A TREATMENT SYSTEM FOR LANDFILL LEACHATE

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A TREATMENT SYSTEM FOR LANDFILL LEACHATE

by

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A TREATMENT SYSTEM FOR LANDFILL LEACHATE

by

GAN CHIN HENG

A Thesis

Submitted to the Postgraduate Studies Programme

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To My Beloved Father, Mother and Sister

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ABSTRACT

Landfill leachate is a potential source of ground and surface water contamination and causes extensive pollution if it is not properly collected, treated and disposed of. The objective of the research was to study a combined advanced oxidation process (AOP) with sequencing batch reactor (SBR) system for treatment of mature landfill leachate so as to meet the discharge standard, particularly in terms of COD, BOD_5 and suspended solids. Fenton and photo-Fenton processes were applied to the preliminary treated (adjusted to pH 3 and 1-h settling) leachate and response surface methodology (RSM) was used to optimize the processes for removal of COD, colour and ammonia nitrogen (NH_3-N). The optimum operating conditions for Fenton treatment were at about H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h reaction time for 51% COD removal, 77% colour removal and 84% NH_3-N removal, whereas the optimum operating conditions for photo-Fenton treatment were H_2O_2/COD molar ratio 3.75, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h irradiation time for 68% COD removal, 81% colour removal and 80% NH_3-N removal. The biodegradability (BOD_5/COD ratio) of the Fenton and photo-Fenton treated leachate were 0.21 and 0.33, respectively under optimum operating conditions. Photo-Fenton treatment under Fenton process optimum operating conditions, i.e. H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 (lower dosages of the Fenton reagent) and 1.5 h irradiation time, was conducted and 65% COD removal, 83% colour removal and 80% NH_3-N removal were achieved, and the biodegradability was 0.35. Aerobic sequencing batch reactor (SBR) treatment of the photo-Fenton treated leachate resulted in soluble COD, BOD_5 and NH_3-N removal of 78, 81 and 94%, respectively. The final effluent characteristics were COD 92 mg/L, soluble COD 71 mg/L, BOD_5 26 mg/L, NH_3-N 7 mg/L, total phosphorus 6.4 mg/L, suspended solids 38 mg/L and colour 46 Pt-Co Units, and met the Malaysian discharge standard (B) (COD 100 mg/L, BOD_5 50 mg/L and suspended solids 100 mg/L). The study shows that combined photo-Fenton-SBR provides effective treatment of a mature landfill leachate.

ABSTRAK

Larut resapan dari tapak pelupusan adalah punca pencemaran yang mendatangkan kesan buruk terhadap air bawah tanah dan air permukaan jika larut resapan tersebut tidak dikumpul, dirawat dan dilepaskan dengan sewajarnya. Objektif kajian ini adalah untuk menghasilkan satu sistem rawatan yang memenuhi syarat-syarat yang terkandung dalam Akta Kualiti Alam Sekitar untuk larut resapan dari tapak pelupusan. Proses-proses Fenton dan foto-Fenton diaplikasikan ke dalam larut resapan olahan awalan (selaraskan ke pH 3 dan enapan selama 1 jam), dan *response surface methodology* (RSM) digunakan untuk mengoptimumkan proses-proses tersebut untuk penyingkiran (COD), warna dan nitrogen ammonia (NH_3-N). Operasi di bawah keadaan optimum untuk olahan Fenton adalah lebih kurang dalam nisbah molar H_2O_2/COD 2.25, nisbah molar H_2O_2/Fe^{2+} 10.0 dan masa tindak balas selama 1.5 jam dengan penyingkiran COD 51%, warna 77% dan NH_3-N 84%, manakala operasi di bawah keadaan optimum untuk olahan foto-Fenton adalah lebih kurang dalam nisbah molar H_2O_2/COD 3.75, nisbah molar H_2O_2/Fe^{2+} 10.0 dan masa tindak balas berserta penyinaran selama 1.5 jam dengan penyingkiran COD 68%, warna 81% dan NH_3-N 80%. Kebolehan biodegradasi (nisbah BOD_5/COD) larut resapan olahan Fenton dan foto-Fenton adalah 0.21 dan 0.33 pada operasi di bawah keadaan optimum masing-masing. Operasi foto-Fenton di bawah keadaan optimum proses Fenton, iaitu dengan reagen Fenton yang lebih rendah dilakukan dan penyingkiran COD 68%, warna 81% dan NH_3-N 83% dicapai, dan nisbah BOD_5/COD adalah 0.35. Olahan aerobik *sequencing batch reactor* (SBR) untuk larut resapan olahan foto-Fenton menghasilkan penyingkiran larut COD, BOD_5 dan NH_3-N sebanyak 78, 81 dan 88% masing-masing. Ciri-ciri efluen akhir adalah COD 92 mg/L, larut COD 71 mg/L, BOD_5 26 mg/L, NH_3-N 13 mg/L, jumlah fosforus 6.4 mg/L, pepejal terampai 38 mg/L dan warna 46 Pt-Co Units, dan memenuhi syarat-syarat dalam Akta Kualiti Alam Sekitar (COD 100 mg/L, BOD_5 50 mg/L dan pepejal terampai 100 mg/L). Kajian ini menunjukkan gabungan foto-Fenton-SBR menghasilkan rawatan yang efektif untuk larut resapan dari tapak pelupusan yang telah beroperasi lama.

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LIST OF ABBREVIATIONS AND NOMENCLATURES

ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
AP	Adequate Precision
BOD_5	Five-Day Biochemical Oxygen Demand
CCD	Central Composite Design
COD	Chemical Oxygen Demand
CV	Coefficient of Variance
HRT	Hydraulic Retention Time
MLSS	Mixed Liquor Suspended Solids
MSW	Municipal Solid Waste
NH_3-N	Ammonia-nitrogen
NO_3^--N	Nitrate-nitrogen
PBL	Pulau Burung Landfill
PLOF	Probability of Lack of Fit
RSM	Response Surface Methodology
SBR	Sequencing Batch Reactor
sCOD	Soluble Chemical Oxygen Demand
STP	Sewage Treatment Plant
TKN	Total Kjeldahl Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solids
VFA	Volatile Fatty Acids
Y_1, Y_2, Y_3	Predicted Results of Removal (COD, Colour and Ammonia-nitrogen)
β	The Sum of a Constant
A, B, C	Parameters in Equation

CHAPTER 1

INTRODUCTION

One of the major consequences of industrialization, urbanization and population growth is the massive generation of solid waste. As a developing country, Malaysia faces solid waste management problems. Solid waste disposal is one of the major environmental problems faced by most municipalities in Malaysia. Each year, there are about 8 million tonnes of solid waste being generated which amounts to each person generating about 1 kg of solid waste per day (Asikir and Agamuthu, 2007). The solid waste generation rate increased to 1.3 kg/day in 2006, and was expected to further increase to 1.5 kg/day in 2007 due to increase in urbanization and change in living standard and consumption pattern (Agamuthu et al., 2006). Currently, more than 19000 tonnes of municipal solid waste is produced daily in Peninsular Malaysia (Agamuthu et al., 2009) and the method of disposal is primarily landfilling – sanitary landfill (30.9%) and dump sites (62.6%), whereas 5.5% is recycled and 1.0% is composted (Agamuthu et al., 2006). However, the landfilling practice in Malaysia is still far from being environmentally sound.

Landfill leachate is composed of the liquid that has entered the landfill from external sources, such as surface drainage, rainfall, groundwater, water from underground springs and the liquid produced from the decomposition of waste, and has percolated through the solid waste and extracted dissolved as well as suspended materials (Tchobanoglous et al., 1993). Leachate is considered as heavily polluted wastewater, presenting significant time and spatial variation in physical-chemical parameters, and a potential source of ground and surface water contamination as it may percolate through soil and subsoil, causing extensive pollution of streams, creeks and water wells (Tatsi et. al., 2003). Leachate contains large amounts of organic matter (biodegradable as well as recalcitrant), humic-type constituents, ammonia-nitrogen, heavy metals, chlorinated organics and inorganic salts. The composition and concentration of the contaminants are influenced by the type and quality of the deposited waste, hydrogeological factors and age of the landfill. Special care is required for efficient treatment and disposal of the leachate.

1.1 Problem Statement

Generation of contaminated leachate remains an inevitable consequence of the solid waste disposal practice by landfill. Landfill leachate is a mixture of high concentration of organic and inorganic contaminants and the contaminants need to be removed due to their toxicity or unfavourable effect on the environment. Several processes such as coagulation-flocculation-filtration, precipitation, ion exchange, adsorption, and air and steam stripping have been applied for treatment of landfill leachate. These processes only transfer the pollutants from one phase to another and do not solve the environmental problem. Biological processes are quite effective when applied to relatively younger (i.e. recently produced) leachate containing mainly volatile fatty acids, but they are less efficient for the treatment of older (i.e. mature or stabilized) leachate (Amokrane et al., 1997). Recalcitrant organics, contained in older leachates, are not amenable to conventional biological processes and the high ammonia content might also be inhibitory to microorganisms (Li et al., 1999). Advanced oxidation processes (AOPs) e.g. Fe^{2+}/H_2O_2 (Fenton), $UV/Fe^{2+}/H_2O_2$ (photo-Fenton), UV/H_2O_2, UV/O_3 and UV/TiO_2 have been used as effective alternative treatment for mineralization of recalcitrant wastewater organics and biodegradability improvement. Biological processes such as activated sludge, sequencing batch reactor and fixed film processes are effective for removal of biodegradable organics and nitrogenous matter from wastewater. Presumably, a complete treatment system for landfill leachate containing recalcitrant organics is a combination of AOP with a biological process.

In Malaysia, 93.5% of the municipal solid waste is disposed by landfilling (30.9% in sanitary landfill and 62.6% in dump sites). A survey of two landfill indicated that treated leachate effluent did not meet the discharge standard. Consequently, development of an integrated method of leachate treatment such as combined AOP with biological process is required. No such investigation has been reported in the literature.

1.2 Objectives of the Study

The main objective of this research is to study a combined advanced oxidation process (AOP) with sequencing batch reactor (SBR) system for effective treatment of a mature landfill leachate. The specific objectives of the study are:

1. To determine optimum operating conditions of advanced oxidation processes (Fenton and photo-Fenton) for effective pretreatment of the leachate.
2. To study the combined advanced oxidation process (AOP)-sequencing batch reactor (SBR) system for effective treatment of the leachate, so as to meet the Malaysian discharge standard (B), particularly in terms of COD, BOD_5 and suspended solids.

1.3 Scope of the Study

This study focuses on a treatment system – combined advanced oxidation process (AOP)-sequencing batch reactor (SBR) – for complete treatment of a mature landfill leachate. Leachate samples are taken from the leachate collection pond of the landfill at Pulau Burung in Nibong Tebal, Penang. The characteristics of the raw leachate are determined and the leachate is subjected to preliminary treatment for pretreatment by advanced oxidation processes (Fenton and photo-Fenton). Optimum operating conditions of the advanced oxidation processes for effective pretreatment of the leachate are determined using response surface methodology (RSM). The AOP-pretreated leachate is subjected to biological treatment by SBR and removal of biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia-nitrogen (NH_3-N), nitrate-nitrogen (NO_3^--N) and total Kjeldahl nitrogen (TKN) are measured with a view to assess the combined system for complete treatment of the leachate.

1.4 Thesis Organization

This thesis has been organized into the following five chapters:

Chapter 1 introduces the solid waste and its disposal, landfill leachate, problem statement, objectives of the study and scope of the study.

Chapter 2 presents a brief review of landfill, landfill leachate and leachate treatment. Typical examples of two landfills in Malaysia and their leachate treatment are included. Basic concept of Fenton and photo-Fenton processes, sequencing batch reactor (SBR) and response surface methodology (RSM) are also discussed.

Chapter 3 presents the methodology of the study – leachate sample, analytical methods, experimental procedure for Fenton, photo-Fenton and SBR treatment, and data analysis.

Chapter 4 presents the results of preliminary treatment, Fenton and photo-Fenton pretreatment and treatment of the pretreated leachate by sequencing batch reactor (SBR), followed by discussion.

Chapter 5 recapped the scope of the study and research method. The results and findings of the study are summarized with conclusions, and suggestions for future work are presented.

CHAPTER 2

LITERATURE REVIEW

2.0 Chapter Overview

This chapter presents a brief review of landfill, landfill leachate and leachate treatment. Typical examples of two landfills in Malaysia and their leachate treatment are included. Basic concept of Fenton and photo-Fenton processes, sequencing batch reactor (SBR) and response surface methodology (RSM) are also discussed.

2.1 Introduction

Increasingly affluent lifestyle, and continuing industrial and commercial growth in the past decades has been accompanied by rapid increase in both municipal and industrial solid waste production. In most countries, sanitary landfill method is nowadays the most common way to dispose municipal solid waste (MSW) and has been widely accepted. However, generation of heavily polluted leachate has caused significant drawback. Moreover, as stricter environmental requirements are continuously imposed, treatment of landfill leachate has become a major environmental issue.

2.2 Landfill

Landfill is the physical facility used for the disposal of residual solid waste in the surface soils on the earth. Landfilling includes monitoring of the incoming solid waste, placement and compaction of the waste and installation of landfill environmental monitoring and control facilities (Tchobanoglous et al., 1993). According to Chong (2001), out of 177 landfills in Peninsular Malaysia, only 6% are sanitary landfills and 50% are open dumping sites as in Table 2.1. According to a more recent estimate (Hua, 2005), among 230 landfills in Malaysia, only 10% are equipped with leachate treatment and gas venting facility while 51% are open dump sites.

Table 2.1 Types of Landfill in Malaysia (Chong, 2001)

State	Open Dump	Controlled Landfill	Sanitary Landfill	Total
Perlis	0	1	0	1
Kedah	7	5	1	13
Pulau Pinang	0	2	1	3
Perak	7	17	2	26
Selangor	7	9	2	18
Negeri Sembilan	7	6	0	13
Melaka	2	2	1	5
Johor	15	15	0	30
Pahang	22	8	2	32
Terengganu	9	8	1	18
Kelantan	14	3	0	17
Kuala Lumpur	0	0	1	1
Total	90	76	11	177

More than 19000 tonnes of municipal solid waste is produced daily in Peninsular Malaysia (Agamuthu et al., 2009). Table 2.2 indicates the current waste management methods in practice since year 2002 and the proposed technologies to be implemented by year 2020. The method of MSW disposal is primarily landfilling – sanitary landfill (30.9%) and dump sites (62.6%), whereas 5.5% is recycled and 1.0% is composted. It is targeted to increase disposal by sanitary landfill to 44.1% by 2020 (Agamuthu et al., 2006).

Table 2.2 Methods of Waste Disposal in Malaysia (Agamuthu et al., 2006)

Treatment	Percentage of Waste Disposed (%)		
	2002	2006	Target 2020
Recycling	5.0	5.5	22.0
Composting	0.0	1.0	8.0
Incineration	0.0	0.0	16.8
Inert Landfill	0.0	3.2	9.1
Sanitary Landfill	5.0	30.9	44.1
Other Disposal Sites	90.0	59.4	0.0
Total	100.0	100.0	100.0

Landfill can be generally classified into few categories as aerobic landfill with forced aeration, anaerobic landfill, anaerobic sanitary landfill with buried leachate collection facilities and semi-aerobic landfill (Hua, 2005). A semi-aerobic system can be achieved through a convection process. The latter involves the decomposition of organic matter inside the landfill and this will cause an increase in temperature. The difference in temperature between inside and outside of the landfill will generate a heat convection current into the landfill through the leachate pipe (Aziz et al., 2004). It is found that the leachate from a semi-aerobic system has slightly lower organic contaminants compared with an anaerobic landfill in terms of BOD and COD (Basri et al., 2000; Aziz et al., 2001).

2.3 Landfill Leachate

Leachate is defined as the aqueous effluent generated as a consequence of rainwater percolation through the landfill, biochemical processes in the landfill and the inherent water content of the waste. Leachate flow rate is closely linked to precipitation, surface runoff and infiltration of groundwater percolating through the landfill. The climate also has a great influence on leachate production because it affects the input of precipitation and losses through evaporation. Besides, leachate production depends on the nature of the waste itself and its degree of compaction into the tip. The production is generally greater whenever the waste is less compacted, since compaction reduces the filtration rate (Lema et al., 1988).

The characteristics of the landfill leachate can usually be represented by the basic parameters of chemical oxygen demand (COD), biochemical oxygen demand (BOD), BOD/COD ratio, pH, total suspended solids (TSS), ammonia-nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN) and heavy metals. There are many factors affecting the characteristics of leachate, i.e., age, precipitation, seasonal weather variation, waste type and composition (depending on the standard of living of the surrounding population and structure of the tip). In particular, the composition of landfill leachate varies greatly depending on the age of the landfill (Baig et al., 1999). Table 2.3 shows landfill leachate classification versus age (Chian and DeWalle, 1976). The data show that the age of the landfill and thus the degree of solid waste stabilization has a significant effect on leachate characteristics. The BOD/COD ratio decreases rapidly with the age of the landfill. This is due to the release of large recalcitrant organic molecules from the solid waste. Consequently, old landfill leachate is characterized by its low BOD/COD ratio and fairly high NH_3-N. Although leachate composition may vary widely within the successive aerobic, acetogenic and methanogenic stabilization stages of the waste, three types of leachates have been defined according to landfill age. The existing relation between the age of the landfill and the organic matter composition may provide useful criteria to choose a suitable treatment process.

Table 2.3 Landfill Leachate Classification Versus Age (Chian and DeWalle, 1976)

	Recent	Intermediate	Old
Age (years)	<5	5-10	>10
pH	6.5	6.5-7.5	>7.5
COD	>10000	4000-10000	<4000
BOD_5/COD	>0.3	0.1-0.3	<0.1
Organic compounds	80% volatile fatty acids (VFA)	5-30% VFA + humic and fulvic acids	Humic and fulvic acids
Heavy metals	Low–medium	-	Low
Biodegradability	Important	Medium	Low

2.3.1 Leachate Generation and Composition

Organic and inorganic contaminants of landfill leachate are derieved from the solid waste due to successive biological, chemical and physical processes. Biodegradable waste can be converted biologically to CH_4 and CO_2. The pathway of conversion can be explained by the following equation:

$$\text{Organic waste} + H_2O + \text{Nutrients} \xrightarrow{\text{Microbes}} CH_4 + CO_2 + NH_3 + H_2S + \text{Biomass} + \text{Heat} + \text{Recalcitrant organic matter}$$

Biodegradation in landfill leachate occurs in sequences of five continuous phases with its predominant products in both leachate and landfill gas as shown in Fig. 2.1.

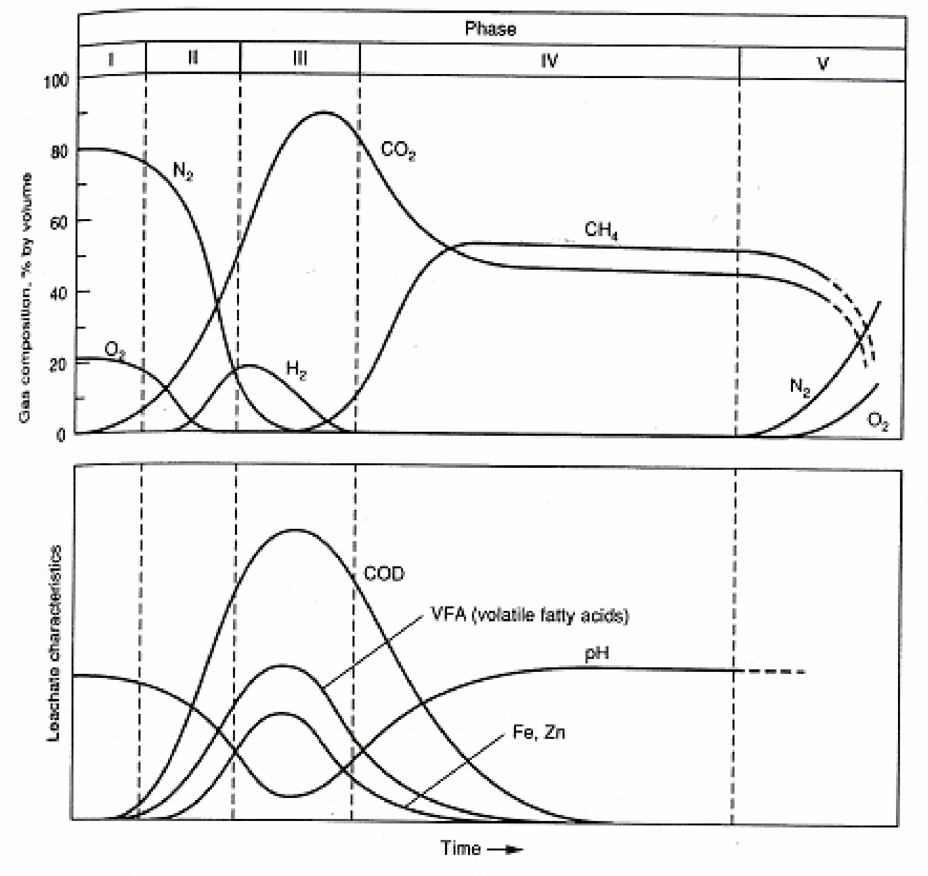

Fig. 2.1 Schematic of Waste Stabilization in a Landfill (Tchobanoglous et al., 1993)

(a) Phase I- Initial adjustment phase (Lag phase)

When the solid waste is buried into the landfill, it takes moisture and air concomitantly with it. Thus, dominant gases are still N_2 and O_2. Biological decomposition occurs under aerobic condition that results in elevation of CO_2 concentration.

(b) Phase II- Transition phase

The transition phase involves the shifting from aerobic to anaerobic environment. Basically, aerobic phase rapidly consumes the confined oxygen and infiltration water by microorganism respiration. Anaerobic conditions result in end products such as volatile fatty acids (VFA) and CO_2. The pH of the leachate decreases due to the presence of VFA and CO_2 solution. The low pH mobilizes heavy metals from the waste into the leachate.

(c) Phase III- Acid phase

Continuous solubilization (hydrolysis) of solid waste, followed by the microbial conversion of biodegradable organic content enhances acetogenic fermentation resulting in high BOD, COD and ammonia-nitrogen concentration. VFA are the main components of the organic matter released (Welander et al., 1997), besides the low pH solubilises heavy metals.

(d) Phase IV- Methane fermentation phase

As a landfill matures, the methanogenic phase occurs. Methanogenic microorganisms develop in the waste, and the VFA are converted to biogas (CH_4, CO_2). In this phase, the leachate composition represents the dynamic equilibrium between the two microbiological mechanisms with lower BOD and COD while the ammonia concentration remains high. Dissolved inorganic materials are continuously released. Occurrence of heavy metals in the leachate tends to decrease because of a high pH value that causes complexation, precipitation and transition to solid phase.

(e) Phase V- Maturation phase

With landfill ageing, waste stabilization takes place. Most of the biodegradable compounds have been decomposed. As the VFA content of leachate decreases parallel to the BOD/COD ratio, the organic fraction in the leachate becomes dominated by recalcitrant compounds such as humic substances (Chian and DeWalle, 1976). Thus, gas production drops and leachate stays at a constant level. The atmospheric gases outside the landfill will permeate through the solid waste, resulting to noticeable amounts of N_2 and O_2 once again.

Lema et al. (1988) proposed an anaerobic degradation scheme for the organic material in a sanitary landfill (Fig. 2.2).

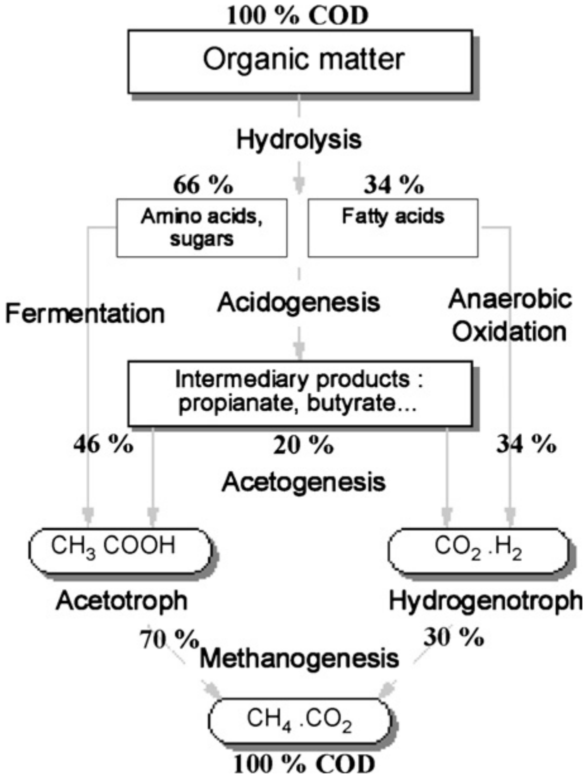

Fig. 2.2 COD Balance of the Organic Fraction During an Anaerobic Degradation in a Sanitary Landfill (Lema et al., 1988).

Typical data on the composition of leachate are reported in Table 2.4 for both new and mature landfills.

Table 2.4 Typical Data on the Composition of Leachate from New and Mature Landfills (Tchobanoglous et al., 1993)

Constituent	Value, mg/L[a]		
	New Landfill (< 2 years)		Mature Landfill (> 10 years)
	Range[b]	Typical[c]	
BOD_5 (5-day biochemical oxygen demand)	2000-30000	10000	100-200
TOC (total organic carbon)	1500-20000	6000	80-160
COD (chemical oxygen demand)	3000-60000	18000	100-500
Total suspended solids	200-2000	500	100-400
Organic nitrogen	10-800	200	80-120
Ammonia-nitrogen	10-800	200	20-40
Nitrate	5-40	25	5-10
Total phosphorus	5-100	30	5-10
Ortho phosphorus	4-80	20	4-8
Alkalinity as $CaCO_3$	1000-10000	3000	200-1000
pH	4.5-7.5	6	6.6-7.5
Total hardness as $CaCO_3$	300-10000	3500	200-500
Calcium	200-3000	1000	100-400
Magnesium	50-1500	250	50-200
Potassium	200-1000	300	50-400
Sodium	200-2500	500	100-200
Chloride	200-3000	500	100-400
Sulfate	50-1000	300	20-50
Total iron	50-1200	60	20-200

[a] Except pH, which has no unit

[b] Representative range of values. Higher maximum values have been reported in the literature for some of the constituents

[c] Typical values for new landfills will vary with the metabolic state of the landfill

It is to be noted that the chemical composition of leachate will vary greatly depending on the age of landfill and the events preceding the time of sampling. For example, if a leachate sample is collected during the acid phase of decomposition (see Fig. 2.1), the pH value will be low and the concentration of BOD_5, TOC, COD, nutrients and heavy metals will be high. If, on the other hand, a leachate sample is collected during the methane fermentation phase (see Fig. 2.1), the pH will be in the range from 6.5-7.5, and the BOD_5, TOC, COD and nutrients concentration values will be significantly lower. Similarly, the concentrations of heavy metals will be lower because most metals are less soluble at neutral pH values. The pH of the leachate will depend not only on the concentration of the acids that are present but also on the partial pressure of the CO_2 in the landfill gas that is in contact with the leachate. The biodegradability of the leachate will vary with time. Changes in the biodegradability of the leachate can be monitored by checking the BOD_5/COD ratio. Initially, the ratios will be in the range of 0.5 or greater. Ratios in the range of 0.4 to 0.6 are taken as an indication that the organic matter in the leachate is readily biodegradable. In mature landfills, the BOD_5/COD ratio is often in the range of 0.05 to 0.2. The ratio drops because leachate from mature landfills typically contains humic and fulvic acids, which are not readily biodegradable (Tchobanoglous et al., 1993).

2.4 Leachate Treatment

Previous studies have confirmed the potential danger of landfill leachate (Pirbazari et al., 1996; Bernard et al., 1997; Sisinno et al., 2000; Marttinen et al., 2002; Silva et al., 2004) and the necessity to treat it so as to meet the discharge standards. Leachate treatment can be classified into five major groups – physicochemical treatment, advanced oxidation process treatment, biological treatment, combined physicochemical and biological treatment and combined advanced oxidation process and biological treatment.

2.4.1 Physicochemical Treatment

Amokrane et al. (1997) reported that the percentage of COD and TOC removal obtained by aluminium sulphate (alum) or ferric chloride coagulation was generally 10-25% with young leachates, but it was higher (50-60%) for stabilized leachate in acidic medium. Similarly, Tatsi et al. (2003) obtained a higher COD removal of 75% for partially stabilized leachate than for young leachate (25-38%). Ahn et al. (2002) investigated treatment of young landfill leachate using reverse osmosis. The results showed about 96-97% removal of COD and NH_3-N. A study on application of reverse osmosis and ultrafiltration for the treatment of a stabilized leachate was compared (Bohdziewicz et al., 2001). The results showed that reverse osmosis gave higher COD removal (97%) than ultrafiltration (52%). Morawe et al. (1995) studied the removal of organic compounds from a stabilized leachate using granular activated carbon (GAC). The results of the column study showed 91% COD removal with an initial concentration of 940 mg/L.

A laboratory-scale study on the treatment of young leachate from a landfill by using ammonium stripping for 12 h was carried out (Calli et al., 2005). About 94% NH_3-N removal was achieved by adding 11 g/L of lime. However, under the same conditions with air stripping, the COD removal was always less than 15%. The results suggest that the process was more effective for the removal of NH_3-N than for organics removal. A comparative study of the removal of NH_3-N from a stabilized leachate was undertaken by using GAC and/or limestone (Aziz et al., 2004). The results showed NH_3-N removal of about 40% with 42 g/L of GAC and 19% with 56 g/L of lime.

Nanofiltration using AFC-30 membrane was employed for the removal of heavy metals from a stabilized landfill leachate and more than 88% metal cations (Pb^{2+}, Zn^{2+} and Cd^{2+}) were removed (Linde and Jönsson, 1995). The treatment of a stabilized leachate using a combination of coagulation and nanofiltration (NF) using MPT-31 membrane with high negative charge was evaluated (Trebouet et al., 2001). The results showed COD and NH_3-N removal of 80 and 21%, respectively. Meier et al. (2002) reported that the combined treatment of NF and powder activated carbon

(PAC) adsorption was able to remove 97% COD with an initial concentration of 1450 mg/L. The results showed better removal compared to the other study carried out by Marttinen et al. (2002) that employed NF alone for removal of about 66% COD with initial concentration of 920 mg/L. Palaniandy et al. (2009) reported that coagulation using ferric chloride ($FeCl_3$) with a dosage of 650 mg/L, followed by dissolved air flotation (DAF) with 20 min retention time was capable of removing turbidity (66%), COD (74%) and colour (93%) of the mature leachate of the Pulau Burung landfill. Sole treatment using coagulation with higher dosage of $FeCl_3$ (1200 mg/L) of the same landfill leachate gave less removal of COD (51%) compared to the combined treatment system using coagulation-DAF (Aziz et al., 2007).

COD removal improved from 48% by using ferric chloride coagulation alone to 73% by using coagulation–Fenton reaction for the treatment of a mature leachate (Yoon et al., 1998). A study on the treatment of stabilized leachate was conducted by comparing coagulation-flocculation with the Fenton oxidation process in combination with GAC adsorption (Zamora et al., 2000). Fenton oxidation pretreatment was found more effective in improving the adsorption capacity of GAC for COD removal. Another study on the treatment of mature leachate was conducted by comparing the combination of coagulation using ferric chloride ($FeCl_3$) and photo-oxidation (UV–vis) and by UV–vis irradiation alone (Wang et al., 2002). This combined treatment was able to remove 64% COD. However, only 31% COD removal was achieved by UV–vis irradiation alone at the wavelength (λ) of 313 nm under the same COD concentration. Rivas et al. (2004) investigated combined sedimentation-chemical oxidation treatment of medium-stabilized landfill leachate with the results: pH adjustment-settling at pH 2 (COD removal $\approx$ 25%), coagulation–flocculation using Fe(III) (0.01 M) at pH 3.5 (COD removal $\approx$ 40% after pH adjustment-settling), Fenton oxidation (Fe(III) = 0.01 M and H_2O_2 = 1.0 M) (COD removal $\approx$ 80% after pH adjustment-settling) and coagulation–flocculation of Fenton's effluent at pH 3.5 (COD removal $\approx$ 90% after pH adjustment-settling). Kurniawan and Lo (2009) investigated the treatment performance of H_2O_2 oxidation, granular activated carbon (GAC) adsorption and combination of H_2O_2 with GAC adsorption for a landfill leachate with a very low biodegradability. The results showed the combined treatment substantially achieved a higher removal (COD 82%, NH_3-N 59%) than the H_2O_2

oxidation (COD 33%, NH_3-N 4.9%) and GAC adsorption (COD 58%). Moreover, the combined treatment significantly improved the biodegradability of the treated leachate from 0.08 to 0.36.

Physicochemical treatments are suitable as pretreatment of mature leachate for further treatment by biological process (Kargi and Pamukoglu, 2004). Physicochemical treatments for the landfill leachate are generally used as additional treatment (pretreatment or post treatment) or to treat a specific pollutant (stripping for ammonia).

2.4.2 Advanced Oxidation Process Treatment

Application of Fenton process on landfill leachate treatment was reported in the literature. COD removal efficiency ranged from 45% (Kim et al., 2001) to 85% (Roddy and Choi, 1999) depending on leachate characteristics and dosage of Fenton reagents. Lopez et al. (2004) investigated Fenton treatment for a raw landfill leachate with an initial COD of 10540 mg/L with the result of 60% COD removal. Zhang et al. (2006) investigated treatment of landfill leachate by Fenton process in a continuous stirred tank reactor and found that the optimum pH was 2.5 and the organic removal increased as H_2O_2/Fe^{2+} molar ratio increased up to 3.0. A study showed that Fenton process applied to landfill leachate treatment increased its biodegradability (Batarseh et al., 2007) and hence Fenton process can be employed for combined advanced oxidation process and biological treatment.

The application of photo-Fenton process for landfill leachate treatment has also been reported. Previous study showed that photo-Fenton was found to be the most efficient treatment among Fenton, Fenton-like and photo-Fenton processes with 78% of COD removal (Primo et al., 2008). Another study showed that the biodegradability of leachate increased from 0.13 to about 0.4 for both UV/H_2O_2 and photo-Fenton treatments (Morais and Zamora, 2005). Kim et al. (2001) investigated photo-Fenton treatment of a mature landfill leachate with reagent dosages 2438 mg/L H_2O_2 and 56 mg/L Fe^{2+} and achieved 70% COD removal. Kim and Vogelpohl (1998) reported that

H_2O_2/Fe^{2+} molar ratio of 26.2:1 and 35.0:1 to be the optimum for photo-Fenton and photo-Fenton-like processes, respectively.

The photocatalytic oxidation with UV/TiO_2 has seldom been investigated for landfill leachate so far. The data indicate that this process allows to remove up to 80% COD from biologically pretreated leachate with COD ranging from 100 to 500 mg/L (Bekbolet et al., 1996; Cho and Choi, 2002). Another study of heterogeneous photocatalysis by titanium oxide (TiO_2) was examined for the removal of COD, TOC and BOD from a biologically pretreated landfill leachate by anaerobic and aerobic processes (Cho et al., 2002). The authors found that the photocatalytic oxidation of COD and TOC had to be operated under the acidic conditions (especially pH 4) and decomposition rate of NH_3-N at alkaline pH was higher than that at acidic pH. A study on application of electro-Fenton for the treatment of stabilized leachate was conducted (Atmaca, 2009). At optimum operating conditions (pH 3.0, H_2O_2 2000 mg/L, duration 20 min and constant DC current 3A), removal of COD, colour, PO_4-P and NH_4-N were 72, 90, 87 and 28%, respectively.

However, it is noted that complete degradation of the pollutants in the treatment of large-scale effluents by AOPs is not economically feasible (Scott and Ollis, 1995; Karrer et al., 1997; Rivas et al., 2003; Koh et al., 2004). The combination with biological treatment would considerably decrease the overall treatment cost and ensure effective removal of undesirable contaminants.

2.4.3 Biological Treatment

Biological processes have been shown to be very effective in removing organic and nitrogenous matter from young landfill leachates.

There are numerous reports describing the effectiveness of the sequencing batch reactor (SBR) for the treatment of landfill leachate (Mace and Mata-Alvarez, 2002). Lo (1996) reached a removal efficiency of NH_3-N in excess of 99% by biological aerobic treatment with retention time of 20 and 40 days. A study by Diamadopoulos et al. (1997) using laboratory-scale SBR showed BOD and overall nitrogen removal of 95 and 50%, respectively and 99% removal of NO_3^--N during denitrification. A study on application of SBR of different modes, in terms of duration of phase, for the treatment of stabilized leachate containing high concentration of ammonia was conducted (Neczaj et al., 2008). The results showed the most effective mode was SBR with aeration time of 19 h and anoxic phase of 2 h with the removals of COD 98%, BOD 97% and TKN 79%. However, the removal efficiency decreased with increased organic loading or decreased HRT. In another study on feasibility of rotating biological contactor (RBC) and upward-flow anaerobic sludge bed (UASB) reactor for the treatment of a landfill leachate, RBC produced COD removal of 53% (retention time 24 h, angular speed 6 rpm), whereas UASB reactor produced COD removal of 62% (volumetric organic load 3273g-COD/m^3day, HRT 54 h) (Castillo et al., 2007). Bohdziewicz et al. (2008) investigated the feasibility of biological treatment of landfill leachate in anaerobic submerged membrane bioreactor (MBR). The results showed 90% COD removal (leachate percentage content 20%, organic loading 2.5 kg/m^3d, HRT 2 days). Tsilogeorgis et al. (2008) investigated biological treatment using membrane sequencing batch reactor (MSBR) for the treatment of mature leachate. The results showed COD removal ranged from 40 to 60%.

2.4.4 Combined Physicochemical and Biological Treatment

A study on application of GAC-nitrification for the treatment of stabilized leachate containing high concentration of ammonia was conducted (Horan et al., 1997). The results showed approximately 93% NH_3-N removal but only 55% COD removal, demonstrating that combined GAC-nitrification was not effective enough in removing recalcitrant organic compounds from the leachate. Pirbazari et al. (1996) investigated a combination of ultrafiltration (UF) and biological activated carbon for the treatment of young landfill leachate and reported 97% COD removal. Neczaj et al. (2005) subjected sonification (field frequency 20 kHz, amplitude 8-16 μm) pretreated leachate to biological treatment using sequencing batch reactor (SBR). The results showed ultrasonic pretreatment with amplitude of 12 μm achieved 90% and 70% COD and ammonia removal in SBR process with up to 25% leachate dilution. In a study on application of combined treatment of chemical precipitation with lime, air stripping of ammonia and aerobic biological treatment in an aeration tank by fed-batch operation for a landfill leachate, nearly 76% COD and 23% NH_4-N removals were obtained after 30 h of operation with a flow rate of 0.21 L/h (Kargi and Pamukoglu, 2003).

Another study on combined aerobic biological treatment and GAC adsorption was evaluated on a stabilized landfill leachate (Schwarzenbeck et al., 2004). The combined treatment was found to remove 65 and 97% of COD and NH_3-N, respectively.

Albers (1992) studied a combination of aerobic pretreatment, GAC adsorption and coagulation for the treatment of a stabilized landfill leachate and showed 92% of COD removal with an initial concentration of 1400 mg/L. A combined treatment consisting of activated sludge as a pretreatment followed by reverse osmosis was developed to treat a young leachate (Baumgarten and Seyfried, 1996). Almost complete removal of both COD and NH_3-N was achieved with initial concentrations of 6440 and 1153 mg/L, respectively. Jans et al. (1992) investigated a combination of an upflow anaerobic sludge blanket (UASB) reactor and reverse osmosis for the treatment of a stabilized landfill leachate. COD and NH_3-N were completely removed from the leachate with initial concentrations of 35000 and 1600 mg/L, respectively.

2.4.5 Combined Advanced Oxidation Process and Biological Treatment

Using AOP as physico-chemical pretreatment for recalcitrant wastewater is important to enhance the biodegradability and produce a new effluent which can be treated biologically (Sarria et al., 2002). Morais and Zamora (2005) subjected raw and UV/H_2O_2 (H_2O_2 3000 mg/L) or photo-Fenton (H_2O_2 2000 mg/L and Fe^{2+} 10 mg/L) pretreated leachate to biological treatment using sequencing batch reactor (SBR). They achieved a maximum COD removal of about 30% for the raw mature leachate and more than 90% for the pretreated leachate at the end of the 72-h cycle. Koh et al. (2004) successfully combined UV/H_2O_2 oxidation and activated sludge process for treatment of a biologically pretreated leachate. This combined treatment effectively removed COD and BOD – effluent COD <200 mg/L and 98% reduction of BOD. Guo et al. (2010) studied treatment of landfill leachate using combined stripping, Fenton, SBR and coagulation process. Air stripping removed 96.6% NH_3-N. Fenton process (pH 3.0, $FeSO_4 \cdot 7H_2O$ 20 g/L and H_2O_2 20 mL/L) produced COD removal of 61% and biodegradability increased from 0.18 to 0.38. Up to 82.8% BOD_5 removal and 83.1% COD removal were achieved in the SBR (aeration 20 h). Ferrous sulphate coagulation (800 mg/L at pH 5) of the SBR effluent reduced COD to 280 mg/L. Lin and Chang (2000) investigated the combined treatment performance of chemical coagulation by polyaluminum chloride (PAC) and polymer, electro-Fenton oxidation and SBR (leachate:sewage = 1:3, 12-h cycle) for a mature landfill leachate with a very low biodegradability. The results showed that chemical coagulation produced good COD and colour removal of over 50% (PAC/polymer ratio of 100:1, pH $\approx$ 5), and electro-Fenton oxidation reduced COD to around 300 mg/L, produced 100% colour removal and biodegradability increased from 0.1 to 0.29, and the treated effluent after SBR met the permissible discharge standards.

2.4.6 Summary of Leachate Treatment

Leachate treatment which can be classified into five major groups – physicochemical treatment, advanced oxidation process treatment, biological treatment, combined physicochemical and biological treatment and combined advanced oxidation process and biological treatment were discussed in the previous section. The strengths and the weaknesses of each of the treatment process were summarized in Table 2.5.

Table 2.5 Treatment Process and its Strengths and Weaknesses

Treatment Process	Strength	Weakness	Reference
Coagulation	Applicable for mature landfill leachate (50-60% COD removal)	Not applicable for young landfill leachate (10-25 % COD removal)	Amokrane et al., 2007; Aziz et al. (2007)
Reverse Osmosis	High removal on COD and NH_3-N (96-97%)	Costly and need extensive pretreatment	Ahn et al., 2002; Tchobanoglous et al., 1993
Ammonium Stripping	94% NH_3-N removal was achieved with 11 g/L of lime	Not effective for the removal of recalcitrant organic compounds (COD removal less than 15%)	Calli et al., 2005; Kurniawan et al., 2006
Nanofiltration	Effective in removing heavy metals (88% for the removal of Pb^{2+}, Zn^{2+} and Cd^{2+}) using AFC-30 membrane, and 66% of COD removal	Useful only as a polishing step	Linde and Jönsson, 1995; Marttinen et al., 2002
Advanced oxidation process (AOP)	Can achieved 45-85% of COD removal and increase the biodegradability of a mature landfill leachate to 0.3-0.6	Not economically feasible for large-scale effluents	Kim et al., 2001; Roddy and Choi, 1999; Scott and Ollis, 1995; Rivas et al., 2003
Sequencing batch reactor (SBR)	Effective in removing organic and nitrogenous matter (BOD removal 95% and nitrogen removal 50%)	High volume of sludge production which requires handling, treatment and disposal	Diamadopoulos et al., 1997

Combinations of two or more treatments have been proved to be more efficient and effective than individual treatment in improving the effluent quality. This could be due to the fact that a two or more-step treatment has the ability to synergize the advantages of individual treatments, while overcoming their respective limitations. It has been proved in the section 2.4.4 and 2.4.5. Recalcitrant organics which contained in mature landfill leachates, are not amenable to conventional biological processes and the high ammonia content might also be inhibitory to microorganisms (Li et al., 1999). As to encounter these problems, advanced oxidation processes (AOPs) have been used as effective alternative treatment for mineralization of recalcitrant wastewater organics and biodegradability improvement. Biological processes are effective for removal of biodegradable organics and nitrogenous matter from wastewater. Presumably, an effective treatment system for mature landfill leachate containing recalcitrant organics is a combination of AOP with a biological process.

2.5 Pulau Burung Landfill

Idaman Bersih Sdn Bhd (IBSB) started operation at the Pulau Burung landfill on 1 July 2001. Pulau Burung landfill (PBL) is located in Mukim II of the Seberang Perai Southern District, Penang. Fig. 2.3 shows the location of the landfill. The sanitary landfill is located in Pulau Burung as well as in the Byram Forest Reserve of Penang State. It covers a total area of 58.35 ha of which 29.28 ha is located in Pulau Burung while the remaining 29.07 ha is located in the adjacent Acacia Mangium plantation of the Byram Forest Reserve (Ranhill, 1994). PBL has a semi-aerobic system and it is one of the only three sites of its kind found in Malaysia. The landfill has been developed semi-aerobically into a sanitary landfill Level II by establishing a controlled tipping technique in 1991. It was further upgraded to a sanitary landfill Level III employing controlled tipping with leachate recirculation in 2001. The landfill receives 1500 tonnes of solid waste per day (Aziz et al., 2004) and the landfill is shown in Fig. 2.4. Table 2.6 shows the characteristics of the raw leachate. From the table, it shows that the PBL leachate is a mature leachate as the BOD_5/COD ratio is low with high concentration of NH_3-N.

Fig. 2.3 Location of Pulau Burung Landfill

Fig. 2.4 Pulau Burung Landfill

Table 2.6 Characteristics of Raw Leachate from Pulau Burung Landfill (Yahaya, 2009)

Parameter	Unit	Min	Max	Average
Temperature	ºC	28	30	30.00
BOD_5	mg/L	8	1020	209
COD	mg/L	879	3363	1800
BOD/COD	-	0.01	0.33	0.11
Suspended solids	mg/L	45	695	174.90
pH	-	7.38	8.78	8.09
Ammonia-nitrogen	mg/L	54	1426	726
Arsenic	mg/L	0.1	0.1	0.10
Cadmium	mg/L	0.02	0.05	0.03
Lead	mg/L	0.02	1.6	0.29
Mercury	mg/L	0.01	0.02	0.01
Copper	mg/L	0.06	0.8	0.25
Manganese	mg/L	0.2	1.2	0.81
Chromium (VI)	mg/L	0.07	0.07	0.07
Chromium (III)	mg/L	0.05	0.4	0.13
Nickel	mg/L	0.1	0.4	0.20
Tin	mg/L	0.1	0.4	0.15
Zinc	mg/L	0.1	3.7	0.79
Boron	mg/L	0.6	7.7	3.58
Iron	mg/L	0.07	9.5	5.31
Phenol	mg/L	0.01	6.8	0.53
Sulphide	mg/L	0.1	2.8	1.45
Oil & grease	mg/L	1	41	10.65

2.5.1 Pulau Burung Landfill Leachate Treatment

PBL leachate treatment system comprises of physicochemical methods – coagulation-flocculation-sedimentation, zeolite filtration and activated carbon filtration (Fig. 2.5). The characteristics of the treated leachate after each treatment unit are shown in Table 2.7. The treated effluent from PBL has high COD and TSS and it did not meet the Malaysian discharge standard (B) (COD 100 mg/L and suspended solids 100 mg/L), indicating that the treatment system did not successfully degrade the organic contaminants. Previous studies show that mature landfill leachate contains recalcitrant organics and must involve a combination of advanced oxidation process (AOP) and biological treatment for complete treatment. The efficiency of combined AOP-biological treatment system has been proved higher than merely combined physicochemical treatment system.

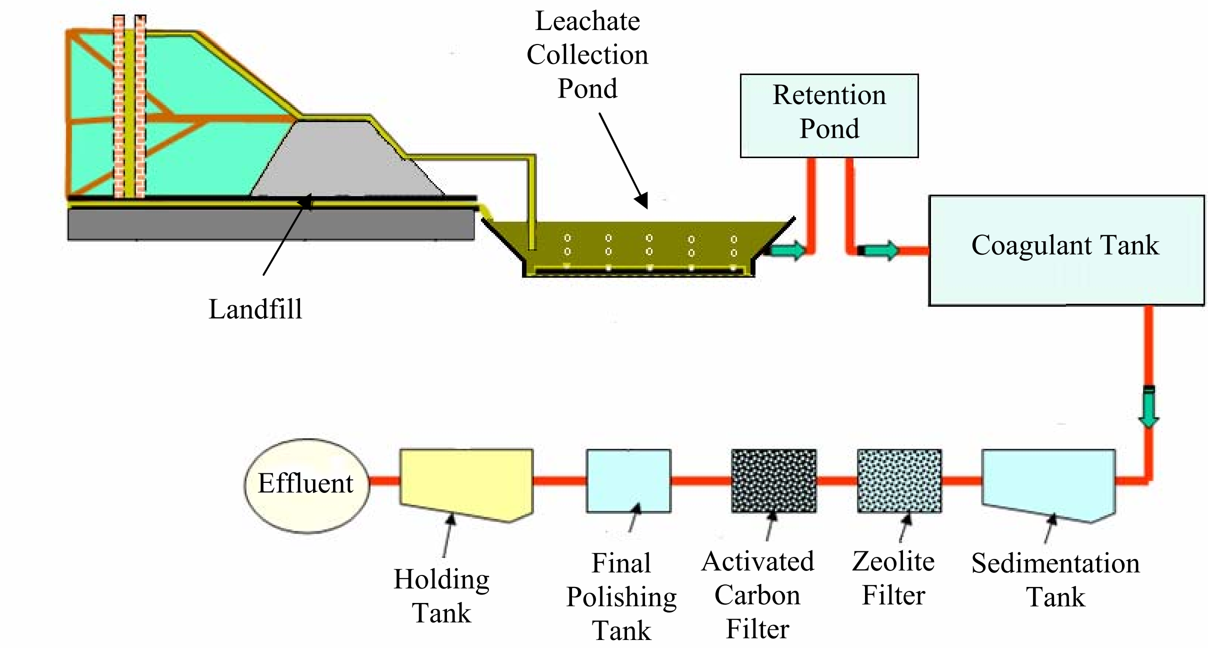

Fig. 2.5 Schematic View of Treatment System in Pulau Burung Landfill (adapted from Yahaya, 2009)

Table 2.7 Characteristics of Treated Leachate after Treatment unit at Pulau Burung Landfill (Yahaya, 2009)

Parameter	Treatment Unit						
	Retention Pond	Coagulant Tank	Sedimentation Tank	Zeolite Filter	Activated Carbon Filter	Final Polishing Tank	Holding Tank
pH	8.14	8.01	7.9	7.69	7.6	7.64	6.1
BOD	138	405	180	90	56	5	36
COD	3813	3365	1813	1250	1021	842	573
Suspended solids	90	385	104	17	98	71	174
Oil and grease	9	13	6	12	2	1	5
Ammonia-nitrogen	2323	2254.6	1052.1	444.1	334.5	327.9	67.5
Mercury	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium	<0.01	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Chromium (VI)	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Arsenic	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cyanide	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
Lead	0.10	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chromium (III)	0.13	0.16	<0.05	<0.05	<0.05	<0.05	<0.05
Copper	0.40	0.2	0.1	<0.1	0.1	<0.1	<0.1
Manganese	0.2	0.1	0.2	0.2	0.4	0.3	0.2

Table 2.7 Characteristics of Treated Leachate after Treatment unit at Pulau Burung Landfill (continued)

Parameter	Treatment Unit						
	Retention Pond	Coagulant Tank	Sedimentation Tank	Zeolite Filter	Activated Carbon Filter	Final Polishing Tank	Holding Tank
Nickel	0.2	0.2	0.1	0.1	<0.1	<0.1	<0.1
Tin	0.2	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
Zinc	0.9	0.7	0.1	<0.1	0.1	<0.1	0.1
Boron	8.6	9.5	4.8	3.6	2.5	3.5	2
Iron	3.8	2.9	0.8	0.2	0.6	0.1	0.2
Phenol	0.2	0.28	0.14	0.09	0.03	<0.01	0.01
Free chlorine	-	-	<0.1	0.9	<0.1	<0.1	0.2
Sulphide	0.2	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
Nitrate	83.6	112.2	40.7	59.8	59.4	138.4	1962.4
Phosphorus	38.2	31.6	5.9	1.9	0.7	0.3	0.2

2.6 Advanced Oxidation Processes (AOPs)

Chemical oxidation is a widely studied method for the treatment of effluent containing recalcitrant compounds such as landfill leachate. Growing interest has been focused on advanced oxidation processes (AOPs). AOPs are defined by Glaze et al., (1987) as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals in sufficient quantity to effect water purification. These processes generate hydroxyl radicals which have a very high oxidation potential to oxidize almost all organic pollutants (Legrini et al., 1993; Andreozzi et al., 1999). In many cases, chemical oxidation is employed as a pretreatment to decompose recalcitrant organic substances and subsequently enhance the biodegradability of the wastewater (Kurniawan et al., 2006; Koh et al., 2004). Most of them, except simple ozonation (O_3), use a combination of strong oxidants, e.g. O_3 and H_2O_2, irradiation, e.g. ultraviolet (UV), ultrasound (US) or electron beam (EB), and catalysts, e.g. transition metal ions or photocatalyst. Table 2.8 lists typical AOP systems (Huang et al., 1993). All these processes have been recently reviewed by Wang et al. (2003) and confirmed that AOP, adapted to old or mature leachate, are applied to:

a) oxidize organics substances to their highest stable oxidation states to carbon dioxide and water (i.e., to reach complete mineralization),

b) improve the biodegradability of recalcitrant organic pollutants up to a value compatible with subsequent economical biological treatment.

Table 2.8 Typical AOP Systems (Huang et al., 1993)

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

However, common drawbacks of AOPs are the high demand of electrical energy for devices such as ozonizers, UV lamps and ultrasounds, which results in rather high treatment costs (Lopez et al., 2004). Besides, for complete degradation (mineralization) of the pollutants to occur, high oxidant doses would be required, rendering the process economically expensive.

Normally the wastewater that has COD value below (≤10 g/L) can be treated with these processes, but if the COD is higher, the requirement of the reagents increases, with negative effect on treatment cost (Andreozzi et al., 1999). Among these processes, Fenton process seems to be the best compromise because the process is technologically simple, there is no mass transfer limitation (homogeneous nature) and both iron and hydrogen peroxide are cheap and non-toxic (Lopez et al., 2004). Fenton and photo-Fenton processes are described as below.

2.6.1 Fenton Process

The Fenton reaction (Eq. 2.1) was first reported by Fenton (1894). The mixture of ferrous salt and hydrogen peroxide is called the Fenton reagent. In Fenton process, Fenton reagent is added to wastewater, generating species that are strongly oxidative with respect to organic compounds present and it degrades recalcitrant and toxic organic compounds and increases biodegradability. Hydroxyl radicals ($^{\bullet}OH$) are traditionally regarded as the key oxidizing species in the Fenton processes (Barb et al., 1951; Yamazaki and Piette, 1991), though high valence iron species and alkoxyl radicals ($RO^{\bullet}$) have also been proposed (Sheldon and Kochi, 1980; Rahhal and Richter, 1988; Bossmann et al., 1998; Buda et al., 2001). The classical Fenton free radical mechanism in the absence of organic compounds mainly involves the sequence of reactions below (Deng and Englehardt, 2006).

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

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO^{\bullet}_2 + H^+ \quad (2.2)$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow HO^{\bullet}_2 + H_2O \quad (2.3)$$

$${}^{\bullet}OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \quad (2.4)$$

$$Fe^{3+} + HO^{\bullet}_2 \longrightarrow Fe^{2+} + O_2 + H^+ \quad (2.5)$$

$$Fe^{2+} + HO^{\bullet}_2 + H^+ \longrightarrow Fe^{3+} + H_2O_2 \quad (2.6)$$

$$2HO^{\bullet}_2 \longrightarrow H_2O_2 + O_2 \quad (2.7)$$

Hydroxyl radicals are rapidly generated through Eq. 2.1. In the above reactions, iron cycles between Fe^{2+} and Fe^{3+}, and plays the role of catalyst. The net reaction of Eq. 2.1–2.7 is the decomposition of H_2O_2 into water and O_2 catalyzed by iron.

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (2.8)$$

Although Fe^{3+} can be reduced to Fe^{2+} through Eq. 2.2, the rate is several orders of magnitude slower than that of Fe^{2+}-Fe^{3+} conversion through Eq. 2.1. Generated Fe^{3+} can be reduced with exceeding H_2O_2 to form Fe^{2+} and more radicals. This process is known as Fenton-like and it is slower than Fenton reaction (Sychev and Isaak, 1995). And the formed Fe^{3+} may precipitate to iron oxyhydroxides, particularly as pH is increased. Consequently, the undesirable iron sludge is generated, which needs proper treatment and disposal in application. In the presence of organic compounds, hydroxyl radicals can attack organics by four pathways: radical addition, hydrogen abstraction, electron transfer and radical combination (SES, 1994). Reported final BOD_5/COD ratio increased from less than 0.10 to values ranging from 0.14 to more than 0.60 (Kim et al., 1997; Lau et al., 2002). However, it should be emphasized that final BOD_5/COD ratio cannot be increased to more than 0.50 in some cases, depending on leachate characteristic and dosages of Fenton reagents (Deng and Englehardt, 2006). The three main factors affecting the Fenton process are described.

2.6.1.1 Effect of pH

Fenton process has a typically preferred pH region in which it is in the acidic range strongly favours oxidation. pH affects the activity of both the oxidant and the substrate, the speciation of iron, hydrogen peroxide decomposition and the hydroxyl radical ($^{\bullet}OH$) production (Solozhenko et al., 1995; Kochany and Lugowski, 1998; Tekin, et al., 2006). Optimal pH value reported for Fenton process for landfill leachate treatment ranges between 2.0 and 3.5 (Kim et al., 2001; Roddy and Choi, 1999; Kim and Huh, 1997). For low pH, the degradation process will become less. This may be due to the formation of complex species $\{Fe(H_2O)_6\}^{2+}$ at pH 1-2, which reacts more slowly with hydrogen peroxide, producing less $^{\bullet}OH$ compared to $\{Fe(OH)(H_2O)_5\}^{2+}$ formed at pH 2-3. In addition, hydrogen peroxide gets solvated in presence of high concentration of hydrogen ion (H^+) to form stable oxonium ion ($H_3O_2^+$). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and reduces substantially its reactivity with Fe^{2+} ion (Kwon et al., 1999). Moreover, at exceptionally low pH can inhibit reaction between Fe^{3+} and H_2O_2, reducing the generation rate of $^{\bullet}OH$ (Pignatello, 1992). On the other hand, at higher pH, it may hindered the generation of hydroxyl radical ($^{\bullet}OH$) because of the formation of the ferric hydroxo complexes, which subsequently form $Fe(OH)_4^-$ (Kochany and Lugowski, 1998). Sedlak and Andren (1991) explained higher hydroxyl radical product yields in the pH range of 2-4 by a reaction involving the organometallic complex where either hydrogen peroxide is regenerated or reaction rates are increased. Literature reported optimal pH for Fenton treated leachate was at 2.0-3.0 (Roddy and Choi, 1999), 2.5 (Gulsen and Turan, 2004; Zhang et al., 2005), 3.0 (Roddy and Choi, 1999; Kim et al., 2001) and 3.5 (Kim and Huh, 1997; Kang and Hwang, 2000).

2.6.1.2 Effect of H_2O_2 Concentration

Generally, percentage of COD removal increases with increasing of H_2O_2 concentration in Fenton process (Kang and Hwang, 2000; Gulkaya et al. 2006). This may be due to the fact that increased amount of H_2O_2 reacts with more $FeSO_4$ and produces more amount of hydroxyl radical leading to more waste degradation. However, excess H_2O_2 results in iron sludge flotation due to O_2 off-gassing caused by auto-decomposition of excess H_2O_2 (Kim et al., 2001; Lau et al., 2001) and residual H_2O_2 may inhibit downstream biological treatment. Previous studies showed that the optimum H_2O_2/COD molar ratio was ranging from 1.5 to 3.0 (Kim and Vogelpohl, 1998; Deng and Englehardt, 2006; Kurniawan et al., 2006).

2.6.1.3 Effect of $FeSO_4$ Concentration

A similar trend is observed for H_2O_2 as removal of organics increases with increasing concentration of iron salt (Fe^{2+}). Higher ferrous concentration causes generation of more hydroxyl ($^{\bullet}OH$) radicals and hence accelerate the redox reaction. Ferrous ion (Fe^{2+}) which converts into ferric ion (Fe^{3+}) as shown in Eq. 2.1 and 2.6, act as a coagulant resulting in improving the COD reduction. In addition, the Fe^{3+} formed can react with H_2O_2 (Eq. 2.2) to generate Fe^{2+} and hydroperoxyl radicals ($HO^{\bullet}_2$) in the reaction medium. The oxidation capacity of $HO^{\bullet}_2$ is less compared to $^{\bullet}OH$, which affects overall COD reduction. However, excess iron salt will destroy the hydroxyl radical ($^{\bullet}OH$) produced (Pignatello et al., 2006) and contributes to an increase of the amount of iron sludge that requires treatment (Gogate and Pandit, 2004). Kim and Huh (1997) found an optimal molar ratio of H_2O_2/Fe^{2+} was 12.5 in batch tests. Another literature showed an optimum molar ratio of H_2O_2/Fe^{2+} was 20 for treatment of a raw leachate in batch tests (Lopez et al., 2004).

2.6.2 Photo-Fenton Process

The principle of the photochemical reaction is the addition of energy for the chemical compound in the form of radiation, which is absorbed by the group of molecules to reach an excited state. In photo-Fenton process, it is a reaction between Fenton reagent, i.e. ferrous salt and hydrogen peroxide, irradiated with UV light. Photo-Fenton is known to be able to improve the efficiency of the dark Fenton reagent by means of the interaction of radiation with the Fenton reagent (Hislop and Bolton, 1999). Hydroxyl radicals ($^{\bullet}OH$) are produced by the decomposition of hydrogen peroxide when reacting with ferrous ions in presence of UV light, which contributes an additional pathway to the generation of free radicals, increasing the concentration of $^{\bullet}OH$ radicals (Benitez et al., 2000).

During the reaction, Fe^{3+} ions accumulate in the system and after Fe^{2+} are consumed, the reaction practically stops. Photochemical regeneration (Eq. 2.9) of Fe^{2+} ions by photo-reduction of Fe^{3+} ions was proposed (Huston and Pignatello, 1999). The newly generated ferrous ion reacts with H_2O_2 generating a second $^{\bullet}OH$ radical and Fe^{3+} and the cycle continues. Thus, it can be used to enhance reduction of Fe^{3+} to Fe^{2+}, and initiate production of $^{\bullet}OH$ radicals through photolysis, so that less Fe^{2+} is required (Deng and Englehardt, 2006).

$$Fe^{3+} + H_2O + hv \longrightarrow {}^{\bullet}OH + Fe^{2+} + H^+ \qquad (2.9)$$

The photo-Fenton process is affected by several factors and are described below.

2.6.2.1 Effect of pH

At pH around 3, highly soluble $Fe(OH)^{2+}$ is the predominant ferric hydroxide complex as opposed to free Fe^{3+}, $Fe(OH)_2^{+}$, and $Fe_2(OH)_2^{4+}$, which are less photoreactive (Faust and Hoigne, 1990). However, amorphous iron oxyhydroxide sludge that may accumulate at pH above 5 prevents the transmission of UV light through the reactor (Kim et al., 1997; Kim and Vogelpohl, 1998). Literature reported optimal pH for photo-Fenton treatment of leachate is 3.0 (Kim et al., 1997; Kim and Vogelpohl, 1998) and 3.0-4.0 (Lau et al., 2002).

2.6.2.2 Effect of H_2O_2 Concentration

COD removal increases with increasing of H_2O_2 concentration as in Fenton process and H_2O_2 dosage depends heavily on initial COD. Generally leachate with high initial COD requires more H_2O_2.

2.6.2.3 Effect of $FeSO_4$ Concentration

The photo-Fenton process can be used to enhance reduction of Fe^{3+} to Fe^{2+}, and initiate production of $^{\bullet}OH$ through photolysis, so that less Fe^{2+} is required. As a result, a higher molar ratio of H_2O_2/Fe^{2+} is employed. The literature showed optimum H_2O_2/Fe^{2+} molar ratio ranging from 7.5 to 26.2 (Kim and Vogelpohl, 1998; Primo et al., 2008).

2.6.2.4 Effect of UV Irradiation

Photolysis occurs when chemical substances absorb light. H_2O_2 is known have maximum absorbance at 210-230 nm and H_2O_2 proteolysis takes place to small extent at wavelength 365 nm (Pignatello et al., 1999). Iron photo-redox also takes place under wavelength $\approx$ 365 nm (Al Momani, 2006). Consequently, degradation of the organic pollutants in leachate samples was found to be the most effective under UV irradiation of wavelength $\approx$ 365 nm when subjected to photo-Fenton.

2.7 Sequencing Batch Reactor (SBR)

Sequencing batch reactor (SBR) is the name given to a wastewater treatment system based on the activated sludge process, operated on a sequence of fill and draw cycles. The reactor acts as a biological reactor and settling tank at various stages of the treatment cycle. The unit operations involved in a SBR is equivalent to those in a conventional activated sludge process. The difference between the systems is that in conventional systems aeration and sedimentation-clarification occur in two different tanks, whereas in SBR, they occur sequentially in the same tank. The SBR process operates on a fill and draw batch system and the process can be divided into five operating steps (Buitron et al., 2001).

a) Step 1: Filling

   The SBR tank is filled with the influent wastewater. In order to maintain suitable F/M (food to microorganism) ratio, the wastewater should be admitted into the tank in a rapid, controller manner. This method functions similarly to a selector, which encourages the growth of certain microorganisms with better settling characteristics.

b) Step 2: Reaction

   During this stage, the aeration period and the sludge mass determines the degree of treatment. The aeration period depends on the strength of the wastewater and the degree of nitrification (conversion of the ammonia to a less toxic form of nitrite or nitrate) in the treatment.

c) Step 3: Settling

   Aeration is stopped and the sludge settles leaving the treated effluent above the sludge blanket. Duration of settling varies from 45 to 60 minutes depending on cycles per day.

d) Step 4: Decanting

   The effluent is removed from the tank without disturbing the settled sludge.

e) Step 5: Idle

   The SBR tank is idle until a batch accumulates and it starts a new cycle again with the filling stage.

In general, this process contains primary sedimentation, biodegradation and secondary sedimentation, as well as nitrogen and phosphorus removal within a single reactor. SBR offers significant advantages as compared to continuous process and includes high degree of process flexibility in terms of cycle time and sequencing, and the ability to incorporate aerobic and anoxic phases in a single reactor (Im et al., 2001).

2.8 Response Surface Methodology (RSM)

Traditionally, optimization in analytical process has been carried out by monitoring the influence of one factor at a time on an experimental response. While only one parameter is changed, others are kept at a constant level. This optimization technique is called one-variable-at-a-time. Its major disadvantage is that it does not include the interactive effects among the variables studied. As a consequence, this technique does not depict the complete effects of the parameter on the response (Lundstedt et al., 1998). Another disadvantage is the increase in the number of experiments necessary to conduct the research, which leads to an increase of time and expenses as well as an increase in the consumption of reagents and materials. In order to overcome this problem, the optimization of analytical procedures is carried out by using multivariate statistical techniques. Among the most relevant multivariate techniques used in analytical optimization is response surface methodology (RSM). Response surface methodology is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data, which must describe the behavior of a data set with the objective of making statistical previsions. It can be well applied when a response or a set of responses of interest are influenced by several variables (Bezerra et al., 2008). Hence, RSM is a technique for designing experiment and it helps researchers to build models, evaluate the effect of several factors and achieve the optimum conditions for desirable responses in addition to reduce the number of experiments (Khuri and Cornell, 1996). The objective is to simultaneously optimize the levels of these variables to attain the best system performance.

RSM comprises of a group of mathematical and statistical techniques based on the fit of empirical models to the experimental data obtained in relation to experimental design. Relevant stages in the application of RSM as an optimization technique are as follows (Bezerra et al., 2008):

a) the selection of independent variables of major effects on the system through screening studies and the delimitation of the experimental region, according to the objective of the study and the experience of the researcher;

b) the choice of the experimental design and carrying out the experiments according to the selected experimental matrix;

c) the mathematic–statistical treatment of the obtained experimental data through the fit of a polynomial function;

d) the evaluation of the model’s fitness;

e) the verification of the necessity and possibility of performing a displacement in direction to the optimal region; and

f) obtaining the optimum values for each studied variable.

The visualization of the predicted model equation can be obtained by the surface response plot as shown in Fig. 2.6. It is possible to find the optimum region through visual inspection of the surfaces.

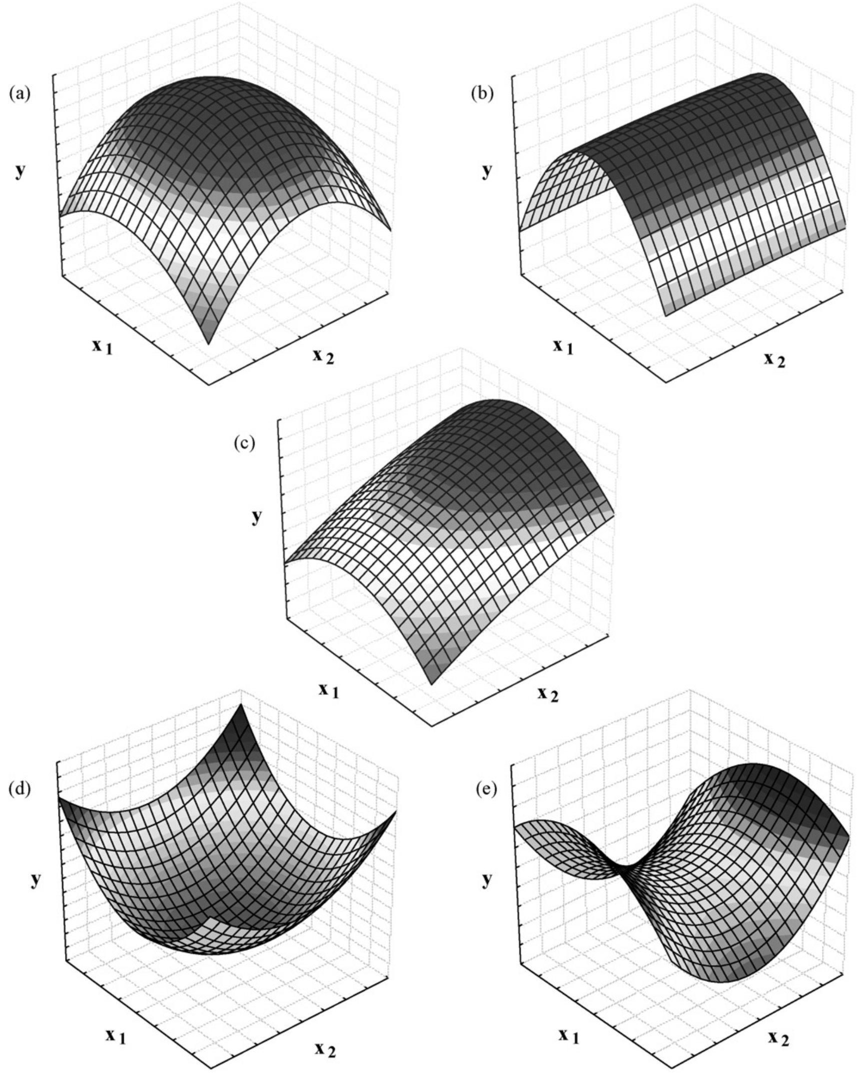

Fig. 2.6 Some Profiles of Surface Response Generated from a Quadratic Model in the Optimization of Two Variables (a) Maximum, (b) Plateau, (c) Maximum Outside the Experimental Region, (d) Minimum, and (e) Saddle Surfaces (Bezerra et al., 2008)

Central composite design (CCD) is used for the RSM in the experimental design for fitting a quadratic surface for process optimization. The central composite design is still the symmetrical second order experimental design most utilized for the development of analytical procedures.

RSM has been applied in numerous studies to optimize the photo-Fenton process (Sarasa et al., 2006; Rozas et al., 2010) and application of RSM on electro-Fenton technique for landfill leachate were reported in the literature (Mohajeri et al., 2010), indicating that RSM is an effective tool for optimization of advanced oxidation processes (Fenton and photo-Fenton) treatment of landfill leachate.

2.9 Chapter Summary and Significance of the Study

In this chapter, landfill, landfill leachate, and its generation and composition are discussed. Five major groups of leachate treatment and its application from previous studies are summarized. Typical examples of two landfills in Malaysia – Pulau Burung landfill (PBL) and Bukit Tagar landfill (BTL), and their leachate treatment are included. Basic concept of Fenton and photo-Fenton processes, operation of sequencing batch reactor (SBR) and response surface methodology (RSM) are also discussed.

The treatment system in both landfills appears to be incomplete, especially the effluent from PBL far exceeds the permissible discharge standards. Previous studies show that mature landfill leachate contains recalcitrant organics and must involve a combination of advanced oxidation process (AOP) and biological treatment for complete treatment. Combined treatment has been proved to be more efficient and effective than individual treatment in improving the effluent quality. Generally, AOPs are used to degrade recalcitrant organics and enhance the biodegradability. Subsequently, biological processes are applied and are very effective in removing organics and nitrogenous matter. Thus, development of a combined AOP-biological process treatment system for landfill leachate assumes significance.

CHAPTER 3

METHODOLOGY

3.0 Chapter Overview

The study was aimed to develop a complete AOP-SBR treatment system for landfill leachate through laboratory experimentation. The following sections describe the leachate sample, analytical methods, experimental procedure and data analysis.

3.1 Leachate Sample

Leachate sample was collected from the Pulau Burung landfill (PBL) located in Nibong Tebal, Penang. Raw leachate was collected from the influent end of the leachate collection pond near the entrance of the landfill (Fig. 3.1) and stored in a cold room in the laboratory at $4^{o}C$ to minimize biological and chemical reactions. The raw leachate was mixed and settled for 2 h as the same operation mode in PBL. The raw leachate was in detention for 2 h before it discharges from the retention pond to the coagulant tank. The purpose of settling the raw leachate is similar to the pre-sedimentation process as to remove the colloidal and suspended matters. Characteristics of the raw and settled (2 h) leachate are presented in Table 3.1.

Fig. 3.1 Pulau Burung Landfill Leachate Collection Pond

Table 3.1 Characteristics of PBL Leachate

Parameter	Unit	Raw	Settled
pH	-	8.4-8.7	8.0-8.8
Colour	Pt-Co	2160-2560	1950-2180
Turbidity	NTU	308-314	208-256
BOD_5	mg/L	83-144	-
COD	mg/L	1960-2880	1350-2740
Total solids	mg/L	6410-6625	-
Total suspended solids	mg/L	175-198	98-122
Total dissolved solids	mg/L	6232-6427	-
Total phosphorus	mg/L	143-168	-
Ammonia-nitrogen	mg/L	730-980	630-878

3.2 Analytical Methods

3.2.1 pH

pH measurement was performed using a pH meter (HACH sension 4, USA) and a pH probe (HACH platinum series pH electrode model 51910, HACH company, USA). The pH meter was calibrated with pH 4.0, 7.0 and 10.0 buffers.

3.2.2 Turbidity

Turbidity was measured by a turbidity meter and reported in nephelometric turbidity unit (NTU).

3.2.3 Colour

Colour was reported as true colour (filtered through 0.45 μm membrane filter) assayed at 455 nm using a HACH spectrophotometer DR 2000 according to Method 2120 C, Standard Methods (APHA, 2005). Colour was reported in Platinum-cobalt (Pt-Co) Units.

3.2.4 Five-Day Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD)

Five-day biochemical oxygen demand (BOD_5) was measured according to Method 5210 B 5-day BOD Test, Standard Methods (APHA, 2005). Dissolved oxygen (DO) was measured using a YSI 5000 dissolved oxygen meter. The bacterial seed for BOD_5 test was obtained from a municipal wastewater treatment plant. Chemical oxygen demand (COD) was measured by the Reactor Digestion HACH Method No. 8000 (HACH, 2003). Low range COD digestion reagent vials were used for this purpose. Colorimetric determination of COD was carried out at 620 nm using a spectrophotometer (HACH DR 2000, USA).

3.2.5 Solids

Solids (total solids, total suspended solids (TSS) and total dissolved solids) were measured according to the Standard Methods (APHA, 2005). Mixed liquor suspended solids (MLSS) was measured by the TSS method.

3.2.6 Ammonia-Nitrogen (NH_3-N), Nitrate-Nitrogen (NO_3^--N) and Total Phosphorus (TP)

Ammonia-nitrogen (NH_3-N) was measured by Nessler Method (Method 8038), nitrate-nitrogen (NO_3^--N) was measured by Cadmium Reduction Method (Medium Range) using HACH Powder Pillow and total Phosphorus (TP) was measured by PhosVer 3 (Ascorbic Acid) Method using HACH Powder Pillow according to HACH Handbook (HACH, 2003).

3.2.7 Total Kjeldahl Nitrogen (TKN)

The macro-Kjeldahl method was used to measure total Kjeldahl nitrogen (TKN) according to Method 4500-N_{org} B Macro-Kjeldahl Method, Standard Methods (APHA, 2005). For digestion, Buchi K-424 Digestion Unit and Buchi B-414 Scrubber Unit were used, whereas for distillation, Buchi K-314 Distillation Unit was used. Selenium catalyst tablets were used in TKN measurement. For ammonia-nitrogen measurement, Method 4500 C Titrimetric Method, Standard Methods (APHA, 2005) was used. Titration was performed using a properly calibrated auto titration unit (Metrohm 702 SM Titrino) at room temperature.

3.3 Experimental Procedure

3.3.1 Preliminary Treatment

The pH adjustment-settling was performed using 250 mL of the leachate sample. The leachate sample was mixed and settled for 2 h, and subjected to pH 2.5, 3, 3.5, 4, 4.5 and 5 using sulphuric acid and mixed for 15 min using a magnetic stirrer. The pH was tested every 5 min using a pH meter. When the pH became constant, the sample was settled for 1 h. Supernatant samples were taken for measurement of COD, TSS, turbidity and colour.

3.3.2 Fenton Pretreatment

Fenton treatment was performed in a 500-mL Pyrex reactor using 250 mL of the preliminary treated leachate. Ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and hydrogen peroxide (H_2O_2) were added according to the selected H_2O_2/COD molar ratio and Fe^{2+}/H_2O_2 molar ratio simultaneously. The mixture was stirred continuously to ensure complete homogeneity during reaction. Aliquots were taken at selected reaction time, adjusted to pH above 10 with sodium hydroxide and mixed for 10 min to reduce interference by H_2O_2 in COD determination (Kuo, 1992; Talinli and Anderson, 1992; Kang et al., 1999; Arslan-Alaton et al., 2004; Andreozzi et al., 2005) and settled overnight for measurement of COD, BOD_5, colour and NH_3-N.

3.3.3 Photo-Fenton Pretreatment

Photo-Fenton treatment was performed in a 500-mL Pyrex reactor using 250 mL of the preliminary treated leachate. Ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and hydrogen peroxide (H_2O_2) were added according to the selected H_2O_2/COD molar ratio and Fe^{2+}/H_2O_2 molar ratio simultaneously. The mixture was irradiated with an UV lamp, emitting radiation at wave length ≈ 365 nm and stirred continuously to ensure complete homogeneity during irradiation. Aliquots were taken at selected irradiation time, adjusted to pH above 10 with sodium hydroxide and mixed for 10 min and settled overnight for measurement of COD, BOD_5, colour and NH_3-N.

3.3.4 Sequencing Batch Reactor (SBR)

The biological treatment system was a 2-L aerobic bench-scale sequencing batch reactor (SBR). The working liquid volume was 1.5 L. The reactor was equipped with an air pump and air diffuser to keep dissolved oxygen level above 3 mg/L and a magnetic stirrer for mixing purpose. Feeding and decanting were performed using two peristaltic pumps. The reactor was inoculated with 300 mL aerobic sludge. The source of seed sludge was the aeration tank in the sewage treatment plant (STP) of the Universiti Teknologi PETRONAS campus. The concentration of biomass in the reactor after inoculation was about 2000 mg/L. In order to acclimate the biomass, hydraulic retention time (HRT) was chosen to be 2 d and the feed was pretreated leachate (adjusted to pH 6.9-7.1) mixed with domestic wastewater obtained from the STP with mixing pretreated leachate : domestic wastewater ratio of 25%:75%, 50%:50%, 75%:25% and 100% and the acclimation period was extended to 8 d. The cycle period was 24 h and divided into five phases: filling (0.25 h), aeration (21.75 h), settling (1.5 h), decant (0.25 h) and idle (0.25 h). Daily analyses of soluble COD (sCOD), ammonia-nitrogen (NH_3-N) and nitrate-nitrogen (NO_3^--N) for both influent and effluent were carried out. Concentration of mixed liquor suspended solids (MLSS) was monitored throughout the operation. A schematic of the experimental setup is shown in Fig. 3.2.

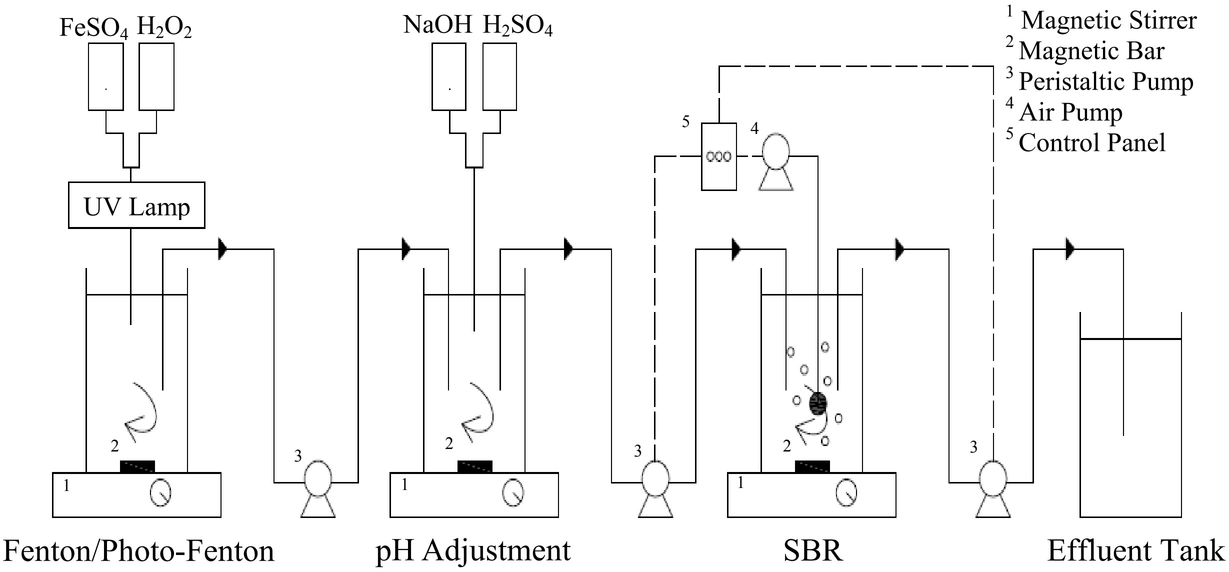

Fig. 3.2 Schematic of Experimental Setup

3.4 Data Analysis

The Design Expert Software (version 6.0.7) was used for the statistical design of experiments and data analysis. Central composite design (CCD) and response surface methodology (RSM) were applied to optimize the three most important operating variables in the Fenton and photo-Fenton processes: H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and reaction/irradiation time. A total of 20 experimental runs were set and the experimental data were fitted to the empirical second order polynomial model of a suitable degree for the optimum operating conditions of leachate treatment by the Fenton and photo-Fenton processes. In order to obtain the optimum H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and reaction/irradiation time, COD removal, colour removal and NH_3-N removal were selected as dependent parameters and were analyzed as responses. Regression analysis, graphical analysis and analysis of variance (ANOVA) were carried out using the Design Expert Software. The coded values for H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B) and reaction/irradiation time (C) were set at five levels: $-\alpha$ (minimum), -1, 0 (central), +1 and $+\alpha$ (maximum). The study ranges were chosen as H_2O_2/COD molar ratio 1.16-2.84, H_2O_2/Fe^{2+} molar ratio 3.18-36.82 and reaction time 0.66 h-2.34 h for the Fenton process; H_2O_2/COD molar ratio 1.32-4.68,

H_2O_2/Fe^{2+} molar ratio 1.59-18.41 and irradiation time 0.66 h-2.34 h for the photo-Fenton process and are shown in Table 3.2. Common reagent dosages employed in the literature range from H_2O_2/COD molar ratio 1.5-3.0 and H_2O_2/Fe^{2+} molar ratio 1.0-26.2 for degradation of leachate (Kim and Vogelpohl, 1998; Deng and Englehardt, 2006; Kurniawan et al., 2006). Experimental results were shown as percentage COD, colour and NH_3-N removal. The optimum region was identified based on the main parameters in the overlay plot.

Table 3.2 Independent Variables and Their Levels for the Central Composite Design used for Fenton and Photo-Fenton Processes

Independent variable	Code	Levels and ranges (Coded)				
		-1.68	-1	0	1	1.68
Fenton Process						
H_2O_2/COD molar ratio	A	1.16	1.5	2	2.5	2.84
H_2O_2/Fe^{2+} molar ratio	B	3.18	10	20	30	36.82
Reaction time (h)	C	0.66	1	1.5	2	2.34
Photo-Fenton Process						
H_2O_2/COD molar ratio	A	1.32	2	3	4	4.68
H_2O_2/Fe^{2+} molar ratio	B	1.59	5	10	15	18.41
Irradiation time (h)	C	0.66	1	1.5	2	2.34

The following equation (Eq. 3.1) was obtained where predicted result (Y) was assessed as a function of H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B) and reaction/irradiation time (C), and calculated as the sum of a constant, three first-order effects (A, B and C), three second-order effects (A^2, B^2 and C^2) and three interaction effects (AB, AC and BC).

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC$$

(3.1)

3.5 Chapter Summary

In this chapter, leachate sample, analytical methods, experimental procedure and method of data analysis have been described. Experimental procedure of preliminary treatment by pH adjustment-settling, Fenton and photo-Fenton processes, and sequencing batch reactor (SBR) is given in detail. Response surface methodology (RSM) used to optimize Fenton and photo-Fenton operating has also been described.

CHAPTER 4

RESULTS AND DISCUSSION

4.0 Chapter Overview

In this chapter, the results of preliminary treatment, Fenton and photo-Fenton pretreatment and treatment of the pretreated leachate by sequencing batch reactor (SBR) are presented and discussed.

4.1 Preliminary Treatment

In preliminary treatment of the landfill leachate, pH adjustment-settling was applied to the 2-h settled leachate. The pH of the leachate sample was adjusted to 2.5, 3, 3.5, 4, 4.5 and 5, and settled for 1 h. Acidic ranges were chosen because pH adjustment was not needed after preliminary treatment and acidic range strongly favours the advanced oxidation processes. Figure 4.1 shows the removal of COD, TSS, turbidity and colour by pH adjustment-settling. Relatively higher removal of COD, TSS, turbidity and colour were observed at pH 3 – COD 45%, TSS 80%, turbidity 59% and colour 68%. Rivas et al. (2004) reported 25% COD removal when pH of a medium-stabilized leachate was adjusted to lower than 3 and settled.

In general, organic colloids are hydrophilic while inorganic colloids are hydrophobic. The primary charge on hydrophilic colloids is due chiefly to the polar groups such as the carboxylic (-COOH) and amine ($-NH_2$) (Sincero and Sincero, 2003). Upon addition of acid, pH is lowered and the H^+ counter-ions neutralize the primary charges reducing the zeta potential and the force of repulsion between particles (O'Melia, 1972). At low pH $\approx$ 3, highest removal of COD, TSS and turbidity occurred resulting from agglomeration and settling of the colloids. Characteristics of the preliminary treated leachate are shown in Table 4.1.

The biodegradability (BOD_5/COD ratio) after pH adjustment-settling was low (0.04) and hence not amenable to biological treatment. Preliminary treated leachate was subjected to advanced oxidation process (Fenton and photo-Fenton) treatment to improve biodegradability so that it is amenable to biological treatment.

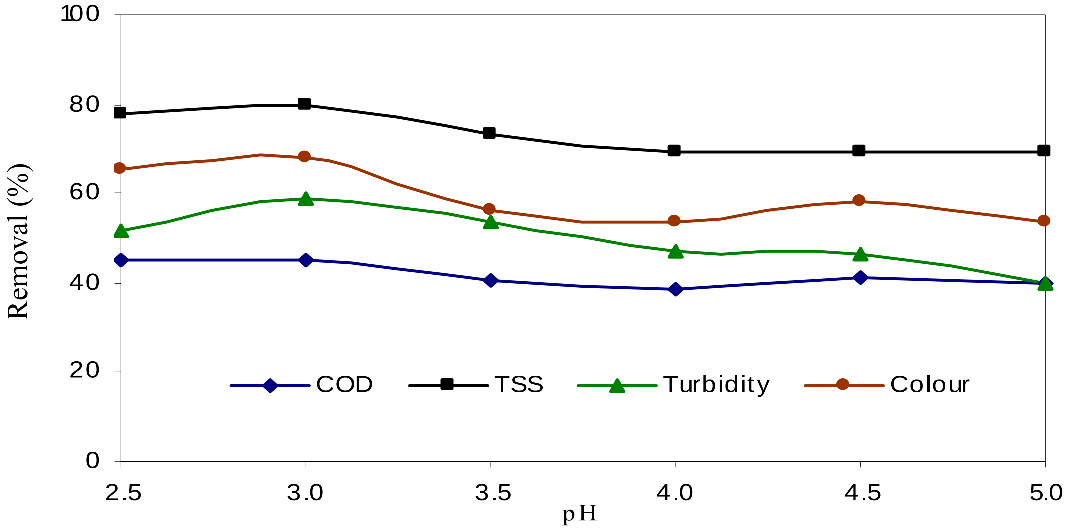

Fig. 4.1 Removal of COD, TSS, Turbidity and Colour by pH Adjustment-Settling

Table 4.1 Characteristics of Preliminary Treated Leachate

Parameter	Unit	Preliminary Treated
Turbidity	NTU	86-105
TSS	mg/L	19-25
Colour	Pt-Co	520-560
COD	mg/L	990-1100
BOD_5	mg/L	40-44
BOD_5/COD	-	0.04
NH_3-N	mg/L	555-680

4.2 Fenton Pretreatment

The optimum pH for Fenton treatment of leachate has been reported to be 2.5 (Gulsen and Turan, 2004; Zhang et al., 2005), 2.0-3.0 (Roddy and Choi, 1999), 3.0 (Kim et al., 2001) and 3.5 (Kim and Huh, 1997; Kang and Hwang, 2000). The preliminary treated leachate (pH adjusted to 3.0 and settled) was used directly for Fenton treatment.

In Fenton treatment, the relationship between the three variables (H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and reaction time) and three process responses (COD, colour and NH_3-N removal) were analyzed using the response surface methodology (RSM).

4.2.1 Statistical Analysis

The study ranges of the parameters (variables) were chosen as H_2O_2/COD molar ratio 1.16-2.84, H_2O_2/Fe^{2+} molar ratio 3.18-36.82 and reaction time 0.66-2.34 h. Common reagent dosages employed in the Fenton process range from H_2O_2/COD molar ratio 1.5-3.0 and H_2O_2/Fe^{2+} molar ratio 1.0-26.2 for degradation of leachate (Kim and Vogelpohl, 1998; Deng and Englehardt, 2006; Kurniawan et al., 2006). The results obtained were analyzed by ANOVA to assess the "goodness of fit". The models for COD, colour and NH_3-N removal (Y_1, Y_2 and Y_3) were significant by the *F*-test at the 5% confidence level if Prob>*F*<0.05. The following fitted regression models (equation in terms of coded values for the regressors) were obtained to quantitatively investigate the effects of H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B) and reaction time (C) on the Fenton process performance.

COD removal:

$$Y_1 = 47.63 + 3.03A - 6.73B + 1.69C - 1.26A^2 + 2.60B^2 - 0.93C^2 - 1.70AB + 0.34AC - 0.11BC \quad (4.1)$$

Colour removal:

$$Y_2 = 75.64 + 6.71A - 7.33B + 2.59C - 6.75A^2 - 3.92B^2 - 3.24C^2 + 0.70AB - 0.46AC - 3.15BC \qquad (4.2)$$

NH_3-N removal:

$$Y_3 = 74.79 + 5.57A - 3.66B + 0.34C - 2.30A^2 + 0.37B^2 - 0.84C^2 - 1.79AB + 0.53AC + 0.26BC \qquad (4.3)$$

In Eq. 4.1, 4.2 and 4.3, the values of the sum of a constant (β_0), 47.63, 75.64 and 74.79 represent the predicted percentage removal of COD, colour and NH_3-N, respectively at “level 0”. The positive sign in first order terms indicates that the parameter (variable) is directly proportional to the responses COD removal, colour removal and NH_3-N removal; on the other hand, the negative sign in first order terms indicates that the parameter inversely proportional to the responses. For example, the decrease of H_2O_2/Fe^{2+} molar ratio (-6.73B, -7.33B and -3.66B) increases the COD, colour and NH_3-N removal. It is to be noted that relatively lower values were found for reaction time (C). It means the variation of reaction time has less effect on the Fenton process compared to H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio.

Table 4.2 shows the central composite design (CCD) in the form of a 2^3 full factorial design with five additional experimental trials (run number 4, 5, 7, 9, 14 and 15) as replicates of the central point and observed (actual) experimental results and predicted results from the model at each assay. The replication of the central points is to get a good estimation of the experimental error. In this table, the parameter levels are presented in terms of molar ratio for H_2O_2/COD and H_2O_2/Fe^{2+}, and h for reaction time, and in addition coded level in parentheses.

Table 4.2 CCD for Study of Operating Conditions of Fenton Process

Run no.	Experimental Design			Removal (%)					
	A:H_2O_2/COD (Code)	B:H_2O_2/Fe^{2+} (Code)	C:Reaction Time (Code)	Observed			Predicted		
				COD	Colour	NH_3-N	COD	Colour	NH_3-N
1	2.00 (0)	3.18 (-1.68)	1.50 (0)	70.0	85.4	85.2	66.3	76.9	82.0
2	2.00 (0)	36.82 (1.68)	1.50 (0)	41.8	56.2	70.1	43.7	52.2	69.7
3	2.84 (1.68)	20.00 (0)	1.50 (0)	50.0	79.8	81.8	49.2	67.9	77.6
4	2.00 (0)	20.00 (0)	1.50 (0)	49.1	76.5	75.9	47.6	75.6	74.8
5	2.00 (0)	20.00 (0)	1.50 (0)	48.2	77.9	74.2	47.6	75.6	74.8
6	2.50 (1)	10.00 (-1)	2.00 (1)	59.1	72.1	80.5	61.7	80.4	83.7
7	2.00 (0)	20.00 (0)	1.50 (0)	45.5	74.0	75.7	47.6	75.6	74.8
8	1.50 (-1)	10.00 (-1)	2.00 (1)	50.9	64.6	66.0	51.5	69.3	67.9
9	2.00 (0)	20.00 (0)	1.50 (0)	45.5	75.4	74.4	47.6	75.6	74.8
10	2.50 (1)	10.00 (-1)	1.00 (-1)	56.4	62.5	79.8	57.4	69.8	82.4
11	2.00 (0)	20.00 (0)	0.66 (-1.68)	43.6	65.8	72.3	42.1	62.1	71.9
12	1.50 (-1)	30.00 (1)	1.00 (-1)	40.0	46.5	65.1	38.8	47.1	64.5
13	1.50 (-1)	30.00 (1)	2.00 (1)	40.9	45.4	64.7	41.2	46.9	64.6
14	2.00 (0)	20.00 (0)	1.50 (0)	50.0	73.7	73.2	47.6	75.6	74.8
15	2.00 (0)	20.00 (0)	1.50 (0)	47.3	74.2	74.8	47.6	75.6	74.8

Table 4.2 CCD for Study of Operating Conditions of Fenton Process (continued)

Run no.	Experimental Design			Removal (%)					
				Observed			Predicted		
	A:H_2O_2/COD (Code)	B:H_2O_2/Fe^{2+} (Code)	C:Reaction Time (Code)	COD	Colour	NH_3-N	COD	Colour	NH_3-N
16	1.50 (-1)	10.00 (-1)	1.00 (-1)	45.5	55.6	68.8	48.6	56.9	68.8
17	1.16 (-1.68)	20.00 (0)	1.50 (0)	40.0	45.8	58.4	39.0	45.3	58.9
18	2.50 (1)	30.00 (1)	1.00 (-1)	40.0	58.7	70.3	40.7	62.3	71.0
19	2.00 (0)	20.00 (0)	2.34 (1.68)	48.2	79.6	76.2	47.8	70.8	73.0
20	2.50 (1)	30.00 (1)	2.00 (1)	46.4	53.3	70.6	44.6	60.1	73.3

Table 4.3 ANOVA for Response Surface Quadratic Model (Fenton Process)

Response	AP	PLOF	CV
COD	15.672	0.1678	5.19
Colour	6.649	0.0005	11.28
NH_3-N	13.093	0.0065	3.67

AP: adequate precision; PLOF: probability of lack of fit; CV: coefficient of variance

The ANOVA for response surface quadratic model is shown in Table 4.3. 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. The AP for all the responses are greater than 4 in the present study. The probability of lack of fit (PLOF) describes the variation of the data around the fitted model. If the model does not fit the data well, this will be significant ($PLOF<0.05$). In this case, COD removal fits the data well. The coefficient of variance (CV) is the ratio of the standard error of estimate to the mean value of the observed response and defines reproducibility of the model. A model normally can be considered reproducible if its CV is not greater than 10% (Beg et al., 2003). A CV of 11.28 indicates colour removal falls short in the model in terms of reproducibility.

Dignostics plots (Fig. 4.2) of the predicted versus actual values can judge the model satisfactoriness by indicating an agreement between the actual data and the one obtained from the model. The R^2 coefficient gives the proportion of the total variation in the response predicted by the model and a value close to 1 is desirable and ensures a satisfactory adjustment of the quadratic model to the experimental data. The R^2 coefficient should be at least 0.80 for a good fit of the model (Olmez, 2009). The R^2 coefficient is found to be close to 1 (0.9392 and 0.9103 for COD and NH_3-N removal, respectively), indicating that the regression models explained the prediction well (Olmez, 2009). The R^2 coefficient of colour removal is low (0.8124) but the value is acceptable. The R^2 values indicate adequate agreement between data obtained from the model and actual data.

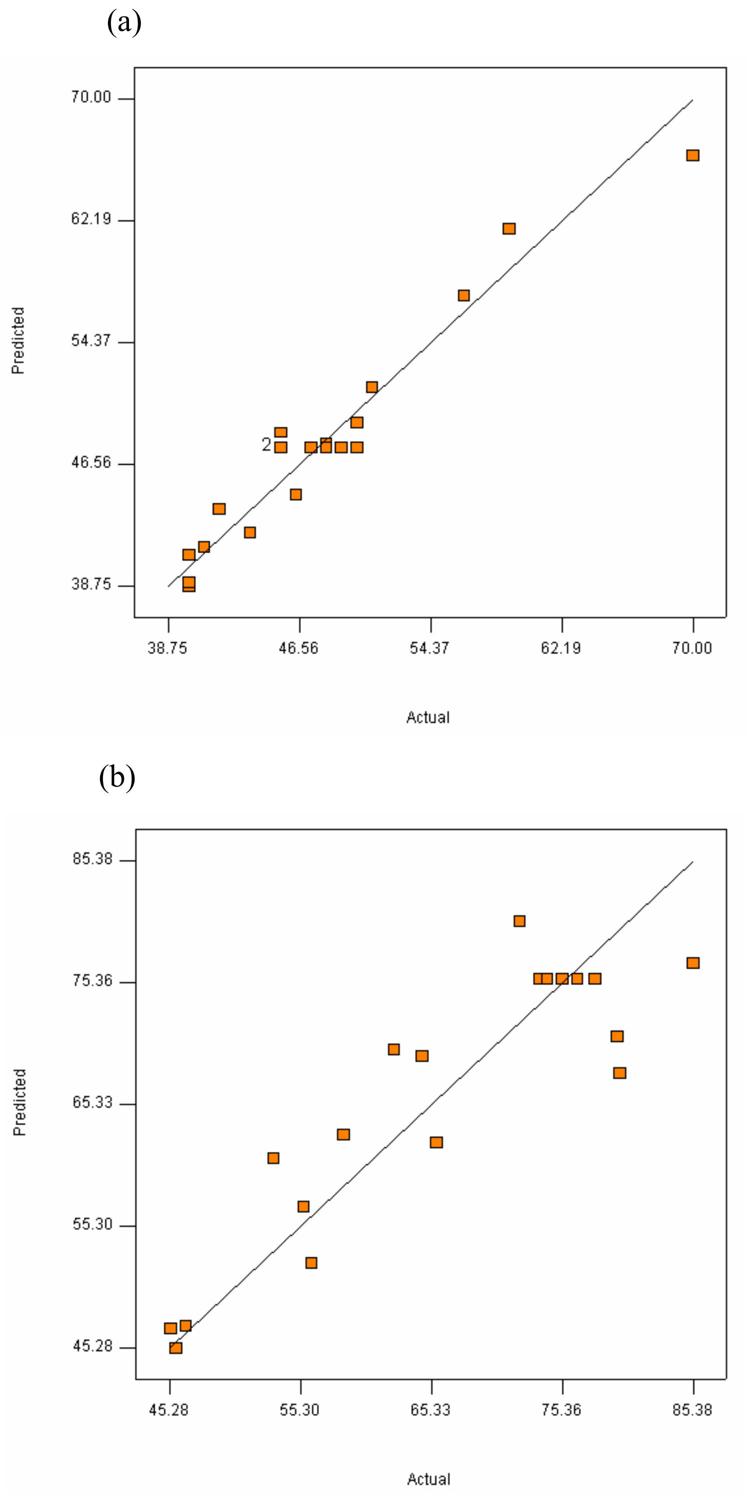

Fig. 4.2 Predicted Versus Actual Plot for (a) COD Removal (R^2 0.9392), (b) Colour Removal (R^2 0.8124), and (c) NH_3-N Removal (R^2 0.9103)

(c)

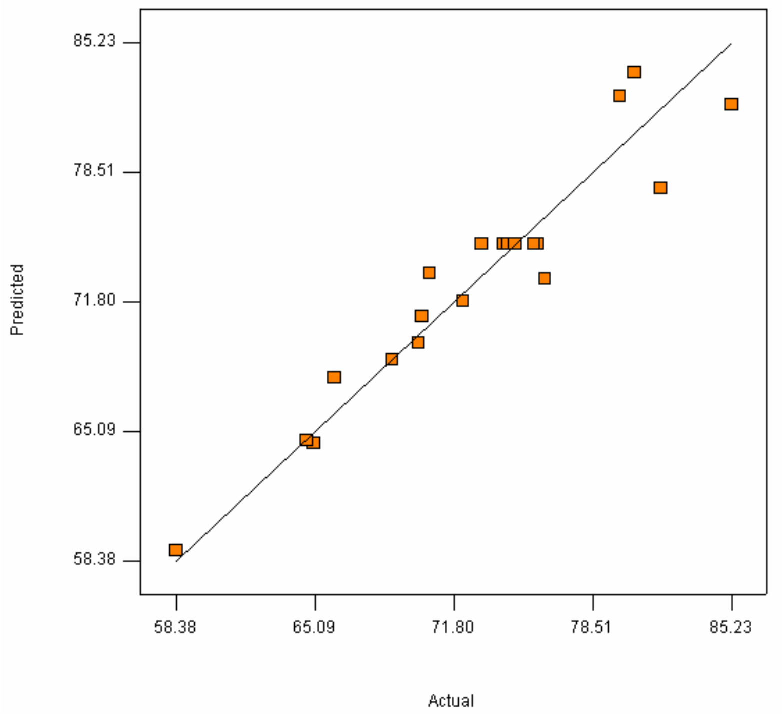

Fig. 4.2 Predicted Versus Actual Plot for (a) COD removal (R^2 0.9392), (b) Colour Removal (R^2 0.8124), and (c) NH_3-N Removal (R^2 0.9103) (continued)

4.2.2 Process Analysis

The response surface plots for COD, colour and NH_3-N removal are shown in the form of two-dimensional contour plots (Fig. 4.3, 4.4 and 4.5). The two-dimensional contour plots represent the responses (COD, colour and NH_3-N removal) on the H_2O_2/COD molar ratio and reaction time (Fig. 4.3), H_2O_2/Fe^{2+} molar ratio and reaction time (Fig. 4.4) and H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio (Fig. 4.5). The plots are approximately circular in shape. The center indicates the range of optimum operating conditions.

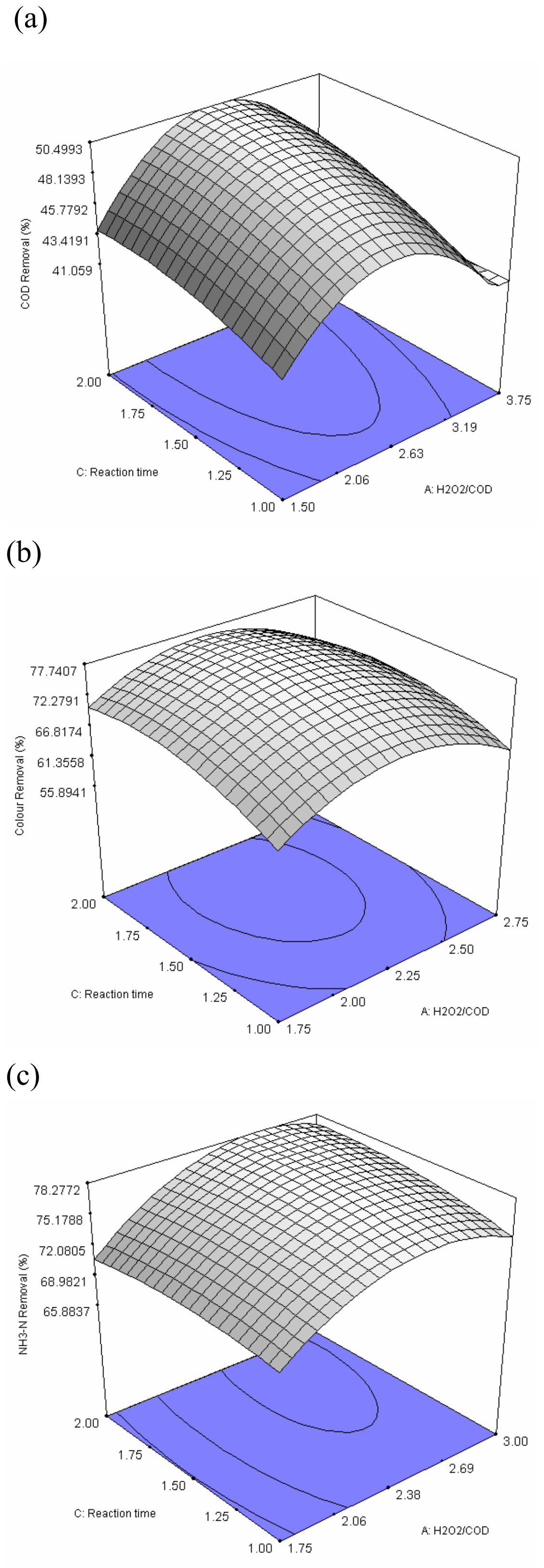

Fig. 4.3 Response Surface Plots of (a) COD, (b) Colour and (c) NH_3-N Removal as a Function of H_2O_2/COD Molar Ratio and Reaction Time at H_2O_2/Fe^{2+} Molar Ratio 20

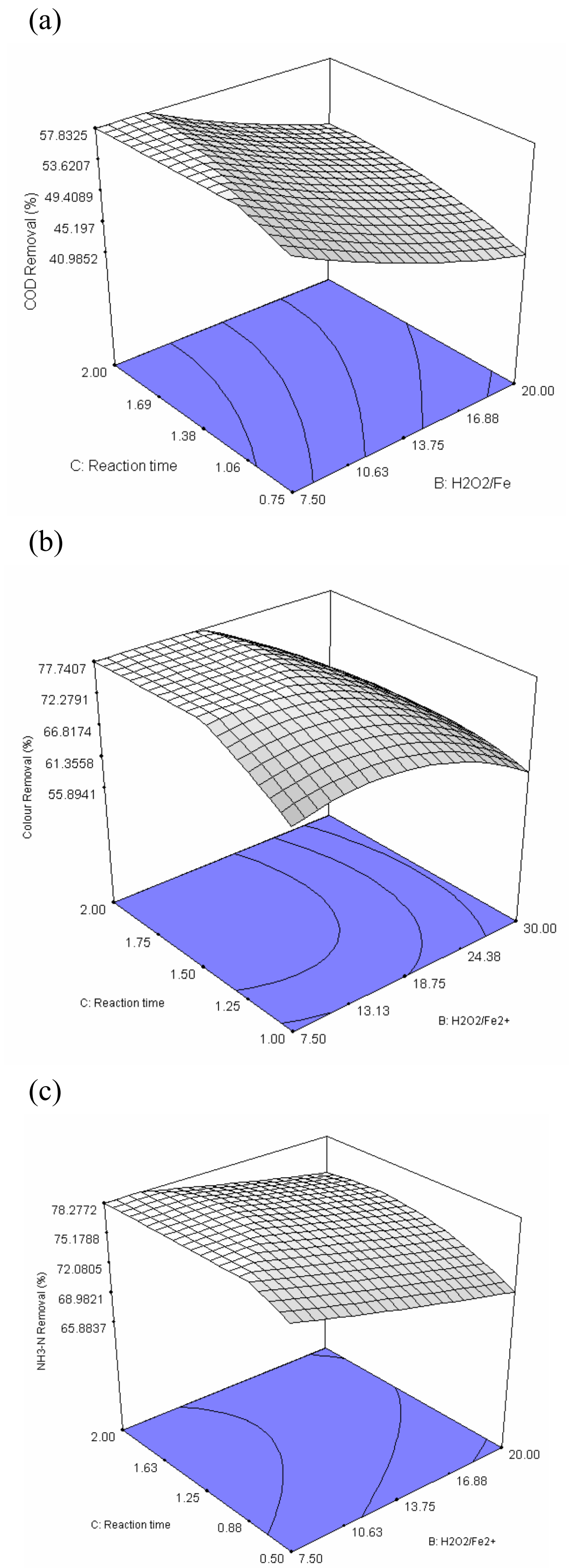

Fig. 4.4 Response Surface Plots of (a) COD, (b) Colour and (c) NH_3-N Removal as a Function of H_2O_2/Fe^{2+} Molar Ratio and Reaction Time at H_2O_2/COD Molar Ratio 2.0

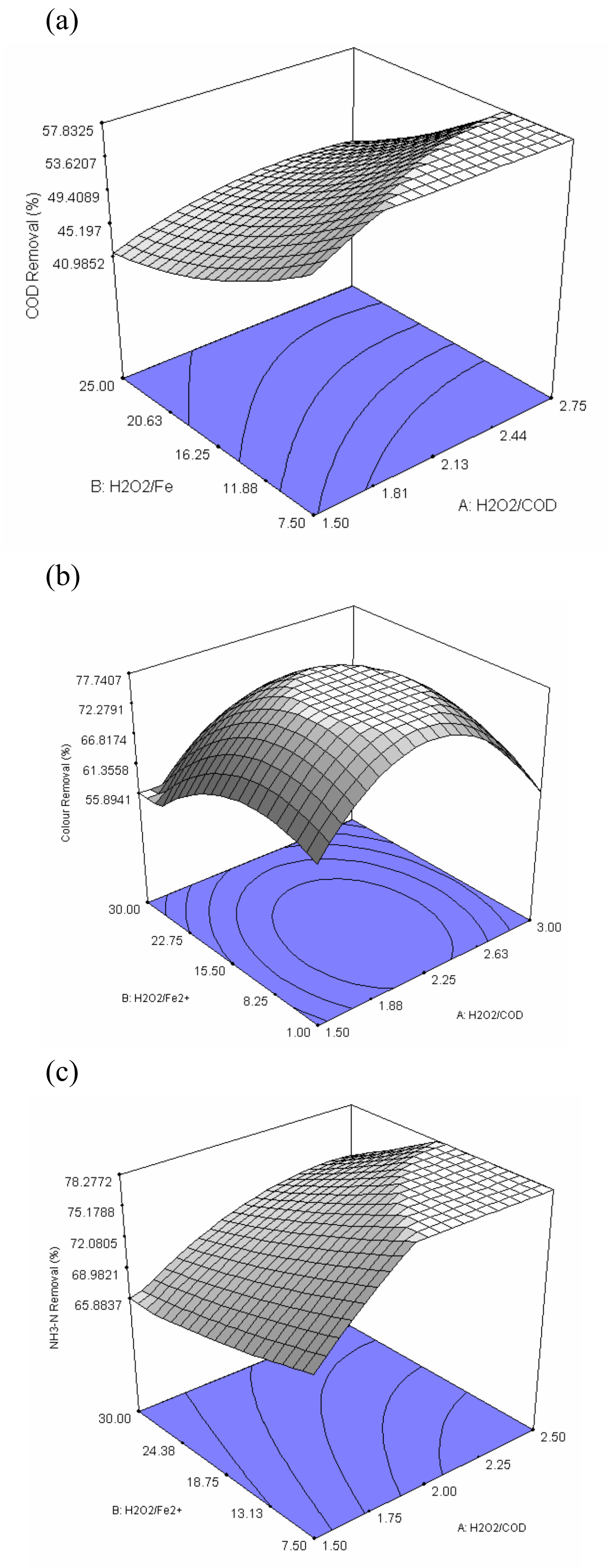

Fig. 4.5 Response Surface Plots of (a) COD, (b) Colour and (c) NH_3-N Removal as a Function of H_2O_2/COD Molar Ratio and H_2O_2/Fe^{2+} Molar Ratio at Reaction Time 1.5 h

4.2.2.1 Effect of H_2O_2/COD Molar Ratio

As can be seen in Fig. 4.3 (a), (b) and (c), the response surface plots have shown a clear peak, indicating that the optimum conditions for maximum values of the COD, colour and NH_3-N removal are attributed to the H_2O_2/COD molar ratio and reaction time variables in the design space. The figure shows that maximum COD, colour and NH_3-N removal were 50.5, 77.7 and 78.3% at about H_2O_2/COD molar ratio 2.0-2.7 at H_2O_2/Fe^{2+} molar ratio 20 and reaction time in the range of 1.5-2.0 h. Figure 4.3 shows that COD, colour and NH_3-N removal increases when the H_2O_2 dosage increases. This may be due to the fact that increased H_2O_2 dosage produces more hydroxyl radicals leading to higher substrate degradation (Deng and Englehardt, 2006). Further increase of H_2O_2 dosage either did not improve the removal efficiency. This may be due to scavenging of $^\bullet OH$ radical by H_2O_2 as in following reaction (Andreozzi et al., 2005). This reaction leads to the production of hydroperoxyl radical, a species with much weaker oxidizing power compared to hydroxyl radical (Ting et al., 2008).

$$^\bullet OH + H_2O_2 \longrightarrow HO^\bullet_2 + H_2O \qquad (2.3)$$

Besides, an excess amount of H_2O_2 can cause the auto decomposition of H_2O_2 to water and oxygen (Eq. 2.8), and the recombination of $^\bullet OH$ radicals (Eq. 4.4) (Mandal et al., 2010), thereby decreasing the concentration of $^\bullet OH$ radicals and reducing degradation efficiency.

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (2.8)$$

$$^\bullet OH + {}^\bullet OH \longrightarrow H_2O_2 \qquad (4.4)$$

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

In Fig. 4.4 (a), (b) and (c), the maximum COD, colour and NH_3-N removal were 57.8, 77.7 and 78.3% at about H_2O_2/Fe^{2+} molar ratio 7.5-13.0 at H_2O_2/COD molar ratio 2.0 and reaction time in the range of 1.5-2.0 h. Figure 4.4 shows that COD, colour and NH_3-N removal increases with increasing Fe^{2+} dosage. These results show increase in COD, colour and NH_3-N removal with decrease in H_2O_2/Fe^{2+} molar ratio up to about 7.5. Further decrease in H_2O_2/Fe^{2+} ratio did not improve the removal efficiency due to direct reaction of ${}^{\bullet}OH$ radical with metal ions at high concentration of Fe^{2+} as in the following reaction (Joseph et al., 2000).

$$ {}^{\bullet}OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^{-} \qquad (2.4) $$

Interaction between H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio on COD, colour and NH_3-N removal are shown in Fig. 4.5 (a), (b) and (c). Maximum COD, colour and NH_3-N removal were 60.4, 80.4 and 83.9% at about H_2O_2/COD molar ratio 2.0-2.7 and H_2O_2/Fe^{2+} molar ratio 7.5-13.0 at reaction time 1.5 h.

4.2.2.3 Effect of Reaction Time

Figure 4.3 (a), (b) and (c) and 4.4 (a), (b) and (c) show that maximum COD, colour and NH_3-N removal were achieved at about reaction time 1.5-2.0 h at H_2O_2/Fe^{2+} molar ratio 20 and H_2O_2/COD molar ratio 2.0. The results showed COD, colour and NH_3-N removal increased when the reaction time increased. However, further increase of reaction time above 1.5 h did not improve the process significantly. This may due to the fact that organics were rapidly degraded by the Fenton reagent and most organics removal occurred in 1.5 h.

Response surface plots indicate the optimum points in the range of H_2O_2/COD molar ratio 2.0-2.7, H_2O_2/Fe^{2+} molar ratio 7.5-13.0 and 1.5 h reaction time with maximum removal of COD 60.4%, colour 80.4% and NH_3-N 83.9%, respectively. Hermosilla et al. (2009) observed that under the optimal conditions, the conventional Fenton process was able to achieve less than 70% COD removal from a mature leachate. Lopez et al. (2004) also investigated the application of the Fenton process as pretreatment for the leachate from a municipal landfill and the maximum COD removal was about 60%, using reagent dosages of 10000 mg/L of H_2O_2 and 830 mg/L of Fe^{2+} (H_2O_2/Fe^{2+} molar ratio 19.8).

4.2.3 Process Optimization

With multiple responses, the optimum operating conditions where all parameters simultaneously meet the desirable removal criteria could be visualized graphically by superimposing the contours of the response surfaces in an overlay plot. Graphical optimization displays the area of feasible response value in the factor space and the regions that do fit the optimization criteria would be shaded (Mason et al., 2003). In order to obtain a moderately precise optimum zone, response limits as the minimum permissible values were chosen for each parameter close to their acquired removal efficiencies – COD 55%, colour 80% and NH_3-N 80% (Fig. 4.6). The shaded region shows the optimum parameters – H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 and reaction time 1.5 h, and constitute the optimum operating conditions. The results agree well with optimum H_2O_2/Fe^{2+} molar ratio of 7.5-26.2 reported in the literature (Kim and Vogelpohl, 1998; Primo et al., 2008).

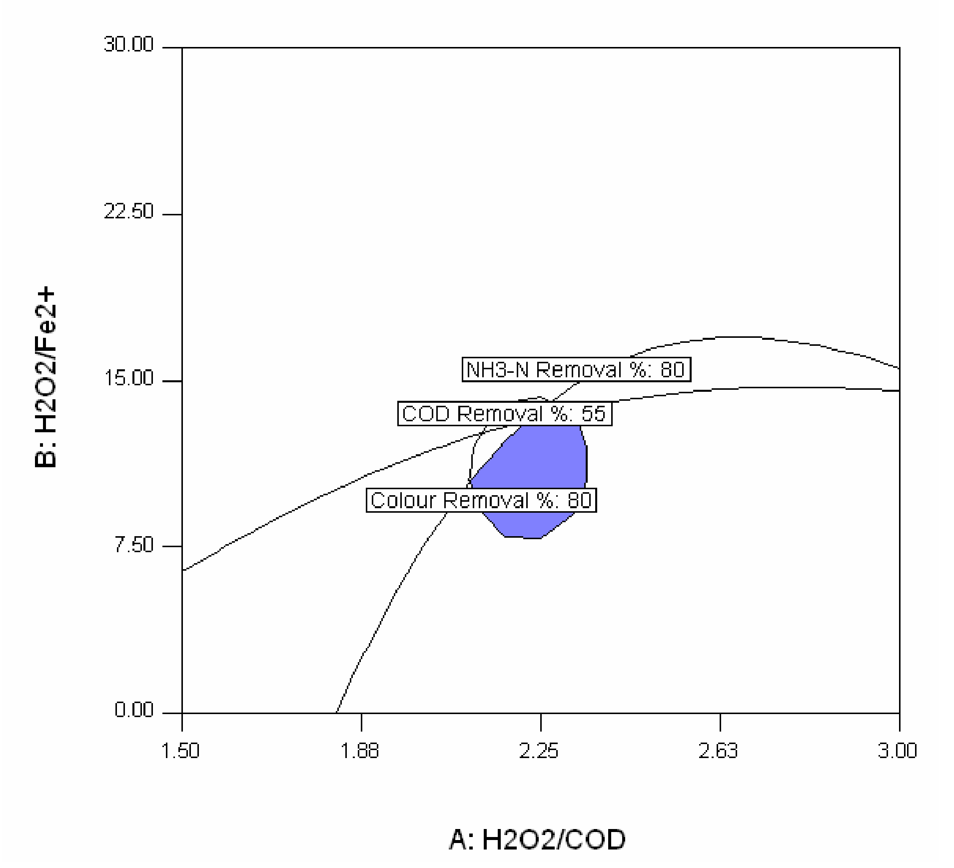

Fig. 4.6 Overlay Plot for Optimal Region at Reaction Time 1.5 h

4.2.4 Model Results Verification

Three additional experiments were conducted applying the optimum operating conditions (H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h reaction time) to verify the results obtained from the model. As shown in Table 4.4, the removal efficiency obtained from the experiment and by the model were in close agreement with less than 5% error.

Table 4.4 Verification Experiments at Optimum Operating Conditions (Fenton Process)

Response	Model Response	Experimental Values	Error
COD removal (%)	55.0	46.3-52.1 (50.5)	-4.5
Colour removal (%)	80.0	72.8-78.4 (76.9)	-3.1
NH_3-N removal (%)	80.0	82.2-84.5 (83.7)	3.7

The characteristics of the Fenton pretreated leachate were: COD 545 mg/L, BOD_5 114.5 mg/L, biodegradability (BOD_5/COD ratio) 0.21, NH_3-N 90.5 mg/L and colour 120 Pt-Co Units. The residual COD is considered high and the biodegradability is low after Fenton pretreatment. Photo-Fenton process which is considered more efficient than Fenton process was chosen as the alternative pretreatment to reduce COD and improve the preliminary treated leachate biodegradability so that it is amenable to biological treatment.

4.3 Photo-Fenton Pretreatment

The preliminary treated leachate (pH adjusted to 3.0 and settled) was used directly for photo-Fenton treatment as the optimum pH for photo-Fenton treatment of leachate has been reported to be 3.0 (Kim et al., 1997; Kim and Vogelpohl, 1998) and 3.0-4.0 (Lau et al., 2002). As in Fenton treatment, the relationship between the three variables (H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and irradiation time) and three process responses (COD, colour and NH_3-N removal) were analyzed using the response surface methodology (RSM).

4.3.1 Statistical Analysis

H_2O_2/COD molar ratio 1.32-4.68, H_2O_2/Fe^{2+} molar ratio 1.59-18.41 and irradiation time 0.66-2.34 h were chosen as the study ranges of the parameters (variables). Previous studies showed that common reagent dosages employed in the photo-Fenton process range from H_2O_2/COD molar ratio 1.5-3.0 and H_2O_2/Fe^{2+} molar ratio 1.0-26.2 for degradation of leachate (Kim and Vogelpohl, 1998; Deng and Englehardt, 2006; Kurniawan et al., 2006). The results obtained were analyzed by ANOVA to assess the "goodness of fit". The models for COD, colour and NH_3-N removal (Y_1, Y_2 and Y_3) were significant by the *F*-test at the 5% confidence level if Prob>*F*<0.05. The following fitted regression models (equation in terms of coded values for the regressors) were obtained to quantitatively investigate the effects of H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B) and irradiation time (C) on the photo-Fenton process performance.

COD removal:

$$Y_1 = 66.48 + 8.90A - 8.44B + 0.83C - 4.48A^2 + 0.019B^2 - 2.23C^2 + 1.14AB - 0.23AC + 1.59BC \qquad (4.5)$$

Colour removal:

$$Y_2 = 69.44 + 8.64A + 15.76B + 2.25C + 6.85A^2 - 14.170B^2 + 4.70C^2 - 6.14AB - 1.76AC + 0.96BC \quad (4.6)$$

NH_3-N removal:

$$Y_3 = 84.81 + 5.41A - 13.90B - 0.27C - 3.04A^2 - 13.69B^2 + 1.72C^2 + 3.44AB - 0.72AC + 0.61BC \quad (4.7)$$

The values of the sum of a constant (β_0), 66.48, 69.44 and 84.81 in Eq. 4.4, 4.5 and 4.6 represent the predicted percentage removal of COD, colour and NH_3-N, respectively at “level 0”. The positive sign in first order terms indicates that the parameter (variable) is directly proportional to the responses COD removal, colour removal and NH_3-N removal; on the other hand, the negative sign in first order terms indicates that the parameter is inversely proportional to the responses. For example, the increase of H_2O_2/COD molar ratio (+8.90A, +8.64A and +5.41A) increases the COD, colour and NH_3-N removal, respectively. It is to be noted that relatively lower values were found for irradiation time (C). It means the variation of irradiation time has less effect on the photo-Fenton process compared to H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio.

Table 4.5 shows the central composite design (CCD) in the form of a 2^3 full factorial design with five additional experimental trials (run number 4, 5, 7, 9, 14 and 15) as replicates of the central point and observed (actual) experimental results and predicted results from the model at each assay. The replication of the central points is to get a good estimation of the experimental error. In this table, the parameter levels are presented in terms of molar ratio for H_2O_2/COD and H_2O_2/Fe^{2+}, and h for irradiation time, and in addition coded level in parentheses.

Table 4.5 CCD for Study of Operating Conditions of Photo-Fenton Process

Run no.	Experimental Design			Removal (%)					
	A:H_2O_2/COD (Code)	B:H_2O_2/Fe^{2+} (Code)	C:Irradiation Time (Code)	Observed			Predicted		
				COD	Colour	NH_3-N	COD	Colour	NH_3-N
1	3.00 (0)	1.59 (-1.68)	1.50 (0)	79.1	-42.9	25.9	80.7	-14.1	27.4
2	3.00 (0)	18.41 (1.68)	1.50 (0)	52.7	73.6	80.3	52.3	60.2	74.2
3	4.68 (1.68)	10.00 (0)	1.50 (0)	73.6	90.4	69.0	68.8	100.0	66.5
4	3.00 (0)	10.00 (0)	1.50 (0)	61.8	69.1	88.2	66.5	69.4	84.8
5	3.00 (0)	10.00 (0)	1.50 (0)	70.9	70.7	85.1	66.5	69.4	84.8
6	4.00 (1)	5.00 (-1)	2.00 (1)	73.6	68.6	43.5	75.0	51.8	45.8
7	3.00 (0)	10.00 (0)	1.50 (0)	67.3	71.1	85.6	66.5	69.4	84.8
8	2.00 (-1)	5.00 (-1)	2.00 (1)	60.0	42.1	66.0	59.9	29.4	65.0
9	3.00 (0)	10.00 (0)	1.50 (0)	65.5	70.4	81.8	66.5	69.4	84.8
10	4.00 (1)	5.00 (-1)	1.00 (-1)	75.5	66.3	51.2	77.0	52.8	49.1
11	3.00 (0)	10.00 (0)	0.66 (-1.68)	54.5	65.2	88.1	58.8	71.7	87.2
12	2.00 (-1)	15.00 (1)	1.00 (-1)	40.9	67.1	84.1	38.7	73.1	85.1
13	2.00 (-1)	15.00 (1)	2.00 (1)	46.4	82.9	81.8	44.0	85.4	87.1
14	3.00 (0)	10.00 (0)	1.50 (0)	67.3	69.3	83.5	66.5	69.4	84.8
15	3.00 (0)	10.00 (0)	1.50 (0)	66.4	68.8	83.8	66.5	69.4	84.8

Table 4.5 CCD for Study of Operating Conditions of Photo-Fenton Process (continued)

Run no.	Experimental Design			Removal (%)					
	A:H_2O_2/COD (Code)	B:H_2O_2/Fe^{2+} (Code)	C:Irradiation Time (Code)	Observed			Predicted		
				COD	Colour	NH_3-N	COD	Colour	NH_3-N
16	2.00 (-1)	5.00 (-1)	1.00 (-1)	67.3	36.4	64.4	61.0	22.3	65.3
17	1.32 (-1.68)	10.00 (0)	1.50 (0)	32.7	65.2	86.8	38.8	70.9	84.7
18	4.00 (1)	15.00 (1)	1.00 (-1)	60.0	83.4	78.2	59.2	85.3	82.5
19	3.00 (0)	10.00 (0)	2.34 (1.68)	64.5	72.3	90.0	61.6	81.2	86.3
20	4.00 (1)	15.00 (1)	2.00 (1)	58.2	86.1	79.4	63.6	89.4	81.7

Table 4.6 ANOVA for Response Surface Quadratic Model (Photo-Fenton Process)

Response	AP	PLOF	CV
COD	12.728	0.0771	7.55
Colour	11.041	<0.0001	22.91
NH_3-N	21.527	0.0018	5.25

AP: adequate precision; PLOF: probability of lack of fit; CV: coefficient of variance

Table 4.6 shows the ANOVA for response surface quadratic model. 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. The AP for all the responses are greater than 4 in the present study. The probability of lack of fit (PLOF) describes the variation of the data around the fitted model. If the model does not fit the data well, this will be significant ($PLOF<0.05$). In this case, COD removal fits the data well. The coefficient of variance (CV) is the ratio of the standard error of estimate to the mean value of the observed response and defines reproducibility of the model. A model normally can be considered reproducible if its CV is not greater than 10% (Beg et al., 2003). A CV of 22.91 indicates colour removal falls short in the model in terms of reproducibility.

Dignostics plots (Fig. 4.7) of the predicted versus actual values can judge the model satisfactoriness by indicating an agreement between the actual data and the one obtained from the model. The R^2 coefficient gives the proportion of the total variation in the response predicted by the model and a value close to 1 is desirable and ensures a satisfactory adjustment of the quadratic model to the experimental data. The R^2 coefficient is found to be close to 1 (0.9177 and 0.9719 for COD and NH_3-N removal, respectively), indicating that the regression models explained the prediction well (Olmez, 2009). The R^2 coefficient of colour removal is low (0.8573) but the value is acceptable. The R^2 values indicate adequate agreement between data obtained from the model and actual data.

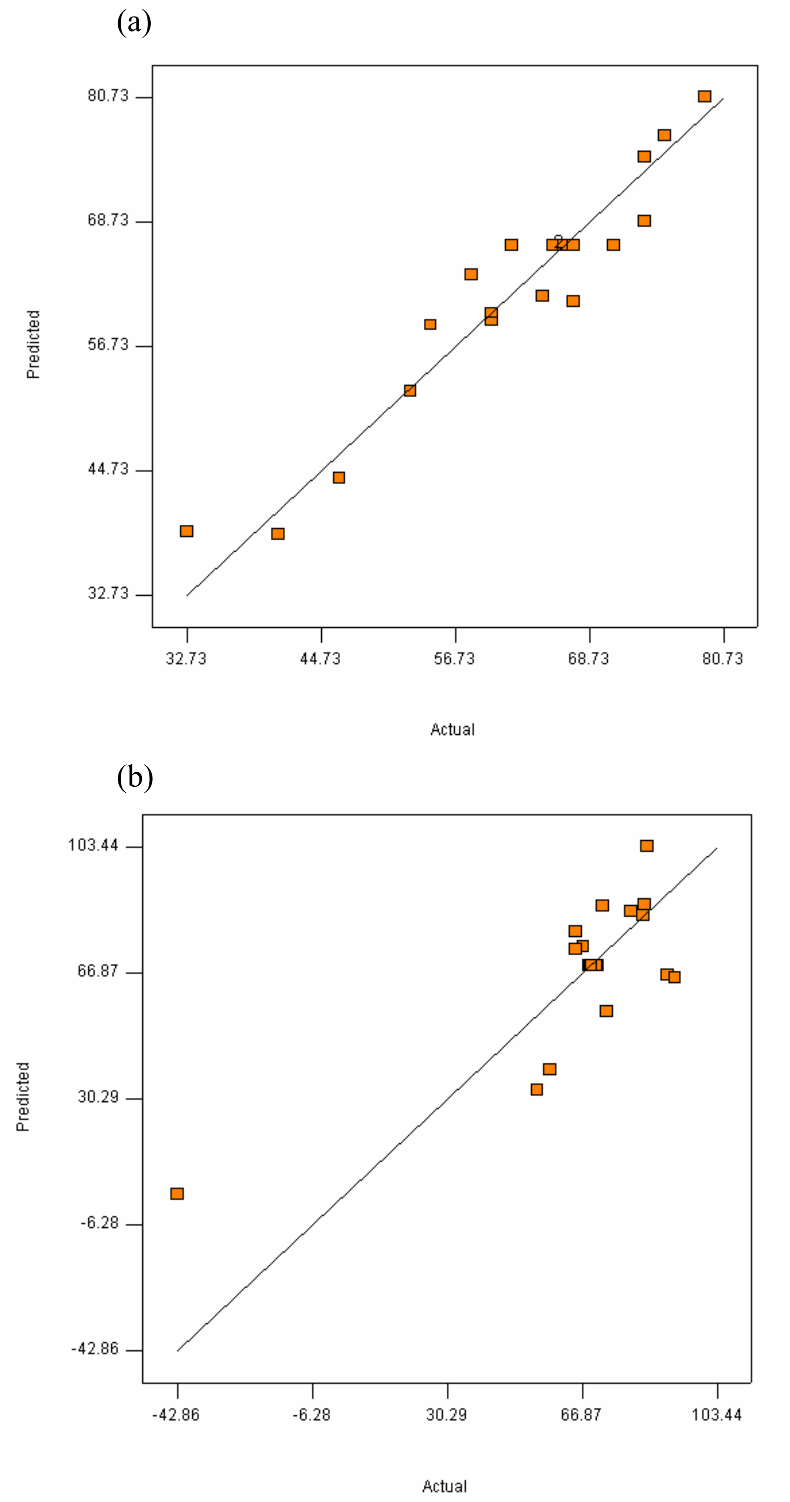

Fig. 4.7 Predicted Versus Actual Plot for (a) COD Removal (R^2 0.9177), (b) Colour Removal (R^2 0.8573), and (c) NH_3-N Removal (R^2 0.9719)

(c)

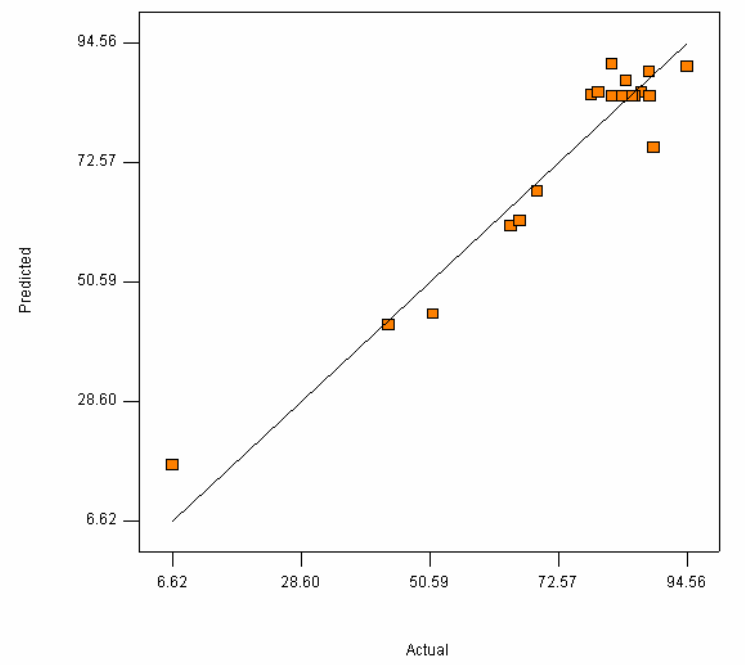

Fig. 4.7 Predicted Versus Actual Plot for (a) COD Removal (R^2 0.9177), (b) Colour Removal (R^2 0.8573), and (c) NH_3-N Removal (R^2 0.9719) (continued)

4.3.2 Process Analysis

Figure 4.8, 4.9 and 4.10 show the response surface plots for COD, colour and NH_3-N removal in the form of two-dimensional contour plots. The two-dimensional contour plots represent the responses (COD, colour and NH_3-N removal) on the H_2O_2/COD molar ratio and irradiation time (Fig. 4.8), H_2O_2/Fe^{2+} molar ratio and irradiation time (Fig. 4.9) and H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio (Fig. 4.10). The center of the plots indicates the range of optimum operating conditions.

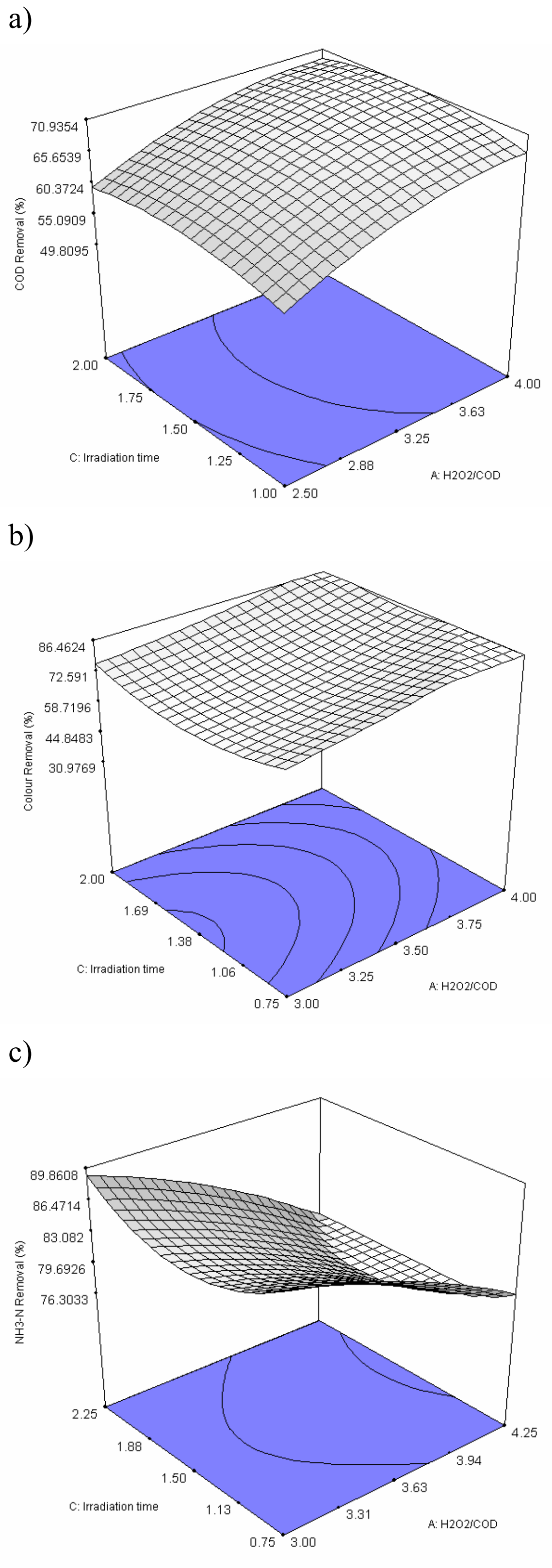

Fig. 4.8 Response Surface Plots of (a) COD, (b) Colour and (c) NH_3-N Removal as a Function of H_2O_2/COD Molar Ratio and Irradiation Time at H_2O_2/Fe^{2+} Molar Ratio 10

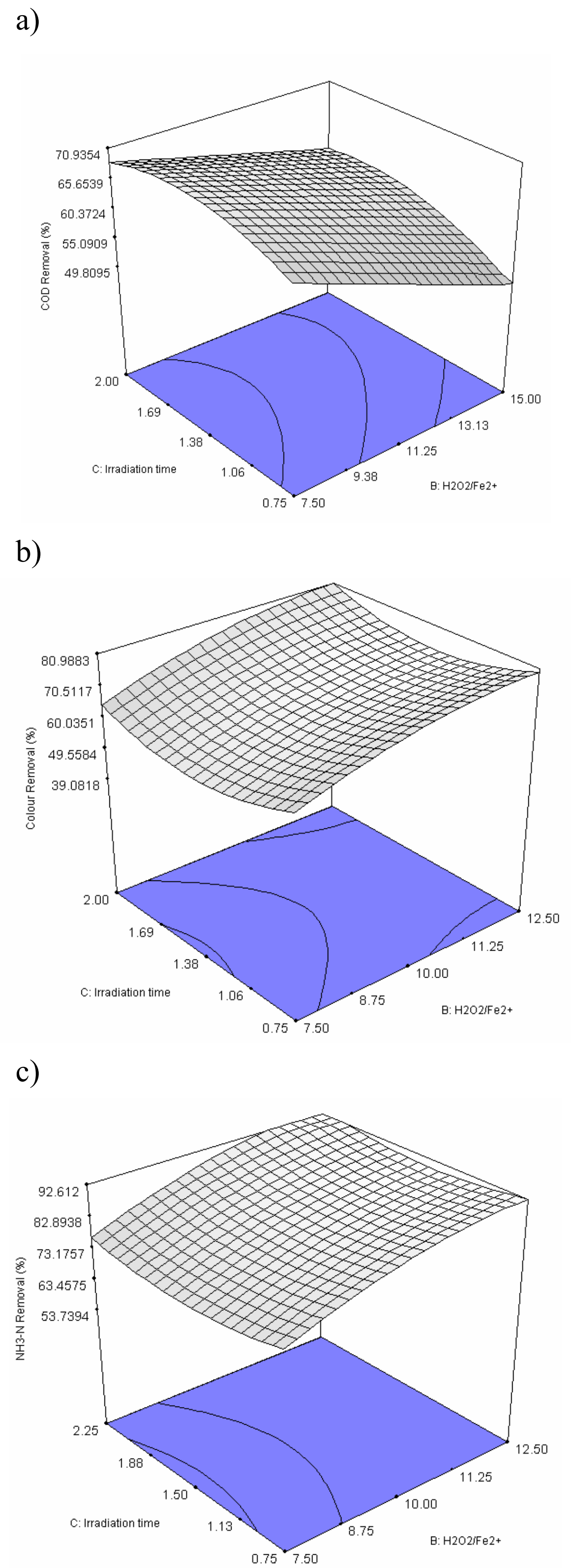

Fig. 4.9 Response Surface Plots of (a) COD, (b) Colour and (c) NH_3-N Removal as a Function of H_2O_2/Fe^{2+} Molar Ratio and Irradiation Time at H_2O_2/COD Molar Ratio 3.0

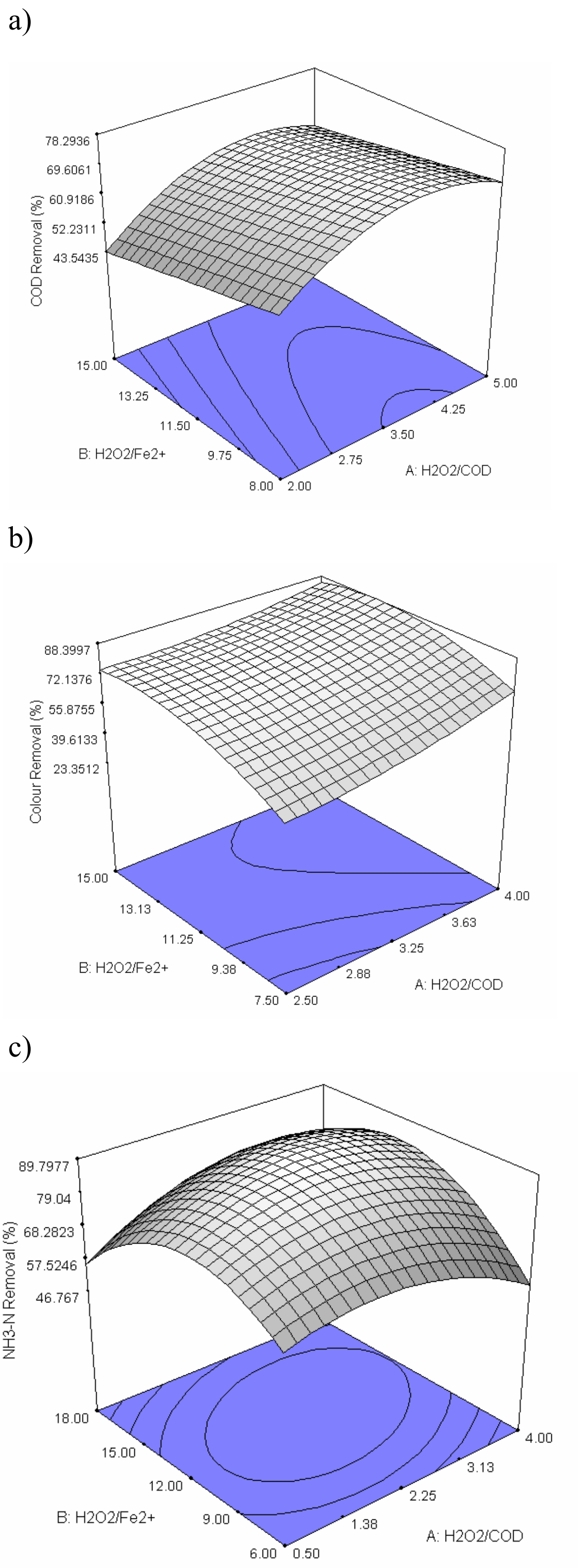

Fig. 4.10 Response Surface Plots of (a) COD, (b) Colour and (c) NH_3-N Removal as a Function of H_2O_2/COD Molar Ratio and H_2O_2/Fe^{2+} Molar Ratio at Irradiation Time 1.5 h

4.3.2.1 Effect of H_2O_2/COD Molar Ratio

Figure 4.8 (a), (b) and (c) show the maximum COD, colour and NH_3-N removal were 70.9, 86.5 and 89.9% at about H_2O_2/COD molar ratio 3.5-4.0 at H_2O_2/Fe^{2+} molar ratio 10. Figure 4.8 shows that COD and colour removal increases when the H_2O_2 dosage increases. This may be due to the fact that increased H_2O_2 dosage produces more hydroxyl radicals leading to higher substrate degradation (Deng and Englehardt, 2006). Further increase of H_2O_2 dosage either did not improve the removal efficiency. This may be due to scavenging of $^{\bullet}OH$ radical by H_2O_2 as in following reaction (Andreozzi et al., 2005). This reaction leads to the production of hydroperoxyl radical, a species with much weaker oxidizing power compared to hydroxyl radical (Ting et al., 2008).

$$^{\bullet}OH + H_2O_2 \longrightarrow HO^{\bullet}_2 + H_2O$$
(2.3)

Besides, an excess amount of H_2O_2 can cause the auto decomposition of H_2O_2 to water and oxygen (Eq. 2.8), and the recombination of $^{\bullet}OH$ radicals (Eq. 4.4) (Mandal et al., 2010), thereby decreasing the concentration of $^{\bullet}OH$ radicals and reducing degradation efficiency.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
(2.8)

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2$$
(4.4)

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

According to Fig. 4.9 (a), (b) and (c), the maximum COD, colour and NH_3-N removal were 70.9, 81.0 and 92.6% at about H_2O_2/Fe^{2+} molar ratio 7.5-15.0 at H_2O_2/COD molar ratio 3.0. Figure 4.9 shows that COD removal increases with increasing Fe^{2+} dosage and the result shows increase in COD removal with decrease in H_2O_2/Fe^{2+} ratio up to about 7.5-10.0. Further decrease in H_2O_2/Fe^{2+} ratio did not improve the removal efficiency due to direct reaction of $^{\bullet}OH$ radical with metal ions at high concentration of Fe^{2+} as in the following reaction (Joseph et al., 2000).

$$^{\bullet}OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^-$$

(2.4)

Figure 4.10 (a), (b) and (c) show interaction between H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios on COD, colour and NH_3-N removal. Maximum COD, colour and NH_3-N removal were 78.3, 88.4 and 89.8% at about H_2O_2/COD molar ratio 3.5-4.0 and H_2O_2/Fe^{2+} molar ratio 8.0-13.0 at irradiation time 1.5 h.

4.3.2.3 Effect of Irradiation Time

According to Fig. 4.8 (a), (b) and (c) and 4.9 (a), (b) and (c), the maximum COD, colour and NH_3-N removal were achieved at about irradiation time 1.0-2.0 h at H_2O_2/Fe^{2+} molar ratio 10 and H_2O_2/COD molar ratio 3.0. The results showed COD, colour and NH_3-N removal increased when the irradiation time increased. However, further increase of irradiation time above 1.5 h did not improve the process significantly. Further increase of irradiation time did not improve process efficiency. This may due to the fact that organics were rapidly degraded by the Fenton reagent and most organics removal occurred in 1.5 h.

Response surface plots indicate the optimum points in the range of H_2O_2/COD molar ratio 3.5-4.0, H_2O_2/Fe^{2+} molar ratio 7.5-12.5 and 1.5 h irradiation time with maximum removal of COD 78.3%, colour 88.4% and NH_3-N 92.6%, respectively. The relatively higher removals of the responses compared to Fenton process were due to the effect of UV irradiation which leading to more hydroxyl radicals production. Primo et al. (2008) investigated application of the photo-Fenton treatment for the leachate from a municipal landfill and the maximum COD removal was about 59%, using reagent dosages of 5000 mg/L of H_2O_2 and 2000 mg/L of Fe^{2+} (H_2O_2/Fe^{2+} molar ratio 4.1). This removal percentage increased to 77% when higher H_2O_2 concentration (15000 mg/L) was used (H_2O_2/Fe^{2+} molar ratio 12.4).

4.3.3 Process Optimization

With multiple responses, the optimum operating conditions where all parameters simultaneously meet the desirable removal criteria could be visualized graphically by superimposing the contours of the response surfaces in an overlay plot. Graphical optimization displays the area of feasible response value in the factor space and the regions that do fit the optimization criteria would be shaded (Mason et al., 2003). In order to obtain a moderately precise optimum zone, response limits as the minimum permissible values were chosen for each parameter close to their acquired removal efficiencies – COD 70%, colour 80% and NH_3-N 80% (Fig. 4.11). The shaded region shows the optimum parameters – H_2O_2/COD molar ratio 3.75, H_2O_2/Fe^{2+} molar ratio 10.0 and irradiation time 1.5 h, and constitute the optimum operating conditions. The results agree well with optimum H_2O_2/Fe^{2+} molar ratio of 7.5-26.2 reported in the literature (Kim and Vogelpohl, 1998; Primo et al., 2008).

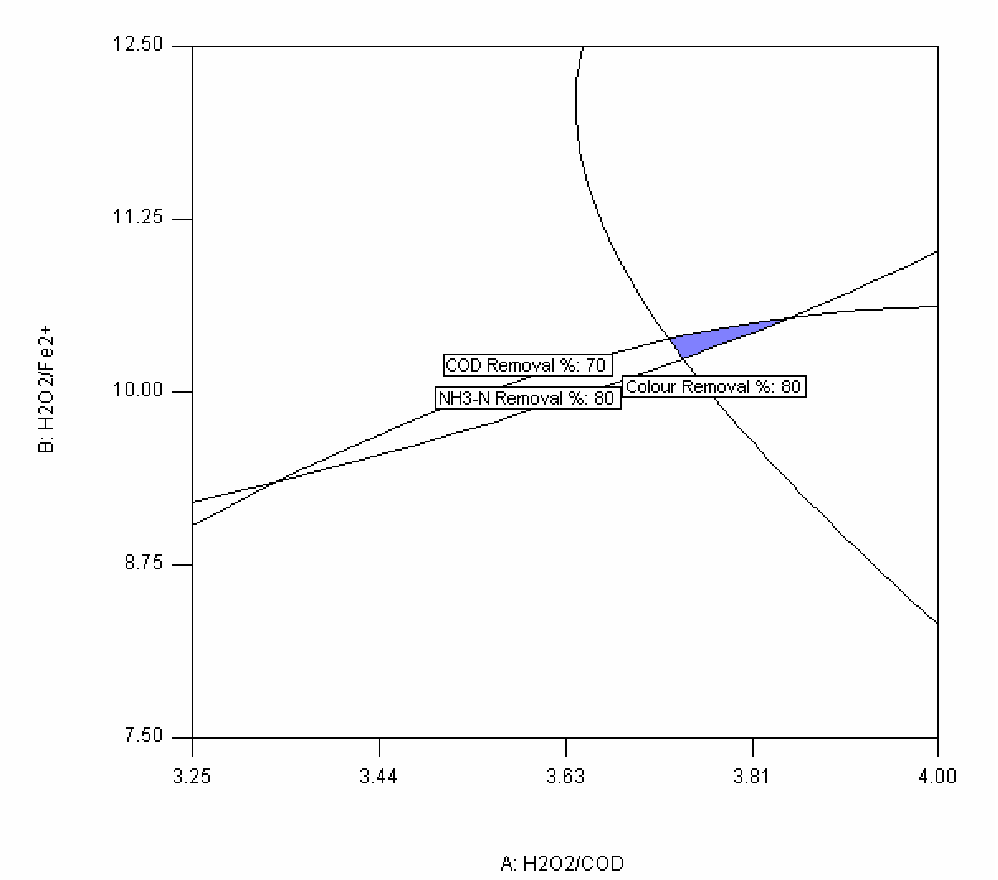

Fig. 4.11 Overlay Plot for Optimal Region at Irradiation Time 1.5 h

4.3.4 Model Results Verification

Three additional experiments were conducted applying the optimum operating conditions (H_2O_2/COD molar ratio 3.75, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h irradiation time) to verify the results obtained from the model. As shown in Table 4.7, the removal efficiency obtained from the experiment and by the model were in close agreement with less than 2% error.

Table 4.7 Verification Experiments at Optimum Operating Conditions (Photo-Fenton Process)

Responses	Model Response	Experimental Values	Error
COD removal (%)	70.0	65.8-73.4 (68.2)	-1.8
Colour removal (%)	80.0	79.2-82.0 (80.7)	0.7
NH_3-N removal (%)	80.0	78.9-81.2 (80.1)	0.1

The characteristics of the photo-Fenton treated leachate were: COD 350 mg/L, BOD_5 116 mg/L, BOD_5/COD ratio 0.33, NH_3-N 112 mg/L and colour 108 Pt-Co Units, and appeared amenable to biological treatment. Hence, photo-Fenton pretreatment proved to be more efficient than Fenton pretreatment.

However, photo-Fenton pretreatment of the leachate under Fenton pretreatment optimum operating conditions, with lower dosages of the Fenton reagent (H_2O_2/COD molar ratio 2.25 and H_2O_2/Fe^{2+} molar ratio 10.0) was conducted. Photo-Fenton which known to be able to improve the efficiency of the dark Fenton reagent by means of the interaction of radiation with the Fenton reagent (Hislop and Bolton, 1999). Hydroxyl radicals ($^{\bullet}OH$) are produced by the decomposition of hydrogen peroxide when reacting with ferrous ions in presence of UV light, which contributes an additional pathway to the generation of free radicals, increasing the concentration of $^{\bullet}OH$ radicals (Benitez et al., 2000). By using photo-Fenton process, the COD removal was significantly increased from 51% to 65% and BOD_5/COD ratio from 0.21 to 0.35 under the same operating conditions (H_2O_2/COD molar ratio 2.25 and H_2O_2/Fe^{2+} molar ratio 10.0) with reaction/irradiation time 1.5 h. Under these operating conditions, the characteristics of the treated leachate were: COD 390 mg/L, BOD_5 136 mg/L, BOD_5/COD ratio 0.35, NH_3-N 112 mg/L and colour 99 Pt-Co Units. Thus, the photo-Fenton process operating under lower dosages of the Fenton reagent with 1.5 h irradiation time was selected as pretreatment for the landfill leachate for further biological treatment.

4.4 Sequencing Batch Reactor (SBR)

The photo-Fenton treated leachate (Table 4.8) was subjected to biological treatment. The biological treatment system was composed of a 2-L aerobic bench scale sequencing batch reactor (SBR).

Table 4.8 Characteristics of Photo-Fenton-Treated Leachate

Parameter	Unit	Photo-Fenton Treated
pH	-	6.9-7.1
BOD_5	mg/L	136
COD	mg/L	390
sCOD	mg/L	330
BOD_5/COD	-	0.35
TKN	mg/L	157
NH_3-N	mg/L	112
NO_3^--N	mg/L	6.8

The SBR was inoculated with 300 mL of aerobic sludge to achieve the design MLSS 2000 mg/L following the procedure describe in section 3.3.4. An acclimation period was necessary to allow expression of appropriate enzyme-producing genes essential for biodegradation of the organics present in the feed. The feeding pattern for acclimation appeared to be successful, and the soluble COD removal of 65% was achieved after 8 d acclimation (Fig. 4.12). The effluent characteristics were sCOD 114 mg/L, TKN 72 mg/L, NH_3-N 48 mg/L and NO_3^--N 17 mg/L. Following acclimation, the SBR was operated for 30 d.

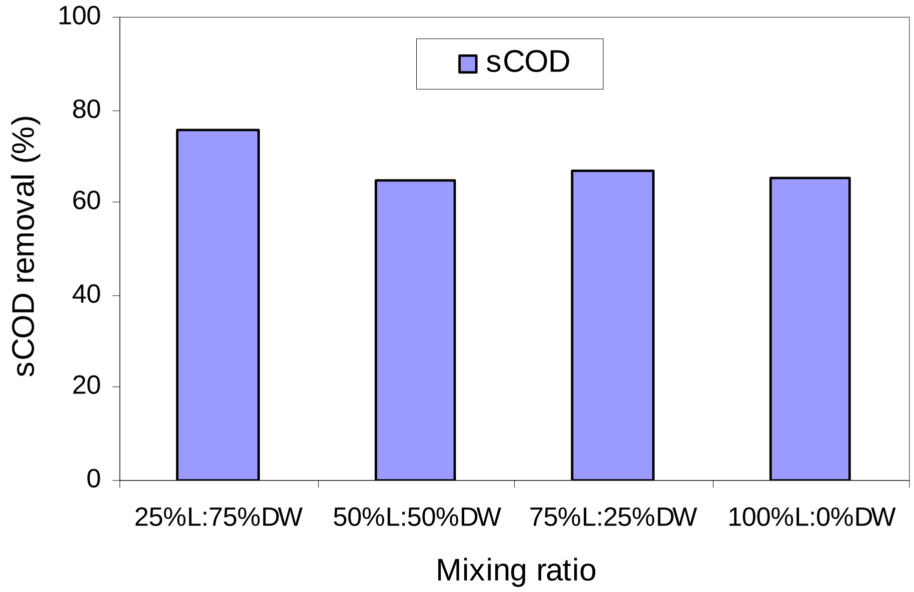

Fig. 4.12 System Performance Versus Leachate (L) : Domestic Wastewater (DW) Mixing Ratio During Acclimation Period

4.4.1 Process Performance

4.4.1.1 Soluble COD (sCOD), MLSS and BOD$_5$

Figure 4.13 shows the effluent soluble COD (sCOD) and MLSS during 30 d operation. Monitoring of MLSS was necessary to ensure that sufficient biomass was maintained in the reactor for biodegradation. The sCOD in the SBR effluent was 71 mg/L (COD 92 mg/L) with the removal percentage of 78%. It is to be noted that the degradation of organics occurred rapidly in the first 6 h (Fig. 4.14). Effluent BOD$_5$ after 30-d treatment was 26 mg/L with removal percentage of 81%. Guo et al. (2010) reported up to 83.1% COD removal and 82.8% BOD$_5$ removal in SBR (20 h aeration) treatment of a Fenton-treated leachate. Morais and Zamora (2005) reported more than 90% COD removal by SBR treatment of a photo-Fenton treated leachate.

It may be noted that the Malaysian Standard (B) for the discharge of treated industrial wastewater into water bodies is 100 mg/L in terms of total COD (EQA, 2007). Assuming that COD contribution by suspended solids is ≈ 20 mg/L, minimum sCOD in the final effluent should be around 80 mg/L. The SBR effluent (COD 92 mg/L, sCOD 71 mg/L and BOD_5 26 mg/L) met the requirement of the Malaysian Standard (B) (COD 100 mg/L, BOD_5 50 mg/L and suspended solids 100 mg/L).

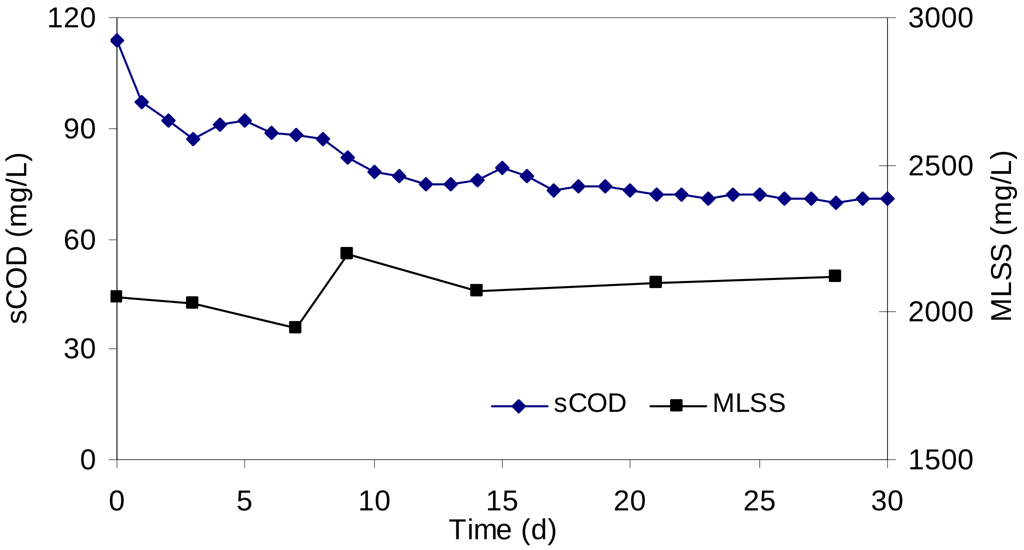

Fig. 4.13 Effluent Soluble COD (sCOD) and MLSS During SBR Operation

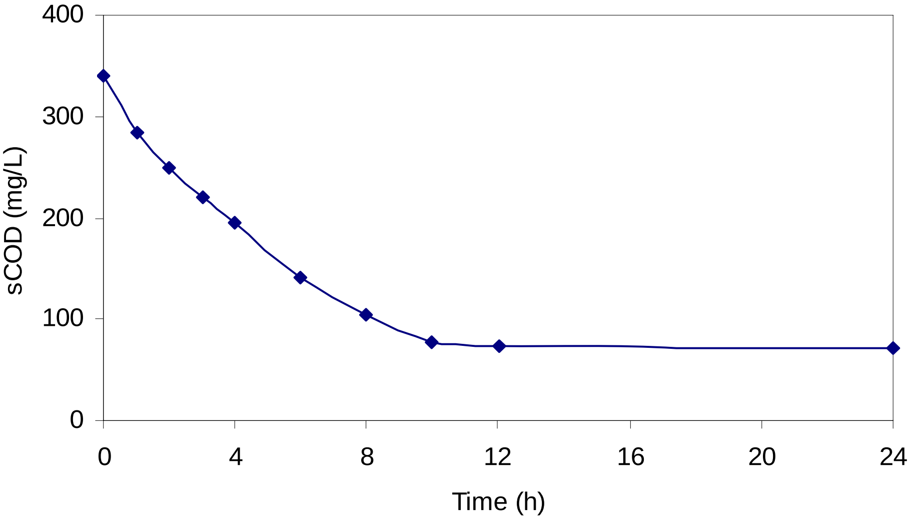

Fig. 4.14 Soluble COD (sCOD) During 24-h Cycle

4.4.1.2 Ammonia-Nitrogen (NH_3-N). Nitrate-Nitrogen (NO_3^--N) and Total Kjeldahl Nitrogen (TKN)

Figure 4.15 shows the effluent ammonia-nitrogen (NH_3-N), nitrate-nitrogen (NO_3^--N) and total Kjeldahl nitrogen (TKN) concentration during the SBR treatment, indicating nitrification (NH_3-N is oxidized to NO_3^--N) and can be shown in the following equation.

$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$
(4.2)

$NO_2^- + 0.5O_2 \rightarrow NO_3^-$
(4.3)

The NH_3-N and TKN gradually reduced from 112 to 7 mg/L and from 157 to 13 mg/L, respectively during the treatment, whereas NO_3^--N increased from 6.8 mg/L to 27 mg/L. Figure 4.16 shows the concentration of ammonia-nitrogen (NH_3-N), nitrate-nitrogen (NO_3^--N) and total Kjeldahl nitrogen (TKN) during a 24-h cycle. Nitrification occurred rapidly with about 75% conversion for both NH_3-N and TKN in the first 4 h.

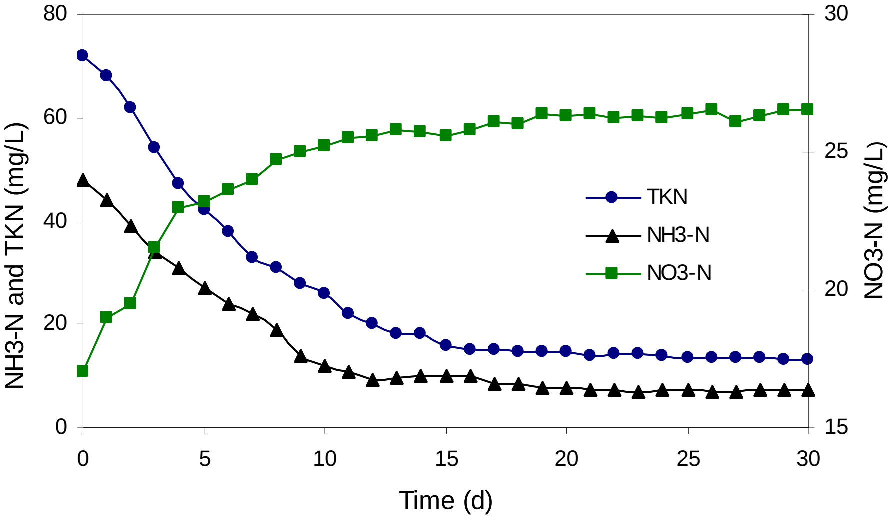

Fig. 4.15 Effluent Ammonia-Nitrogen (NH_3-N), Nitrate-Nitrogen (NO_3^--N) and Total Kjeldahl Nitrogen (TKN) During SBR Operation

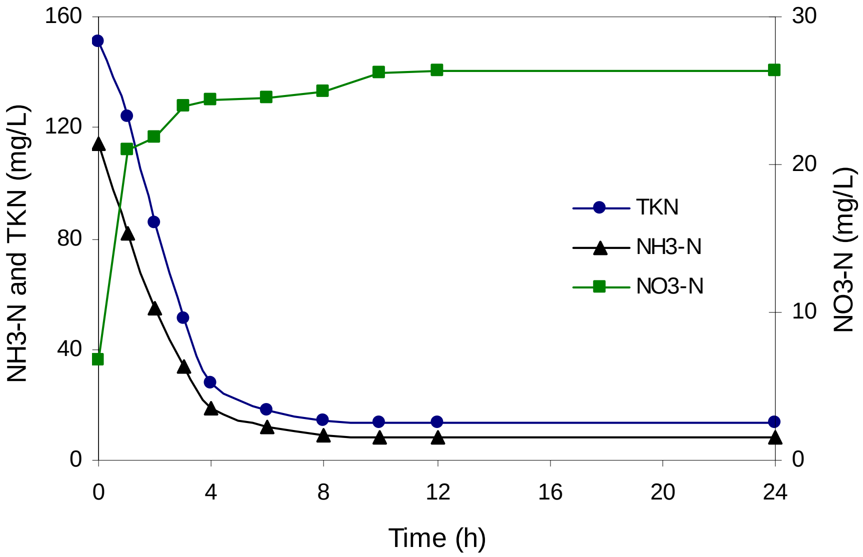

Fig. 4.16 Ammonia-Nitrogen (NH_3-N), Nitrate-Nitrogen (NO_3^--N) and Total Kjeldahl Nitrogen (TKN) During 24-h Cycle

Aerobic sequencing batch reactor (SBR) treatment of the photo-Fenton treated leachate resulted in sCOD, BOD_5 and NH_3-N removal of 78, 81 and 94%, respectively. The final effluent characteristics were COD 92 mg/L, sCOD 71 mg/L, BOD_5 26 mg/L, NH_3-N 7 mg/L, NO_3^--N 27 mg/L, TKN 13 mg/L and total suspended solids

38 mg/L. The effluent met the Malaysian discharge standard (B) (COD 100 mg/L, BOD_5 50 mg/L and suspended solids 100 mg/L).

4.5 Chapter Summary

In this chapter, the results of preliminary treatment, Fenton and photo-Fenton pretreatment and treatment of the pretreated leachate by sequencing batch reactor (SBR) have been presented and discussed.

The preliminary treated leachate (pH adjusted to 3.0 and settled) was subjected to advanced oxidation process (Fenton and photo-Fenton) pretreatment to improve biodegradability. The optimum operating conditions for Fenton treatment were H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h reaction time; and for photo-Fenton treatment were H_2O_2/COD molar ratio 3.75, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h irradiation time. Photo-Fenton treatment of the leachate under Fenton optimum operating conditions and 1.5 h irradiation time, produced an effluent of COD 390 mg/L, BOD_5 136 mg/L, BOD_5/COD ratio 0.35, NH_3-N 112 mg/L and colour 99 Pt-Co Units.

Aerobic sequencing batch reactor (SBR) treatment of the photo-Fenton treated leachate resulted in soluble COD, BOD_5 and NH_3-N removal of 78, 81 and 88%, respectively. The final effluent characteristics were COD 92 mg/L (sCOD 71 mg/L), BOD_5 26 mg/L, NH_3-N 7 mg/L, NO_3^--N 27 mg/L, TKN 13 mg/L, total phosphorus 6.4 mg/L, suspended solids 38 mg/L and colour 46 Pt-Co units, and met the Malaysian discharge standard (B) in terms of COD, BOD_5 and suspended solids.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.0 Chapter Overview

In this chapter, the scope of the study and research method are recapped, the results and findings of the study are summarized with conclusions and suggestions for future work are presented.

5.1 Conclusions

This study focused on a combined system – advanced oxidation process (AOP)-sequencing batch reactor (SBR) – for effective treatment of a landfill leachate. Leachate samples were taken from the leachate collection pond of the Pulau Burung landfill in Nibong Tebal, Penang. The leachate was subjected to preliminary treatment (pH adjustment and settling) for pretreatment by advanced oxidation processes (Fenton and photo-Fenton). Optimum operating conditions of the Fenton and photo-Fenton processes for effective pretreatment of the leachate were determined using response surface methodology (RSM). It was applied to optimize the three operating conditions of the Fenton and photo-Fenton processes: H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and reaction/irradiation time. The AOP-pretreated leachate was subjected to biological treatment by aerobic sequencing batch reactor (SBR). Removal of five-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended solids (TSS), ammonia-nitrogen (NH_3-N), nitrate-nitrogen (NO_3^--N) and total Kjeldahl nitrogen (TKN) were measured with a view to assess the combined system for effective treatment of the leachate.

The results and findings of the study are summarized below with conclusions:

1.3 pH adjustment-settling of the leachate resulted in removal of COD (45%), TSS (80%), turbidity (59%) and colour (68%) at pH 3. pH adjustment-settling appeared to be an adequate preliminary treatment for further pretreatment of the leachate by advanced oxidation process(es) operating at low pH such as Fenton and photo-Fenton processes.

1.3 Using RSM, the optimum operating conditions for Fenton treatment of the leachate was H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h reaction time with COD, NH_3-N and colour removal of 51, 84 and 77%, respectively. The characteristics of the Fenton pretreated leachate were: COD 545 mg/L, BOD_5 114.5 mg/L, biodegradability (BOD_5/COD ratio) 0.21, NH_3-N 90.5 mg/L and colour 120 Pt-Co Units. The residual COD was considered high and biodegradability of the Fenton pretreated leachate was low and hence not amenable to biological treatment.

1.3 Using RSM, the optimum operating conditions for photo-Fenton treatment of the leachate was H_2O_2/COD molar ratio 3.75, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h irradiation time with removal of COD, NH_3-N and colour 68, 80 and 81%, respectively. The characteristics of the photo-Fenton pretreated leachate were: COD 350 mg/L, BOD_5 116 mg/L, BOD_5/COD ratio 0.33, NH_3-N 112 mg/L and colour 108 Pt-Co Units. Hence, photo-Fenton pretreatment proved to be more effective than Fenton pretreatment and the pretreated leachate appeared amenable to biological treatment.

1.3 Removal efficiencies obtained from the experiment and by the model were in close agreement with less than 5% and 2% error for the Fenton and photo-Fenton processes, respectively. This study revealed that RSM was an effective tool to optimize the processes.

1.3 Under photo-Fenton pretreatment at the optimum operating conditions found in Fenton pretreatment, the characteristics of the photo-Fenton treated leachate were: COD 390 mg/L, BOD_5 136 mg/L, BOD_5/COD ratio 0.35, NH_3-N 112 mg/L and colour 99 Pt-Co Units. Thus, the photo-Fenton process operating under H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 and 1.5 h irradiation time was selected as pretreatment for the landfill leachate for further biological treatment.

1.3 Aerobic sequencing batch reactor (SBR) treatment (HRT 24 h, MLSS 2000 mg/L) of the photo-Fenton treated leachate resulted in sCOD, BOD_5 and NH_3-N removal of 78, 81 and 94%, respectively. The final effluent characteristics were COD 92 mg/L, sCOD 71 mg/L, BOD_5 26 mg/L, NH_3-N 7 mg/L, total phosphorus 6.4 mg/L, total suspended solids 38 mg/L and colour 46 Pt-Co Units. The effluent met the Malaysian discharge standard (B) (COD 100 mg/L, BOD_5 50 mg/L and suspended solids 100 mg/L) in terms of COD, BOD_5 and suspended solids..

1.3 The study showed that combined photo-Fenton-SBR provides effective treatment of a mature landfill leachate.

5.2 Suggestions for Future Work

Suggestions for future work for possible improvements and new directions:

1. To assess the potential of reusing the iron sludge formed during neutralization of the photo-Fenton treated leachate.

2. To evaluate TiO_2/UV photocatalysis as pretreatment for biological treatment of landfill leachate.

3. To study the use of solar irradiation for UV-based advanced oxidation processes such as photo-Fenton and TiO_2 photocatalysis for leachate treatment.

4. To study the feasibility of using other physicochemical processes such as coagulation-flocculation-carbon adsorption for complete treatment of landfill leachate.

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PUBLICATIONS AND ACHIEVEMENT DERIVED FROM THIS WORK

Conference Paper

1. **Heng, G. C.**, Elmolla, E. S. and Chaudhuri, M. 2009. Physicochemical pretreatment of landfill leachate. Presented at 2nd International Conference on Engineering Technology (ICET 2009). 8-10 December, 2009, Legend Hotel, Kuala Lumpur.

2. **Heng, G. C.**, Elmolla, E. S. and Chaudhuri, M. 2010. Optimization of the photo-Fenton process for removal of chemical oxygen demand from sanitary landfill leachate by response surface methodology. Presented at 1st International Conference on Sustainable Building and Infrastructure (ICSBI 2010). 15-17 June, 2010, Kuala Lumpur Convention Centre, Kuala Lumpur.

Achievement

1. Silver medal in Engineering Design Exhibition (EDX 24). Application of response surface methodology (RSM) to the treatment of landfill leachate by photo-Fenton process. 21-22 October, 2009, Universiti Teknologi PETRONAS.