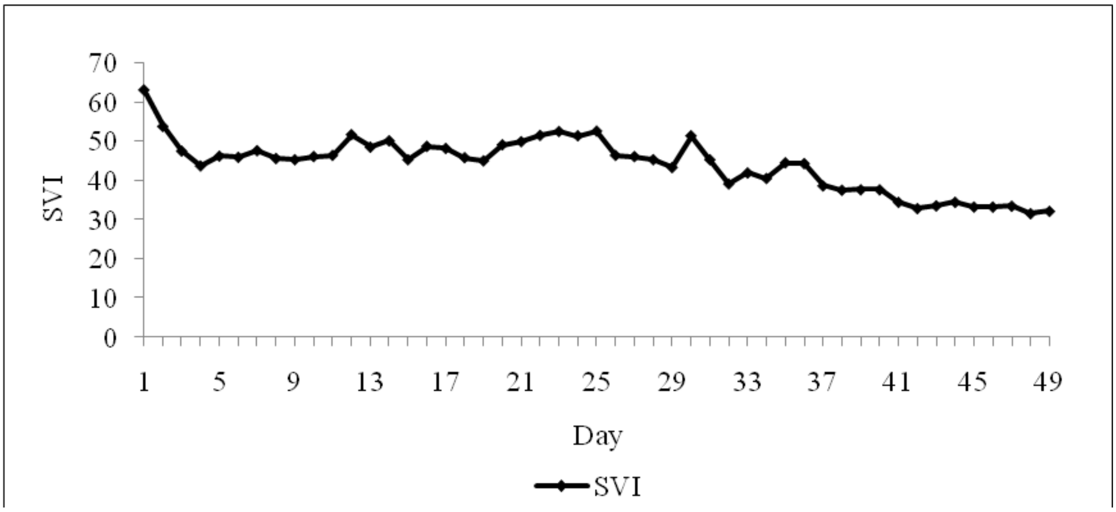


Figure 4.16: SVI Analyses

4.3.3 Comparison of the Final Effluent with the Malaysia Standard Limit

The effluent from SBR has been characterized based on COD, TSS, BOD_5, oil and grease, colour, ammonia nitrogen, phenols and sulphide. The results were summarized and compared with the discharge limits established by the DOE as shown in Table 4.4. While the COD, TSS, oil and grease, colour, and phenol discharge values were less than the discharge limit in Standard B, the values for BOD_5, ammonia nitrogen and sulphide were less than the limited amounts in Standard A. The results of the effluent from SBR contained a bit high total solid content which was organic matter, thus, effecting the TSS value and COD concentration. Oil and grease and phenol concentrations did not achieve the Standard A due to the characteristics of the wastewater itself. The crude oil contained extremely high oil and grease concentrations and phenol, hence they were not sufficiently removed to be put in the Standard A after undergoing the treatment process. In addition, phenol in the dispersed oil was difficult to remove so the effluent from SBR still showed a higher phenol concentration than Standard A. However, overall, all the parameters followed the allowable discharge limits.

This study demonstrated the efficiency of the AOP-SBR system for the treatment of the petroleum refinery wastewater in providing a high quality of treated wastewater according to the required discharge standards. The application of AOP-SBR was considered a successful combination based on the good achievement of the effluent quality. The main reason for this was that the application of AOP as a pretreatment provided the less toxic wastewater to SBR. Moreover, AOP was responsible for turning the less biodegradable wastewater into more suitable biodegradability for the SBR system. AOP was also able to reduce the solid content through the oxidation processes. Therefore, SBR was received readily biodegradable, less toxic wastewater, thus, its effluent showed an acceptable quality standard. Treating less toxic wastewater also gave less of a shock load impact to the system and helped in the bacterial adaptation and degrading process.

Other studies also reported the useful combination of the AOP-SBR system. The combination of AOP-SBR achieved the best option for textile wastewater treatment as compared to SBR alone or SBR-AOP by giving colour and total phosphorus removal of around 80 % and COD and TKN reduction greater than 90 % [88]. Meanwhile, the study on the pharmaceutical wastewater reported that AOP with the Fenton reagent as a pretreatment played a very important role by providing better biodegradability at about 3-5 times increment [94]. The toxicity test also indicated that the toxicity level was greatly reduced by the pretreatment. The results showed that the effluent from SBR reveals a high removal efficiency of about 98% for COD and BOD.

Table 4.4: Comparison of SBR Effluent and Discharge Standard

Parameters	Values	Removal (%)	Standard	
			A	B
COD	174^{b}	70	80	200
TSS	75^{b}	76	50	100
BOD_5	12^{a}	96	20	50
Oil and grease	3^{b}	96	1	10
Colour	108^{b}	97	100	200
Ammonia Nitrogen	4.2^{a}	90	10	20
Phenols	0.002^{b}	100	0.001	1
Sulphide	$0.35^{a,b}$	98	0.5	0.5

All the units are in mg/L, except Color (Pt Co)
[a] Achieving Standard A
[b]Achieving Standard B
ND: Not detected

4.4 Summary

The observation on the characteristics of petroleum refinery wastewater shows low biodegradability and exceeds the discharge limit standard. Therefore, Fenton process was applied for pretreatment of petroleum refinery wastewater and shows biodegradability improved up to 0.44. Statistical analysis of RSM shows an attractive method to determine the optimum operating variables in shorter time with 0.95% of R^2. Then, SBR system was selected and shows good performance in producing high quality of final effluent within 49 days. Finally, the final effluent of SBR was analyzed and showed acceptable quality compared to Malaysia Standard Limit.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Petroleum refinery wastewater treatment is important worldwide. Discharging of untreated petroleum refinery wastewater may give negative effects to human health and the environment as well. Fenton process was applied to improve the biodegradability of the petroleum refinery wastewater.

- The results show improvement in the biodegradability from approximately 0.27 to 0.44. The preliminary analysis were conducted and the optimum operating conditions of the Fenton process were achieved at the H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 5 and reaction time 60 min. Furthermore, the optimization of the Fenton process was carried out using the Response Surface Methodology (RSM). RSM suggested the optimum condition at H_2O_2/COD molar ratio 2.8, H_2O_2/Fe^{2+} 4 and reaction time of 71 min, with BOD_5/COD 0.44 which was economically unfeasible as compared to the preliminary experiment achievements. In addition, ANOVA showed acceptable and satisfactory results with P: <0.0001, R^2: 0.95 $Adj.R^2$: 0.91, AP: 16.479 and CV: 6.09). Moreover, the H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} were the most significant factors in the Fenton process of the petroleum refinery wastewater.

- The pretreated petroleum refinery wastewater was then treated by the Sequencing Batch Reactor to meet the standard limit. It was found that, the system took 49 days to achieve stability based on the effluent COD, COD removal efficiency, mixed liquor suspended solids (MLSS), mixed liquor

- volatile suspended solids (MLVSS) and SVI. Fluctuation of the COD removal efficiency could be observed during the SBR operation. Fluctuation of the real petroleum refinery wastewater on the treatment system caused a significant effect on the microorganism growth in the reactor. Consequently, once the microorganisms were well adapted to the wastewater content, they showed stability by gradual increase in MLSS and MLVSS. Adaptation also could be identified by constant COD removal efficiency of about 58 – 70%.

- Effluent of AOP-SBR was analyzed and showed that its quality meets the Standard B of Malaysia Standard Limit instructed by DOE.

Therefore, the AOP-SBR system can be an attractive and suitable method for the petroleum refinery wastewater treatment.

5.2 Recommendations

The results and observations from this project show the potential of the AOP-SBR system to become one of the alternatives for petroleum refinery wastewater treatment in Malaysia. Based on the experiments and knowledge during this study, the recommendations for future work are as follows:

- To apply low cost catalyst such as iron-clays and volcanic sand for the Fenton process.
- To use the most active bacteria in the sequencing batch reactor. Application of active bacteria enhances the stability of the system in a shorter time.

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PUBLICATIONS AND AWARDS

C.1 Publications

1. S. Ishak, A. Malakahmad, M. Hasnain Isa. 2012. Application of Sequencing Batch Reactor (SBR) for Post Treatment of Petroleum Refinery Wastewater. *Proceeding of International Conference on Construction, Offshore and Environmental Engineering (ICCOEE),* 12nd – 14th June 2012, Kuala Lumpur Convention Center, Malaysia.

2. A. Malakahmad, S. Ishak, M. H. Isa. 2012. Refinery Wastewater Biological Treatment: A Short Review. *Journal of Scientific & Industrial Research (JSIR),* 71(4)251-256.

3. A. Malakahmad, S. Ishak, U. N Nasoha, M. H. Isa, S. R. Kutty. 2011. Application Sequencing Batch Reactor (SBR) for treatment of refinery wastewater containing nickel, *Proceeding of the third international conference on management of natural resources , sustainable development and ecological hazards, Ravage of the planet (RAV) 2011 organized by Wessex Institute of Technology (WIT),* 13rd – 15th December 2011, Shah Alam, Malaysia.

4. S. Ishak, A. Malakahmad, M. H. Isa 2010. Biological Treatment of Refinery Wastewater: A Review. *Proceeding of International Conference on Sustainable Building and Infrastructure (ICSBI),* 15th – 17th June 2010, Kuala Lumpur Convention Center, Malaysia.

C.2 Awards

Gold medal 2011. Universiti Teknologi PETRONAS (UTP) Science and Engineering Design Exhibition (SEDEX).

APPENDIX A

EXPERIMENTAL DARTA ACHIEVEMENT DURING LABORATORY WORKS

A.1 Preliminary analysis of the Fenton process using the different reaction time at a constant H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio.

Reaction time (min)	Final BOD (mg/L)	Final COD (mg/L)	BOD removal (%)	COD removal (%)	BOD_5/COD
0	648	1667	0	0	0.39
20	181.7	454	72	73	0.40
40	148	353	77	79	0.42
60	150.3	342	77	79	0.44
80	180.3	418	72	75	0.43
100	210.1	516	68	69	0.41
120	178.7	457	72	73	0.39

A.2 Preliminary analysis of the Fenton process using different H_2O_2/COD molar ratio at the constant H_2O_2/Fe^{2+} molar ratio and reaction time.

H_2O_2/COD molar ratio	Final BOD (mg/L)	Final COD (mg/L)	BOD removal (%)	COD removal (%)	BOD_5/COD
0	648	1667	0	0	0.39
2	150.3	342	77	79	0.44
4	118.7	295	82	82	0.4
6	113.4	303	83	82	0.37
8	62.8	208	90	88	0.30
10	57.8	169	91	90	0.34
12	68	174	90	90	0.39

A.3 Preliminary analysis of the Fenton process using different H_2O_2/Fe^{2+} molar ratio at constant H_2O_2/COD molar ratio and reaction time.

Reaction time	Final BOD (mg/L)	Final COD (mg/L)	BOD removal (%)	COD removal (%)	BOD_5/COD
0	648	1667	0	0	0.39
5	150.3	342	77	79	0.44
10	160	486	75	71	0.33
15	146.8	491	77	71	0.3
20	157.3	514	75	69	0.31
25	115.7	541	82	68	0.21
30	165.8	499	74	70	0.33

A.4 Results for Response Surface Methodology

Standard Order	Numerical factors			Response factor	
	H_2O_2/COD	H_2O_2/Fe^{2+}	Reaction time	Actual	Predicted
1	1.0	3	40	0.26	0.24
2	3.0	3	40	0.40	0.42
3	1.0	7	40	0.35	0.35
4	3.0	7	40	0.41	0.40
5	1.0	3	80	0.22	0.23
6	3.0	3	80	0.44	0.44
7	1.0	7	80	0.35	0.33
8	3.0	7	80	0.38	0.40
9	0.3	5	60	0.16	0.17
10	3.7	5	60	0.4	0.38
11	2.0	2	60	0.36	0.35
12	2.0	8	60	0.42	0.42
13	2.0	5	26	0.40	0.40
14	2.0	5	94	0.41	0.40
15	2.0	5	60	0.39	0.42
16	2.0	5	60	0.44	0.42
17	2.0	5	60	0.42	0.42
18	2.0	5	60	0.39	0.42
19	2.0	5	60	0.43	0.42
20	3.0	7	80	0.44	0.42

A.5 FIT SUMMARY

Design Summary

Study Type: Response Surface Experiments:20
Initial Design: Central Composite Blocks: No Blocks
Design Model: Quadratic

Response	Name	Obs	Minimum	Maximum	Trans	Model
Y1	BOD/COD	20	0.16	0.44	None	Quadratic

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	H_2O_2/COD	(mr)	Numeric	1.00	3.00	-1.000	1.000
B	H_20_2/FE^{2+}	(mr)	Numeric	3.00	7.00	-1.000	1.000
C	Reaction time	(min)	Numeric	40.00	80.00	-1.000	1.000

Response: BOD/COD

A.6 Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	2.79	1	2.79			
Linear	0.059	3	0.020	6.18	0.0054	
2FI	9.537E-003	3	3.179E-003	1.00	0.4222	
Quadratic	0.036	3	0.012	23.17	< 0.0001	Suggested
Cubic	2.457E-003	4	6.14E-004	1.35	0.3518	Aliased
Residual	2.721E-003	6	4.535E-004			
Total	2.90	20	0.14			

"Sequential Model Sum of Squares": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

A.7 Lack of Fit Tests

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Linear	0.048	11	4.366E-003	8.14	0.0157	
2FI	0.038	8	4.811E-003	0.0136	8.97	
Quadratic	2.495E-003	5	4.989E-004	0.93	0.5309	Suggested
Cubic	3.788E-005	1	3.788E-0	0.071	0.811	Aliased
Pure Error	2.683E-003	5	5.367E-004			

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit.

A.8 Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted	PRESS	
Linear	0.056	0.5367	0.4498	0.2465	0.082	
2FI	0._056	0.6238	0.4502	0.0860	0.10	
Quadratic	0.023	0.9527	0.9101	0.7699	0.025	Suggested
Cubic	0.021	0.9751	0.9213	0.8884	0.012	Aliased

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

A.9 ANOVA Results

Response: BOD/COD

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	0.10	9	0.012	22.38	< 0.0001	significant
A	*0.053*	*1*	*0.053*	*103.05*	*< 0.0001*	
B	*5.374E-003*	*1*	*5.374E-003*	*10.38*	*0.0092*	
C	*1.272E-005*	*1*	*1.272E-005*	*0.025*	*0.8786*	
A^2	*0.036*	*1*	*0.036*	*68.57*	*< 0.0001*	
B^2	*1.664E-003*	*1*	*1.664E-003*	*3.21*	*0.1033*	
C^2	*4.266E-004*	*1*	*4.266E-004*	*0.82*	*0.3854*	
AB	*9.112E-003*	*1*	*9.112E-003*	*17.60*	*0.0018*	
AC	*3.125E-004*	*1*	*3.125E-004*	*0.60*	*0.4552*	
BC	*1.125E-004*	*1*	*1.125E-004*	*0.22*	*0.6511*	
Residual	5.178E-003	10	5.178E-004			
Lack of Fit	*2.495E-003*	*5*	*4.989E-004*	*0.93*	*0.5309*	*not significant*
Pure Error	*2.683E-003*	*5*	*5.367E-004*			
Cor Total	0.11	19				

The Model F-value of 22.38 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, A^2, AB are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 0.93 implies the Lack of Fit is not significant relative to the pure error. There is a 53.09% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	0.023	R-Squared	0.9527
Mean	0.37	Adj R-Squared	0.9101
C.V.	6.09	Pred R-Squared	0.7699
PRESS	0.025	Adeq Precision	16.479

The "Pred R-Squared" of 0.7699 is in reasonable agreement with the "Adj R-Squared" of 0.9101.
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 16.479 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.42	1	9.281E-003	0.40	0.44	
A-$_2O_2$/COD	0.063	1	6.157E-003	0.049	0.076	1.00
B-H_20_2/FE^{2+}	0.020	1	6.157E-003	6.17E-003	0.034	1.00
C-Reaction time	-9.652E-004	1	6.157E-003	-0.015	0.013	1.00
A^2	-0.050	1	5.994E-003	-0.063	-0.036	1.02
B^2	-0.011	1	5.994E-003	-0.024	2.612E-003	1.02
C^2	-5.441E-003	1	5.994E-003	-0.019	7.915E-003	1.02
AB	-0.034		1 8.045E-003	-0.052	-0.016	1.00
AC	6.250E-003		1 8.045E-003	-0.012	0.024	1.00
BC	-3.750E-003		1 8.045E-003	-0.022	0.014	1.00

Final Equation in Terms of Coded Factors:

BOD/COD =
+0.42
+0.063 * A
+0.020 * B
-9.652E-004 * C
-0.050 * A^2
-0.011 * B^2
-5.441E-003 * C^2
-0.034 * A * B
+6.250E-003 * A * C
-3.750E-003 * B * C

Final Equation in Terms of Actual Factors:

BOD/COD =
-0.22729
+0.32667 * H_2O_2/COD

+0.076154 * H_2O_2/FE^{2+}
+1.42771E-003 * Reaction time
-0.049635 * H_2O_2/COD^2
-2.68601E-003 * H_2O_2/FE^{2+2}
-1.36019E-005 * Reaction time^2
-0.016875 * H_2O_2/COD * H_2O_2/FE^{2+}
+3.12500E-004 * H_2O_2/COD * Reaction time
-9.37500E-005 * H_2O_2/FE^{2+} * Reaction time

A.10 Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	0.26	0.24	0.020	0.670	1.530	0.475	1.658	19
2	0.40	0.42	-0.020	0.670	-1.530	0.475	-1.659	6
3	0.35	0.35	-4.671E-003	0.670	-0.357	0.026	0.341	5
4	0.41	0.40	0.010	0.670	0.789	0.126	0.773	8
5	0.22	0.23	-0.013	0.670	-0.999	0.203	-0.999	9
6	0.44	0.44	1.922E-003	0.670	0.147	0.004	0.140	1
7	0.35	0.33	0.017	0.670	1.320	0.353	1.378	18
8	0.38	0.40	-0.023	0.670	-1.740	0.614	-1.977	20
9	0.16	0.17	-0.013	0.607	-0.907	0.127	-0.898	11
10	0.40	0.38	0.017	0.607	1.180	0.215	1.206	3
11	0.36	0.35	5.306E-003	0.607	0.372	0.021	0.355	17
12	0.42	0.42	-1.417E-003	0.607	-0.099	0.002	-0.094	7
13	0.40	0.40	-4.679E-003	0.607	-0.328	0.017	-0.313	12
14	0.41	0.40	8.568E-003	0.607	0.601	0.056	0.581	4
15	0.39	0.42	-0.028	0.166	-1.369	0.037	-1.441	14
16	0.44	0.42	0.022	0.166	1.037	0.021	1.042	16
17	0.42	0.42	1.555E-003	0.166	0.075	0.000	0.071	13
18	0.39	0.42	-0.028	0.166	-1.369	0.037	-1.441	10
19	0. 43	0.42	0.012	0.166	0.556	0.006	0.536	2
20	0.44	0.42	0.022	0.166	1.037	0.021	1.042	15

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

1) Normal probability plot of the studentized residuals to check for normality of residuals.

2) Studentized residuals versus predicted values to check for constant error.

3) Outlier t versus run order to look for outliers, i.e., influential values.

4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

A.11 Data Optimization

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
H_2O_2/COD	is in range	1	3	1	1	3
H_2O_2/FE^{2+}	is in range	3	7	1	1	3
Reaction time	is in range	40	80	1	1	3
BOD_5/COD	maximize	0.16	0.44	1	1	3

Solutions

Number	H_2O_2/COD	H_2O_2/FE^{2+}	BOD/COD	Reaction time	Desirability	
1	2.8	4	71	0.439248	0.997	Selected
1	2.8	4	71	0.439248	0.997	

2 Solutions found

Number of Starting Points 10

H2O2/COD	H202/FE2+	Reaction time
1.5	6	67
1.9	6	71
2.1	7	46
1.6	6	53
2.7	3	51
1.6	7	46
1.2	6	67
2.5	6	51
1.1	4	60
1.6	7	77

A.12 Preliminary Analysis of Sequencing Batch Reactor

F/M	COD*i*	COD, mg/L (day 1)	COD removal (%)	COD, mg/L (day 2)	COD removal (%)	COD, mg/L (day 3)	Final COD removal (%)
0.05	166	106	36	90	45	105	37
0.10	231	141	38	76	67	91	61
0.15	248	99	60	111	55	117	53
0.20	291	203	30	111	62	170	42
0.25	320	158	51	110	66	126	60

COD*i* = Initial COD

A.13 Reactor performance of Sequencing Batch Reactor

Date	Influent COD	Effluent COD	COD removal (%)	MLSS	MLVSS	SVI
10.6.2011	386	306	21	5907	5147	63.0
11.6.2011	386	253	34	3627	3087	53.7
13.6.2011	367	137	63	2533	2120	47.4
14.6.2011	367	123	66	2293	1933	43.6
15.6.2011	367	124	66	2170	1790	46.1
17.6.2011	380	115	70	2313	1873	45.8
20.6.2011	375	116	69	2167	1780	47.5
21.6.2011	375	139	63	2087	1747	45.5
22.6.2011	375	138	63	1880	1633	45.2
23.6.2011	375	144	62	1847	1540	46.0
24.6.2011	375	137	63	1620	1373	46.3
27.6.2011	104	72	31	1550	1360	51.6
28.6.2011	104	52	50	2067	1740	48.4
29.6.2011	104	51	50	2000	1727	50.0
30.6.2011	104	73	30	2100	1730	45.2
1.7.2011	104	77	30	2160	1947	48.6
5.7.2011	107	60	44	2080	1867	48.1
6.7.2011	107	55	49	2300	2170	45.7
7.7.2011	107	47	56	2227	2040	44.9
11.7.2011	121	42	65	1940	1860	49.0
12.7.2011	121	65	46	2007	1900	49.8
13.7.2011	121	89	26	1947	1793	51.4
14.7.2011	121	71	41	1907	1840	52.4
15.7.2011	121	86	29	1853	1853	51.3
18.7.2011	121	63	48	1620	1313	52.5
19.7.2011	121	64	47	1727	1433	46.3
20.7.2011	341	135	60	1745	1450	46.0
21.7.2011	341	143	58	1767	1540	45.2
22.7.2011	341	128	62	1853	1767	43.2
25.7.2011	341	131	62	1560	1260	51.3

A.13 *(Cont),* Reactor performance of Sequencing Batch Reactor

26.7.2011	341	143	58	1993	1750	45.2
27.7.2011	348	140	60	2207	1813	39.0
28.7.2011	348	141	60	2153	1920	41.8
29.7.2011	348	139	60	2227	1907	40.4
01.8.2011	348	136	61	2140	2073	44.4
02.8.2011	348	121	65	2260	2167	44.2
03.8.2011	378	147	61	3113	2847	38.5
04.8.2011	378	135	64	3207	2913	37.4
05.8.2011	378	134	64	3200	2940	37.5
08.8.2011	378	130	66	3200	2873	37.5
09.8.2011	378	126	67	3640	3280	34.3
12.8.2011	378	133	65	3827	3493	32.7
15.8.2011	378	138	63	3742	3370	33.4
16.8.2011	373	142	62	3647	3247	34.3
18.8.2011	373	139	63	3927	3560	33.1
19.8.2011	373	147	61	3927	3600	33.1
22.8.2011	373	139	63	3907	3493	33.3
23.8.2011	383	118	69	4080	3533	31.4
24.8.2011	383	139	64	4060	3767	32.0

APPENDIX B

LIST OF EXPERTS AND VISITED SITES

D.1 List of Expert

The following experts were consulted for the purpose of knowledge acquisition at various stages of this study.

1. Dr. Amirhossein Malakahmad, Department of Civil Engineering, Universiti Teknologi PETRONAS (UTP).

2. AP.Dr. Mohamed Hasnain Isa, Department of Civil Engineering, Universiti Teknologi PETRONAS (UTP).

3. Prof. Dr. Malay Chaudhuri, Department of Civil Engineering, Universiti Teknologi PETRONAS (UTP).

4. Prof. Dr Bassim H.Hameed, School of Chemical Engineering, Universiti Sains Malaysia (USM).

5. Noor Azahari B Arshad Department of HSE, PETRONAS Penapisan (Melaka) Sdn Bhd.

6. Pn. Rohaida Che Man, Faculty of Chemical Engineering and Natural Resources, Universiti Malaysia Pahang (UMP).

7. Pn Zatilfarihiah Rasti, Faculty of Applied Science, Universiti Teknologi MARA (UiTM), Kuala Pilah.

D.2 List of Visited Site

The following site was visited for the purpose of knowledge acquisition regarding petroleum refinery wastewater treatment in Malaysia.

1. PETRONAS Penapisan (Melaka) Sdn Bhd.
2. Ulu Kinta Water Treatment Plant
3. Sultan Idris Shah II water treatment plant