TREATMENT OF STABILIZED LANDFILL LEACHATE BY THE COMBINATION OF COAGULATION-FLOCCULATION AND ADVANCED OXIDATION PROCESSES

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THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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TREATMENT OF STABILIZED LANDFILL LEACHATE BY THE COMBINATION OF COAGULATION-FLOCCULATION AND ADVANCED OXIDATION PROCESS

ABSTRACT

The stabilized landfill leachate (SLL) is complex wastewater that containing the high concentration of bio-recalcitrant organic matter. The application of conventional biological treatment was often found to be inefficient in reducing the organic content of SLL. Improper treated SLL can emerge into the environment and cause the soil and water pollution. Therefore, it is critical to apply the efficient treatment method to treat this hazardous wastewater before releasing it into the environment. The objective of this research was to develop and investigate the hydroxyl radical (•OH) and sulfate radical based advanced oxidation process (SR-AOP) for the treatment of SLL after coagulation-flocculation pretreatment. Coagulation-flocculation is a crucial pretreatment process to improve the effectiveness of AOP. In this study, the effectiveness of three coagulants, ferric chloride ($FeCl_3$), aluminium sulfate ($Al_2(SO_4)_3$) and polyaluminum chloride (PACL), in the removal of chemical oxygen demand (COD) was evaluated. The result indicated that the removal of COD was more favorable when the coagulation-flocculation was performed in the slightly acidic condition. Among the selected coagulants, $FeCl_3$ is the most efficient coagulant which produced 65-75% COD removal. However, it was found that the concentration of COD after pretreatment was still not complying with the maximum discharge standard of many countries indicating the requirement of further treatment. Pre-treated SLL was further treated with Fenton (Fe^{2+} & H_2O_2) and SR-AOP. In Fenton treatment, the result showed that 55% of COD was successfully reduced. However, the ecotoxicity of the Fenton reaction treated SLL was found to be higher than the pre-treated SLL due to the presence of H_2O_2 residue. In SR-AOP treatment, sulfate radical was generated using Fe(II) and Ultraviolet (UV) activation of persulfate (PS) and peroxymonosulfate (PMS). By using the optimized condition, more than 30 and 60% of COD concentration in the pre-treated leachate was successfully removed using Fe(II) and UV based SR-AOP, respectively. Since UV/SR-AOP showed higher efficiency in COD removal as compared to Fe(II)/SR-AOP, UV-based treatment was selected as the treatment for the development of laboratory scale continuous flow wastewater treatment system (CFWTS). In addition, PS was selected as the oxidants due to lower toxicity effluent production. In the continuous mode treatment, the COD removal was consistent with the previous UV/PS batch experiment. However, it required longer reaction time due to a higher volume of treated SLL. Since the changes of pH did not significantly affect the COD removal, the initial pH was adjusted to 11.5 for simultaneous removal of ammoniacal nitrogen (NH_3N). In this study, 91% COD and 68% of NH_3N were successfully removed from SLL. These findings indicated that the combination of coagulation-flocculation and SR-AOP could be an alternative method to be applied in a full-scale leachate treatment system.

Keywords: leachate, coagulation-flocculation, advanced oxidation process, Fenton reaction, sulfate radical

RAWATAN CECAIR LARUT RESAP STABIL MENGGUNAKAN KOMBINASI KOAGULASI-FLOKULASI DAN PROSES PENGOKSIDAAN TERMAJU

ABSTRAK

Cecair larut resap stabil (SLL) daripada pusat pelupusan sisa pepejal adalah sisa kumbahan yang kompleks dan mengandungi bahan bio-organik yang sukar terurai. Penggunaan rawatan konvensional secara biologi didapati tidak effektif bagi mengurangkan kandungan bahan organik di dalam SLL. Rawatan SLL yang tidak sesuai boleh menyebabkan pencemaran alam sekitar seperti pencemaran tanah dan air. Oleh itu, pengendalian SLL yang effektif adalah penting untuk merawat sisa kumbahan berbahaya ini sebelum dilepaskan ke persekitaran. Tujuan utama kajian ini adalah untuk mengkaji dan membangunkan sistem rawatan SLL menggunakan proses pengoksidaan termaju berteraskan hidroksi radikal ($\bullet$OH) dan sulfat radikal (SR-AOP) selepas proses rawatan koagulasi-flokulasi. Rawatan awal koagulasi-flokulasi adalah sangat penting untuk meningkatkan lagi keberkesanan proses pengoksidaan termaju. Di dalam kajian ini, keberkesanan tiga bahan penggumpal, ferric klorid ($FeCl_3$), aluminium sulfat ($Al_2(SO_4)_3$) dan polialuminium klorid (PACL) di dalam mengurangkan kepekatan keperluan oksigen kimia (COD) dinilai. Dapatan kajian menunjukkan pengurangan COD bagi proses koagulasi-flokulasi yang paling cekap adalah pada keadaan sedikit berasid. Di antara bahan penggumpal yang dinilai, $FeCl_3$ adalah bahan yang paling berkesan dengan menghasilkan 65-75% pengurangan COD. Walau bagaimanapun, kepekatan COD selepas koagulasi-flokulasi masih tidak mematuhi piawai pelepasan maksimum bagi kebanyakan negara dan memerlukan rawatan lanjut. Setelah dirawat menggunakan kaedah koagulasi-flokulasi, cecair larut resap seterusnya dirawat menggunakan SR-AOP dan Fenton. Di dalam rawatan Fenton (Fe^{2+}/H_2O_2), 55% daripada kepekatan COD berjaya dikurangkan. Walau bagaimanapun, SLL yang dirawat menggunakan rawatan Fenton menunjukkan kadar eko-ketoksikan yang lebih tinggi kerana lebihan H_2O_2 selepas rawatan. Di dalam rawatan SR-AOP pula, radikal sulfat dihasilkan menggunakan pengaktifan persulfat (PS) dan peroximonosulfat (PMS) oleh Fe(II) dan sinar ultralembayung (UV). Pada keadaan optimum, lebih daripada 30 dan 60% daripada kepekatan COD berjaya dikurangkan dengan menggunakan pengaktifan Fe(II) dan sinar UV. Rawatan UV/SR-AOP dipilih untuk membangunkan rawatan sisa kumbahan berterusan (CFWTS) kerana sistem ini menunjukkan keberkesanan yang lebih tinggi dalam menyingkirkan COD berbanding Fe (II)/SR-AOP. Tambahan itu, PS telah dipilih sebagai agen pengoksidaan kerana menghasilkan sisa kumbahan yang kurang toksik. Di dalam CFWTS, penyingkiran COD adalah konsisten dengan kajian eksperimen UV/PS tetapi memerlukan masa yang lebih panjang kerana isipadu SLL yang lebih tinggi digunakan. Oleh kerana perubahan pH tidak mempengaruhi pengurangan kepekatan COD, pH asal telah diubahsuai kepada 11.5 untuk sekaligus menyingkirkan ammoniacal nitrogen (NH_3N). Dapatan kajian mendapati, 91% COD dan 68% NH_3N berjaya disingkirkan dari SLL. Penemuan kajian mendapati kombinasi rawatan koagulasi flokulasi dengan SR-AOP boleh dijadikan sebagai rawatan alternatif dan berpotensi diaplikasikan di dalam sistem rawatan larut resap berskala penuh.

Kata kunci: Cecair larut resap, koagulasi-flokulasi, proses pengoksidaan termaju, Fenton, sulfat radikal.

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LIST OF SYMBOLS AND ABBREVIATIONS

AOP : Advanced Oxidation Process

BOD : Biochemical Oxygen Demand

COD : Chemical Oxygen Demand

CFWTS : Continuous Flow Water Treatment System

DAF : Dissolve Air Flotation

GAC : Granular Activated Carbon

LC$_{50}$: Lethal concentration

MDS : Maximum Discharge Standard

MSW : Municipal Solid Waste

MBBR : Moving Bed Biofilm Reactor

NH$_3$N : Ammoniacal Nitrogen

NF : Nanofltration

OECD : Organization for Economic Co-operation and Development

PACL : Polyaluminum Chloride

PS : Persulfate

PMS : Peroxymonosulfate

PAC : Powder Activated Carbon

RSM : Response Surface Methodology

RBC : Rotating Biological Contactor

RO : Reverse Osmosis

SBR : Sequential Batch Reactor

SR : Sulfate Radical

TOC : Total Organic Carbon

TF : Trickling Filter

TU : Toxicity Unit

UASB : Upflow Anaerobic Sludge Blanket

UV : Ultraviolet

WHO : World Health Organization

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CHAPTER 1: INTRODUCTION

1.1 Background of study

Rapid economic transition and urbanization have accelerated municipal solid waste (MSW) generation in developing countries (Guerrero et al., 2013). Mismanagement of MSW can cause adverse effect to the environmental, risk the public health, and other socio-economic related problems (Gupta et al., 2015). Numerous new waste management technologies for solid waste treatments such as incineration and biological composting have been adopted in recent years. However, the oldest method, landfilling is still the preferred option for MSW disposal especially in developing countries (Samsudin and Don, 2013). In general, up to 95% of MSW is disposed in landfills worldwide (Scott et al., 2005). Landfilling is among the cheapest method to manage solid waste as it does not require expensive machineries or high-technological equipment (Malek and Shaaban, 2008). Today, disposal of MSW in landfills remains an integral component in solid waste management even with the implementation of waste reduction, recycling, and transformation technologies (Tchobanoglous et al., 1993).

While landfilling provides a simple and economic means of waste disposal, if not properly managed, it can lead to severe environmental pollution. The greatest concern of landfilling is the contamination of surrounding ground and surface waters by landfill leachate (Wang et al., 2016). Landfill leachates are highly polluted effluent that are formed when liquid, usually water that seeps through the landfill (Emenike et al., 2012). As the water percolates through the solid waste, waste products are leached into the water, forming the leachate. Typically, municipal landfill leachates are containing high concentrations of organic substances, ammoniacal nitrogen (NH_3N), suspended solid, heavy metals, and inorganic salts (Bashir et al., 2015). Highly contaminated leachate may seep through the unsaturated soil layers at the bottom of the landfill into the groundwater, and then to surface water through hydraulic connections. Landfill leachate may also pollute the environment from the discharge of partially treated leachate from ineffective leachate treatment plants or from untreated leachate that are directly released into the environment without treatment (Ismail, 2013).

In recent decades, the development of leachate treatment technologies has caught up with the increasing waste generation and demand for the need of environmental protection (Amiri and Sabour, 2014; Oloibiri et al., 2015; Verma and Kumar, 2016; Asaithambi et al., 2017). With more restrictive effluent discharge standards, leachate treatment is becoming more sophisticated and complex. At present, no single treatment process is sufficient for the complete and proper leachate treatment because the pollutants to be treated are simply too varied and concentrated (Wu et al., 2011). Leachate treatment plants are usually applied a combination of different processes such as biological, chemical, and physicochemical treatment (Ahmed and Lan, 2012; Gupta et al., 2014; Liu et al., 2015) to treat the leachate. The combined processes have the ability to synergize the advantages of each single process, and this has been documented as effective treatment method for treating landfill leachate (Wu et al., 2011).

Based on previous literature, leachate characteristics will change with time, and extensive modification on leachate treatment process are required as the landfill aged (Bashir et al., 2015). For example, conventional biological treatment such as the treatment that involved activated sludge was efficient in the removal of biodegradable organic substance from fresh landfill leachate. However, it was unable to remove the recalcitrant organic compounds such as humic acid, fulvic acid and hydrophilic fractions that frequently exist in the matured landfill leachate (Wang et al., 2012). Other conventional treatments such as coagulation-flocculation, clarification and filtration are also insufficient to reach the level of purification needed to fully remove the negative impact of landfill leachates on the environment. Therefore, new alternatives treatment must be employed in dealing with the recalcitrant substances in matured leachate or so-called stabilized landfill leachate (SLL).

Advanced treatment processes such as advanced oxidation processes (AOPs) are increasingly being studied as a polishing step after the physical or biological treatment of wastewater (Deng and Zhao, 2015). AOPs are recognized tools to destroy recalcitrant compounds or, at least, to transform them into biodegradable species (Ribeiro et al., 2015). AOPs was first defined as the oxidation processes involving the generation of sufficient hydroxyl radicals (•OH) for the destruction of organic or inorganic contaminants in water and wastewater (Ghanbari and Moradi, 2017). Later, the AOPs concept was extended to include other oxidative radicals such as sulfate radicals (SR) (Deng and Zhao, 2015). When AOPs are applied for wastewater treatment, the radical species act as a powerful oxidizing agent to decompose organic compounds into simpler and benign products such as CO_2, H_2O, and organic acids (Al-Sarawy and Wali, 2005). Among the AOPs, Fenton reaction has been frequently applied in the treatment of various wastewaters including landfill leachate (Lucas et al., 2012; Amor et al., 2015; Durán et al., 2015; Expósito et al., 2016; Verma and Kumar, 2016; Perez et al., 2017). This method applies H_2O_2 as an oxidizing reagent and Fe(II) as a catalyst to generate the •OH. Due to low energy consumption and modest integration with other treatment methods, Fenton reaction has been widely used in full-scale wastewater treatment (Bautista et al., 2008). In addition, the toxicity of the effluent before and after treatment was usually ignored in most of the studies. Most studies on leachate treatment system has been focused on the chemical oxygen demand (COD) removal without considering the toxicity of the effluent. In some cases, high organic removal efficiency does not always reflect the toxicity removal of the effluent (Ishak et al., 2017).

Besides Fenton, sulfate radical based advanced oxidation process (SR-AOP) has drawn increasing attention for the degradation of a broad spectrum of organic pollutants (Asaithambi et al., 2017). During SR-AOP, SR ($E^{o} = 2.5$-3.1 V) is the main reactive species that degrade organic compounds. SR can be generated from persulfate (PS) and peroxymonosulfate (PMS) through various activation methods such as heat, addition of transition metals, or exposure to ultraviolet light (UV) (Zhou et al., 2015). Compared to $\bullet$OH which can be deactivated easily by water matrices, SR reacts selectively with organic compounds through electron transfer reaction (Matzek and Carter, 2016). SR-AOP was found to be efficient in removing organic pollution such as pharmaceuticals, herbicides, phenols, perfluorinated compounds, and bacteria in water treatment and groundwater remediation (Anipsitakis et al., 2006). However, most of these studies were only focused on the treatment of individual compounds in water (Olmez-Hanci and Arslan-Alaton, 2013; Ghanbari et al., 2016). The application of SR-AOP in real wastewater treatment which involves complicated water matrices such as landfill leachates is still rarely reported. The treatment of the real wastewater is important in providing information on the applicability of the treatment method. Recently, Fagier et al. (2016) reported that the high efficiency of SR-AOP in the treatment of distillery wastewater. This study showed that the organic content of the distillery wastewater can be removed at neutral pH. Therefore, SR-AOP is a method with high potential for industrial scale water treatment (Ghanbari and Moradi, 2017). To date, there is only very limited literature on the usage of SR-AOP for the treatment of landfill leachate and UV-based SR-AOP has not been reported elsewhere.

In this work, the feasibility of two AOP technologies; Fenton and SR-AOP in the treatment of pre-treated SLL were evaluated. The efficiency of each treatment process in the removal of total organic carbon (TOC), COD, colour, and turbidity of pre-treated SLL were studied. In addition, the toxicity study for the treated leachate was also evaluated. In this study, the acute toxicity of raw and treated SLL was measured using zebrafish (*Danio rerio*). Zebrafish has been classified as a model vertebrate for chemical (Hill et al., 2005) and aquatic toxicity studies (Moșneang et al., 2014). As reported by Hollert and Keiter (2015), numerous critical pathways that regulate vertebrate development are highly conserved between humans and zebrafish and therefore, zebrafish can be used as a prominent model organism for the study of the effects of pollutant towards humans and the environment. Different living organisms may respond differently to the toxicity of the tested substances. Therefore, multi-species testing is crucial for evaluating toxicity variation during treatment processes (Kuang et al., 2013). In addition, the relative toxicity of leachate and treated leachate based on seed germination of ladies fingers (*Abelmoschus esculentus*) and mung beans (*Vigna radiata*) was also evaluated.

The optimized treatment conditions from the batch study was then used to develop a modular type laboratory-scale continuous-flow water treatment system (CFWTS). The system consists of a coagulation-flocculation reactor, AOPs treatment (ammonia stripping-UV/PS system), and cation exchange column. The aim of this system is to provide an alternative and improved method to currently available leachate treatments. This modular feature of the treatment system allows it to be retrofitted to existing systems in laboratory and for future different water treatment system to be installed in conjunction.

1.2 Objectives of the research

The objectives of this study were:

1. To assess the efficiency of coagulation-flocculation as a pretreatment prior to Fenton, and SR-AOP treatment.
2. To evaluate the efficiency of Fenton treatment in the removal of TOC, COD, turbidity, and toxicity of pre-treated SLL.
3. To evaluate the efficiency of SR-AOP in the removal of TOC, COD, turbidity, and toxicity of pre-treated SLL.
4. To develop a CFWTS based on the optimization of previous objectives.

1.3 Outlines of thesis

This thesis is organized into five chapters. Chapter 1 gives a brief introduction on the research background and research objectives. A review of the related literature is presented in Chapter 2. Chapter 3 presents the experimental and analytical procedure used in this study. Chapter 4 discusses the optimization of coagulation-flocculation, Fenton, and SR-AOP for leachate treatment. The performance of each treatment in terms of COD, TOC, colour, turbidity, and toxicity reduction are presented in this chapter as well. Finally, the overall conclusions, together with recommendations of future works are provided in Chapter 5.

CHAPTER 2: LITERATURE REVIEW

2.1 Municipal Solid Waste (MSW) Management

The Organization for Economic Co-operation and Development (OECD) (2018) has defined municipal solid waste (MSW) as the waste collected and treated by, or for municipalities. This includes waste from households, commerce and trade, office buildings, institutions and small businesses, yard and garden, street sweepings, contents of litter containers or market cleansing. The population growth, economic development, higher rate of urbanization, and the rise in community living standards are among the factors that increased the global MSW (Guerrero et al., 2013). Improper MSW management often caused harmful effect to the environment. It has becoming a serious threat for most of the local authorities (Sharholy et al., 2008).

Table 2.1 shows the worldwide MSW production in 2012, and its projection for 2025 by region (Hoornweg and Bhada-Tata, 2012). The OECD region was the largest MSW contributor in 2012, generating 44% of the total global MSW whereby 1.57 million tonne of solid waste per day was generated with an estimated per capita value of 2.2 kg/capita/day. The East Asia and Pacific regions came to the second place for MSW contribution of 0.74 million tonne/day with an average per capita waste generation of 0.95 kg/capita/day. It was noted that more than 70% of the waste generated in the East Asia and Pacific region was contributed by China (Hoornweg et al., 2005). In Table 2.2, it is depicted that high-income countries produce more waste per capita than low income countries due to their higher rate of urbanization. However, the data for lower and upper middle-income countries were skewed due to the classification of China and India in the lower middle-income group. These countries have disproportionately high urban waste generation rates per capita relative to overall economic status as they have large relatively poor rural populations that tend to dilute national figures. Overall, it was projected that the global MSW to increase almost 3-fold to approximately 6.1 million tonne/day by 2025 compared to the recent 2012 MSW data.

Malaysia has risen from the ranks of a lower income economy in the 1970s to an upper middle-income economy in 1992 (Economic Planning Unit, 2010). With the economic booming and urbanization, waste generation in Malaysia has been increasing drastically. The solid waste generation was estimated to increase from 21,918 tonne/day in 2012 to the estimated 51,655 tonne/day in 2025 (Agamuthu and Victor, 2011). An average waste generation per capita in Malaysia was 1.52 kg/capita/day and expected to reach 1.90 kg/capita/day by 2025 (Hoornweg and Bhada-Tata, 2012). These values are found to be higher than the projected per capita value for the world and East Asia Pacific region (Table 2.1). Therefore, MSW has become such an attentive issue in this country.

Table 2.1: Waste generation projection for 2025 by region (Hoornweg and Bhada-Tata, 2012).

Region	**Current Available Data**			**Projections for 2025**			
	Total Population (millions)	Per Capita (kg/capita/day)	Total (tonne/day)	Total Population (millions)	Urban population (millions)	Per Capita (kg/capita/day)	Total (Tonne/day)
Africa region (AFR)	260	0.65	196 119	1 152	518	0.85	441 840
East Asia and Pacific (EAP)	777	0.95	738 958	2 124	1 229	1.50	1 865 379
Europe & Central Asia (ECA)	227	1.10	254 389	339	239	1.50	354 810
Latin America & Caribbean (LAC)	399	1.10	437 545	681	466	1.60	728 392
Middle East & North Africa (MENA)	162	1.10	173 545	379	257	1.43	369 320
Organization for Economic Co-operation and Development (OECD)	729	2.20	1 566 286	1 031	842	2.10	1 742 417
South Asia Region (SAR)	426	0.45	192 410	1 938	734	0.77	567 545
Total	**2 980**	**1.10**	**3 559 252**	**7 644**	**4 285**	**1.40**	**6 069 703**

Table 2.2: Waste generation projection for 2025 by income level (Hoornweg and Bhada-Tata, 2012).

	Current Available Data			**Projections for 2025**			
Income Level	Total Population (millions)	Per Capita (kg/capita/day)	Total (tonne/day)	Total Population (millions)	Urban population (millions)	Per Capita (kg/capita/day)	Total (Tonne/day)
Lower Income	343	0.60	204 802	1637	676	0.86	584 272
Lower Middle Income	1 293	0.78	1 012 321	4 010	2 080	1.3	2 618 804
Upper Middle Income	572	1.16	665 586	888	619	1.6	987 039
High Income	774	2.13	1 649 547	1 112	912	2.1	1 879 590
Total	**2 982**	**1.20**	**3 532 256**	**7 647**	**4 287**	**1.50**	**6 069 705**

The increased of MSW generation throughout the world requires an urgent implementation of efficient MSW management. In recent decades, an integrated approach based on the hierarchy of solid waste management has been increasingly implemented (Menikpura et al., 2013; Othman et al., 2013). Waste management hierarchy was first introduced in the European Union's Second Environment Action Programmed in 1977 (Marshall and Farahbakhsh, 2013). The hierarchy comprises the following elements: source reduction and reuse, recycling and composting, energy recovery, and treatment and disposal. The hierarchy ranks the various management strategies from the most to the least environmentally preferable ways to manage solid waste with the aim to extract the maximum practical benefits from products and to generate the minimum amount of waste (Figure 2.1). Although source separation, recycling, composting, and energy recovery technology may undoubtedly have decreased the amount of MSW generated, but the most practical and commonly employed method for MSW management in developing and poor countries is still landfilling (Ismail, 2013). As in other developing countries, Malaysia too disposes 95% of MSW in landfills (Moh and Abd Manaf, 2014).

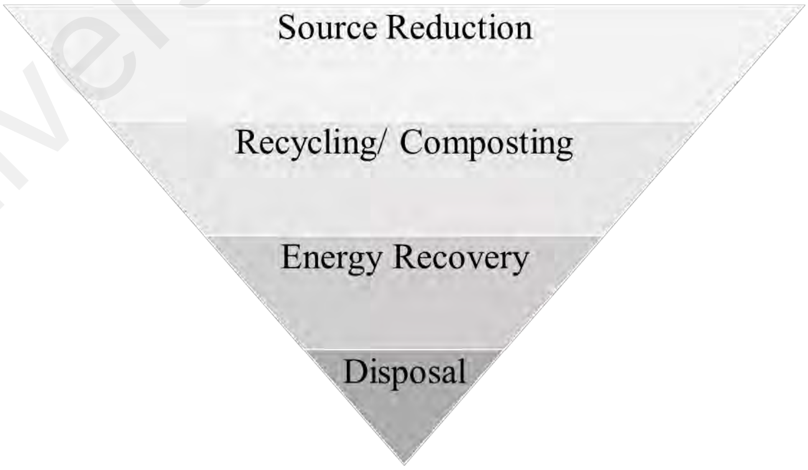


Figure 2.1: Integrated Solid Waste Management hierarchy (Marshall and Farahbakhsh, 2013).

2.2 Landfilling

According to a report by Hoornweg and Bhada-Tata (2012), more than 300 million tonne of MSW ends up in landfills every year, worldwide (Figure 2.2). The versatility and simplicity of landfilling in terms of technical requirements and socio-economic aspects makes it an attractive technique for waste management (Malek and Shaaban, 2008). The landfilling process comprises the monitoring of the incoming waste stream, placement, and compaction of the waste. Installation of landfill environmental monitoring and control facilities are necessary to ensure the continuous operation of the landfill (Tchobanoglous et al., 1993).

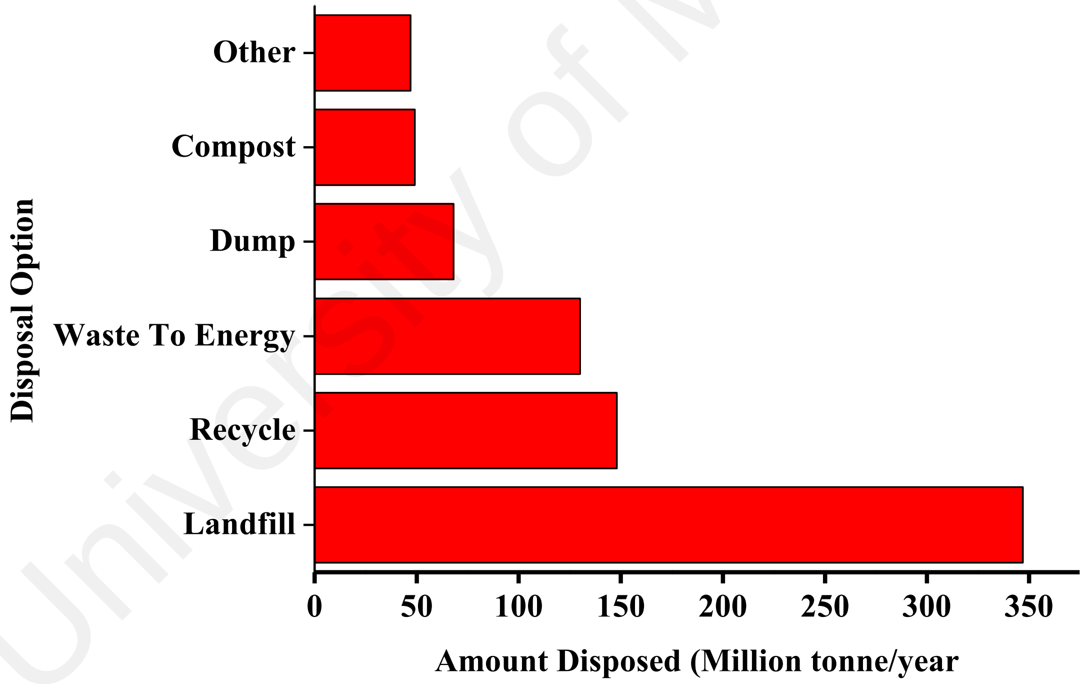


Figure 2.2: Total MSW disposed worldwide (Hoornweg et al., 2012).

Current landfilling practices throughout the world ranging from uncontrolled "open dumps" to modern sanitary landfills. In high income countries, sanitary landfills that utilized liners, leak detection, leachate and gas collection, and treatment systems are used intensively (Hoornweg and Bhada-Tata, 2012). A sanitary landfill is a landfill that is designed to protect public health and to minimize environmental pollution (Tchobanoglous et al., 1993). However, in middle income countries, less than 5% of MSW are deposited in sanitary landfills while in lower income countries, the bulk of collected MSW are simply disposed in "open dumps" (Modak et al., 2010). An "open dump" is defined as a land disposal site at which MSW are disposed of in a manner that does not protect the environment, are susceptible to open burning, and are exposed to disease vectors and scavengers (Agamuthu, 2001).

In Malaysia until now, there are about 156 operational landfills (Table 2.4). Only 23 of these landfills are classified as sanitary landfills and the remaining are constructed without a proper long-term plan (SWCop, 2018). In the 1988 Action Plan, the Malaysian government has tried to improve these disposal sites stepwise by forming four targeted levels of improvement (Noor et al., 2013). The levels are shown in Table 2.3. All current landfilling practices in Malaysia is required to achieve level 4 within a given time frame or else they would be requested to cease the operation in specific dates (Fauziah and Agamuthu, 2012). In addition, the prohibition of new non-sanitary and open dumping area through the Malaysian Solid Waste and Public Cleansing Management (SWPCM) Act 2007 has minimized pollution emissions from these dumping grounds and resulted in a better management and monitoring system of landfills in the country.

Table 2.3: Level of Sanitary Landfill System.

Level	Descriptions
1	Controlled dumping
2	Sanitary landfill with daily cover
3	Sanitary landfill with leachate circulation
4	Sanitary landfill with leachate treatment

Table 2.4: Operational and non-operational landfill sites in Malaysia (SWCorp, 2018).

State	Operational landfill	Non-Operation Landfill Site	Total
Johor	14	25	37
Kedah	8	8	15
Kelantan	13	9	20
Melaka	2	7	8
Negeri Sembilan	7	14	19
Pahang	16	16	32
Perak	17	15	31
Perlis	1	1	2
Pulau Pinang	2	1	3
Sabah	19	1	23
Sarawak	49	17	63
Selangor	8	15	23
Terengganu	8	12	21
WP Kuala Lumpur	0	7	7
WP Labuan	1		
Total	**156**	**148**	**304**

2.3 Potential environmental and public health impacts of landfills

Despite its advantages, landfilling might potentially cause some negative effects not only on the public health but also to the environment. Landfills attract various scavengers such as birds, rodents (e.g. rats) and insects (e.g. houseflies) at the site. These scavengers may act as vectors of infectious diseases such as typhoid, cholera, and dysentery (Kimbugwe and Ibitayo, 2013). In addition, landfills also contribute to dust and malodours to the local vicinity (Al-Khatib et al., 2015). These issues can be mitigated by the use of proper compaction and covering of the solid waste (McBarnette, 2011).

Another main environmental concern is the formation of uncollected methane gas. Methane is a greenhouse gas and a by-product of anaerobic degradation of organic matter. Overall methane formation originating from landfills makes up 5% of the total anthropogenic greenhouse gas emissions (Bogner et al., 2008). In high income countries, the organic content of waste ending up in landfills is typically low and when coupled with pre-treatment of the waste, uncollected methane generation is only at the minimum level. However, in middle and low income countries, high unprocessed organic content in waste especially from uncontrolled open dumps cause higher methane emissions (Christensen, 2011).

2.4 Leachate generation

A landfill leachate is the residual liquid generated during the biochemical decomposition of MSW or as the result of water percolation through solid wastes undergoing the degradation process (Vedrenne et al., 2012). Water from rainfall, underground source, or a nearby water body can leach various toxic inorganic and organic compounds from the MSW that it comes into contact with. This leachate generation has become the main problem associated with the landfilling (Ahmed and Lan, 2012).

There are many factors that affects the quality and composition of landfill leachates. These factors are waste characteristics, landfill age, precipitation and seasonal weather variation (Bashir et al., 2015). In a typical landfill, there are three basic phases of MSW decomposition (Tchobanoglous et al., 1993). These three phases lead to the different characteristics and compositions of landfill leachates. Phase I is the initial aerobic stage in which the biodegradable components in the MSW undergo microbial decomposition. In this phase, biological decomposition occurs under aerobic conditions. This process involves the hydrolysis of higher molecular mass compounds such as lipids, protein and nucleic acid by microorganisms for their metabolic processes (Tchobanoglous et al., 1993). The high moisture content in the MSW in Phase I induces Phase II, which is the acetogenic fermentation process (Renou et al., 2008). In this process, the matter from Phase I undergoes microbial conversion into lower molecular mass intermediate compounds to the large fraction of acetic acid (CH_3COOH) and a low concentration of fulvic acid and some other more complex organic acids (Renou et al., 2008). Carbon dioxide (CO_2) is the principle gas generated during Phase II. If the leachate is collected during this phase, the pH value would be low due to the presence of organic acids and elevated concentrations of CO_2. In this phase, the low pH also causes several inorganic constituents such as heavy metals to be solubilized. Subsequently, the BOD, COD, and TOC will be high due to the dissolution of the organic acids in the leachate (Renou et al., 2008). In Phase III, as the landfill matures, methanogenic fermentation process occurs. Methanogenic microorganisms convert the acetic acid from Phase II to methane and carbon dioxide. The organic fraction in the leachate becomes rich with recalcitrant compounds of high molecular weights such as humic and fulvic-like material (Renou et al., 2008). The removal of acetic acid causes the leachate to become more neutral with the pH range of 6.8 to 8. Meanwhile, the BOD, COD, and TOC values will also be reduced. The increase in pH value would also precipitate out heavy metals from the leachate.

The mentioned three phases will result in the changes of physical, chemical and biological characteristics of leachate which will further determine its classification. Lower pH, higher organic concentration but more biodegradable is classified as a fresh or young leachate, whereas, old or stabilized landfill leachate (SLL) is characterized by higher pH, lower organic concentration but less biodegradable. Table 2.5 showed the typical leachate classification based on the age of the landfills.

Table 2.5: Landfill leachate classification (Bashir et al 2015).

Parameter	**Type of Leachate**		
	Young	**Intermediate**	**Stabilized/Old**
Age (year)	<5	5-10	>10
pH	<6.5	6.5-7.5	>7.5
COD (mg/L)	>10 000	4000 – 10 000	<4000
BOD_5/COD	>0.3	0.1-0.3	<0.1
Content of Organic compounds	80% acetic acid	5-30% Acetic acid + Humic and Fulvic acids	Humic and Fulvic acids
Concentration of metal	Low-medium	Low	Low
Biodegradability of organic compound	High	Medium	Low

2.5 The treatment of landfill leachate

Landfill leachate can have a relatively variable composition. The type of pollutants present in its composition must be taken into consideration when selecting the appropriate treatment technology. There is no single treatment method that can adequately treat the myriad of pollutants present in landfill leachate. Often, a combination of two or more different treatment methods are needed depending on the type and severity of the pollutant. In the previous decade, the aim of landfill leachate treatments was simply the reduction of COD and NH_3N content. Today, the aim of landfill leachate treatment has been extended toward the removal of non-biodegradable organic substances as well as to meet the requirement of more stringent effluent discharge limits. Indeed, many leachate treatment plants have upgraded to more sophisticated systems by utilizing a combination of many different treatment technologies.

Generally, the leachate treatments can be classified as biological treatment, physical treatment, physicochemical treatment and advanced oxidation processes (AOPs). The selection of appropriate treatment's combination would provide better treatment efficiency with the cost-effectiveness (Christensen, 2011). Several common combination of leachate treatments was illustrated in Figure 2.3. The following sections highlight some treatment technologies that have been applied for the treatment of landfill leachate.

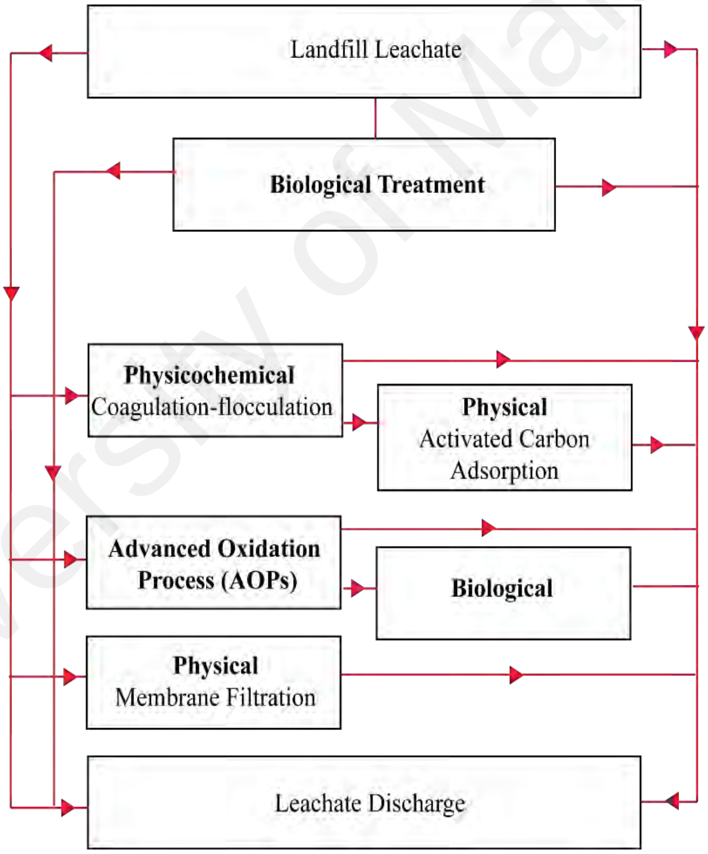


Figure 2.3: Several combination of leachate treatment technologies.

2.5.1 Biological treatment

Biological treatment relies on microorganisms to break down the organic matter under aerobic or anaerobic conditions. Both aerobic and anaerobic biological treatments can be further categorized as either suspended or attached growth system. Aerated lagoon activated sludge process, sequential batch reactor and Upflow anaerobic sludge blanket (UASB) are the common suspended biological treatment for landfill leachate.

The aerated lagoon is a classic aerobic system that is relatively simple in terms of plant construction, maintenance costs, and quick start-up. Robinson and Grantham (1988) reported that almost 97% removal of COD from landfill leachate was removed using aerated lagoon. In another study conducted by Mehmood et al. (2009), 80% of NH_3N and 75% of COD were successfully removed from landfill leachate with retention times varying from 11 to 254 days. Although the aerated lagoon ensures high removal of pollutants, this method is always associated with long retention time (Aziz et al., 2014). In addition, the lagoon temperature is a limiting factor as it retards bacterial growth and thus reducing the overall effectiveness of the treatment system (Bove et al., 2015).

Activated sludge process is different from conventional aerated lagoons where it has a separate settling tank after the aeration reactor for the biomass to settle and return to the aeration tank as activated sludge. Bae et al. (1999) reported the successful removal of 98% of BOD during the 72 h batch test using activated sludge process. This finding was in agreement with a report by Al-Jlil (2009) which used the same method, indicating that 92, 98 and 84% of BOD, COD and NH_3N removal, respectively. Although activated sludge process ensures effective removal, the concentration of COD and BOD after the treatment still above the standard regulation and required additional leachate treatment (Aziz et al., 2014). In addition, there are some drawbacks of this method in treating landfill leachates such as insufficient sludge sedimentation, high energy consumption and excessive sludge production (Bove et al., 2015).

The sequential batch reactor (SBR) is another technology based on the modification of the activated sludge process. Zouboulis et al. (2001) studied the laboratory-scale SBR for the treatment of sanitary landfill leachate. The results showed that almost 70, 40 and 60% of the removal of BOD, COD and NH_3N, respectively. In another study conducted by Uygur and Kargı (2004), 44% of NH_3N and 75% of COD were reported to be removed from landfill leachate within 21 h using SBR. The performance of SBR in leachate treatment is relatively weaker in industrial wastewater treatment (Aziz et al., 2014). In addition, this technology also required a higher level of maintenance due to its more sophisticated control system (Mahvi, 2008).

The most widely used anaerobic suspended method for leachate treatment is Upflow Anaerobic Sludge Blanket (UASB) (Anand and Singh, 2014). Kettunen and Rintala (1995) conducted a pilot-scale UASB for the treatment of municipal landfill leachate. The removal efficiencies of COD and BOD_5 were found to be 65-75% and up to 95%, respectively. Another study conducted by Kennedy and Lentz (2000) reported the COD removal efficiency of 92% from landfill leachate using UASB reactor. Although the efficiency of these reactors is impressive, it has been reported to be unsuitable for landfill leachate because it inhibits granular sludge formation and sludge methanogenic activity. Furthermore, landfills regularly deal with high leachate flow rates and continuous flow could cause active sludge washout (Wangnai et al., 2014).

An alternative approach to suspended biological leachate treatment is the used of attached growth system. A few examples of attached growth system use in leachate treatments are rotating biological contactor (RBC), trickling filter (TF) and moving bed biofilm reactor (MBBR). The RBC makes used of a series of disc with biofilm on its surface. Castillo et al. (2007) reported the feasibility of small-scale RBC for the treatment of landfill leachate. A COD removal of about 52% was obtained within 24 h retention time with a rotational speed of 6 rpm. In another study conducted by Kulikowska et al. (2010) using a two-stage RBC, the overall removal of NH_3N was reported to be 74.4% and 71.6%, respectively. High bacterial density makes RBC useful for the degradation of refractory pollutants in the landfill leachates. However, frequent mechanical failures associated with RBC limits its application for leachate treatment (Kawan et al., 2016).

TF is a fixed-film reactor with a non-submerged medium over which leachate is continuously sprinkled on it (Aluko and Sridhar, 2013). Mondal and Warith (2008) conducted a suitability study of shredded tire materials in a trickling filter system to treat the landfill leachate. BOD_5, COD and NH_3N removal were obtained in the range of 81 to 96%, 76 to 90% and 15 to 68%, respectively. In another study, NH_3N removal from municipal landfill leachate by TF was examined by Jokela et al. (2002). This study found that over 90% removal of NH_3N was achieved by TF and they concluded that TF appeared to be applicable for the removal of NH_3N in landfill leachate. However, TF was reported to have clogging issues which prevented their widespread use especially in leachate treatment plants (Bove et al., 2015).

The MBBR is the recent attached type technology that has been developed to overcome the clogging problem and mechanical failure of TF and RBC. Chen et al. (2008) investigated the performance of a MBBR system to treat landfill leachate for simultaneous removal of COD and NH_3N. The results indicated that MBBR played a major role in COD and NH_3N removal. The contribution of the MBBR to total removal efficiency of COD and NH_3N were 91 and 97%, respectively. The disadvantage of this technology is that the membrane tends to foul out easily and it is difficult for the waste matter to settle down from the treated leachate (Chen et al., 2016).

In general, biological treatments provide good to average treatability for fresh and intermediate leachate but they are not suitable for treating stabilized landfill leachate due to the presence of bio-recalcitrant substances (Anand and Singh, 2014; Amor et al., 2015; Oloibiri et al., 2015; Rahim Pouran et al., 2015). Because of its simplicity, reliability, and high-cost effectiveness, biological treatment is mainly employed to treat landfill leachate (Aziz et al., 2014). However, temperature variation, high loading rates, and the presence of toxins and metal inhibits the activity of microorganism and consequently, reduced the efficiency of organic matter removal (Zhang and Surampalli, 2016).

2.5.2 Physical treatment

Physical method of leachate treatment refers to the removal of substances by the use of naturally occurring forces, such as gravity, electrical attraction, or van der Waal forces (Christensen, 2011). In general, the mechanisms in physical treatment do not result in changing the chemicals structure in leachate. The two common physical treatments for landfill leachate are membrane separation and adsorption. Sedimentation and flotation are also a part of physical approaches but usually are co-joined with another non-physical method such biological and chemical process during leachate treatment.

Membrane separation can be defined as the separation of solid immiscible particles from liquid or gaseous stream predominantly according to the size difference (Anand and Singh, 2014). The membrane acts as a semi-permeable layer and regulates the transportation of leachate between the two phases. Specifically, the filter will let the water flow through the membrane, while it retains suspended solids and other substances (Padaki et al., 2015). A few types of membrane separation technologies have been used for leachate treatment. These separation technologies are such as microfiltration, ultrafiltration, nanofiltration, forward osmosis and reverse osmosis. Reverse osmosis (RO) and nanofiltration (NF) are the most widely used membrane methods for leachate treatment (Smol et al., 2015). Košutić et al. (2015) investigated the feasibility of the combination of NF and RO membranes for the treatment of landfill leachate from Jakuševec, Zagreb, Croatia. This study indicated that the combination of NF and RO managed to decrease the COD, TOC and NH_3N concentration by 94.6, 92.5 and 37.1%, respectively. In another study, Wang et al. (2016) investigated the feasibility of NF and RO for the treatment of leachate from the Taizhou municipal landfill plant (China). The NF membrane exhibited excellent colour removal of 93.75% meanwhile RO membrane held a steadier and higher flux with high salt rejection capability. The final permeate from RO was proved to exceed related qualification for reutilization and can easily be recycled. Di Palma et al. (2002) applied two different membranes: the AD membrane (thin two-ply film of polyamide) and the SC membrane (thin three-ply film of polyamide) for the treatment of landfill leachate. This study reported the reduction of organic content of about 88% and 80% when AD and AC membranes were used. As regards to NH_3N, comparable reductions of over 97% were reported for both types of membrane in optimal conditions.

In general, RO membranes can remove more than 99% organic macromolecules and colloids from feed water and up to 99% of the inorganic ions (Smol et al., 2015). RO membrane removed both organic and inorganic contaminants that dissolved in water with rejection rates of 98–99%, thus being useful for purifying of liquid wastes such as leachate (Zhang and Surampalli, 2016). It is undeniable that membrane technology is one of the most direct, effective and feasible approach for treatment of landfill leachate. However, the cost of this technology is very high which is in the range of 40-60 % above the baseline cost of landfills (Zhang and Surampalli, 2016).

The other physical treatment which has been used for leachate treatment is adsorption process that refers to the transfer of organic substances from a liquid onto a solid phase.

The chemical and physical properties of the soluble substances and the solid surface determine the efficiency of the adsorption processes. The most commonly used adsorbent in landfill leachate treatment is activated charcoal (Christensen, 2011). Activated carbon consists of carbon materials from various sources such as coal, wood and peat which have a very large surface area (800 -1200 m^2/g). Usually, activated carbon adsorption was applied as tertiary treatment to reduce the residual COD. Li et al. (2010) investigated the efficacy of the combined process of coagulation-flocculation and powder activated carbon (PAC) adsorption to treat stabilized landfill leachate. The adsorption experiments showed the removal of 86, 97.6, 99.7 and 78%, of COD, Pb, Fe and toxicity of the stabilized landfill leachate respectively using 10 g/L PAC and the contact time of 90 min. In another study, Oloibiri et al. (2015) investigated the efficiency of granular activated carbon (GAC) in the adsorption of organic matter after coagulation–flocculation and ozonation pretreatment of biologically stabilized landfill leachate. The result indicated that subsequent activated carbon adsorption resulted in 77, 53 and 8% of total COD removal after treatment of 6 bed volumes. The result clearly showed the requirement of leachate pretreatment before GAC adsorption. The activated carbon is effective to adsorb pollutants better than chemical methods, but carbon regeneration is an issue that limit its application in real leachate treatment (Zhang and Surampalli, 2016). Unlike a sand filter, the carbon material must be changed once its maximum capacity has been reached.

2.5.3 Physicochemical treatment

Physicochemical treatment or coagulation-flocculation refers to the application of both physical and chemical process for the reduction of suspended solids, colloidal particles, and floating material in the water. This treatment is widely used as a pretreatment or final treatment as well as specific treatment for various wastewaters. Coagulation is a process that involved the destabilization of colloidal suspension and consequently giving rise to particles aggregations (Smaoui et al., 2015). On the other hand, flocculation assists the coagulation process by clumping the destabilized particles together into larger aggregates to ease the separation via sedimentation (Verma and Kumar, 2016). The particles destabilization in coagulation-flocculation can be accomplished by the addition of chemical coagulants. These coagulants can be classified into two categories, namely hydrolyzing metal coagulants or polymeric flocculants (Teh et al., 2016). The mode of action of these coagulants is via the charge neutralization of negatively charged colloids by cationic hydrolysis products and the precipitation of amorphous hydroxide (Duan and Gregory, 2003).

In recent years, several studies have investigated the application of coagulation-flocculation for leachate pretreatment. These studies have evaluated different types of coagulants, dosage and pH condition to obtain the optimum removal of inorganic and organic pollutant. Maleki et al. (2009) applied $FeCl_3$ and $Al_2(SO_4)_3$ as coagulants for the removal of COD and heavy metal in landfill leachate. It was found that $FeCl_3$ shows better COD removal efficiency as compared to $Al_2(SO_4)_3$. 28% of COD was removed by 2.0 g/L of $FeCl_3$ at pH 10 meanwhile only 18% of COD removal was observed when 1.4 g/L $Al_2(SO_4)_3$ was used at pH 6.5. Heavy metal removal using $FeCl_3$ was also found to be better than $Al_2(SO_4)_3$.

In another study, Li et al. (2010) investigated the performance of 4 types of coagulants; $Al_2(SO_4)_3$, $FeCl_3$, PACL, and polyferricsulphate (PFS) prior to activated carbon adsorption for the removal of COD in landfill leachate. The optimum pH for the tested coagulants was in the range of 5.5 to 6.0. The performance of selected coagulants in COD removal was PFS > $FeCl_3$ > PACL> $Al_2(SO_4)_3$. In this study, PFS was found to be the most effective coagulant. PFS showed the highest COD removal efficiency (70%) with the lowest dosage of 0.3 g/L. Meanwhile, $FeCl_3$, PACL and $Al_2(SO_4)_3$ removed 68, 61 and 53% of COD using 0.6 g/L dosage.

Oloibiri et al. (2015) used $FeCl_3$ and PACL to pretreat biologically stabilized landfill leachate prior to GAC adsorption. The experiment was conducted without pH adjustment and the result was reported in term of the ratio of coagulant to initial COD content (COD_0). When landfill leachate was treated with $FeCl_3$, larger fraction of organic matter was removed as compared to PACL. At optimum ratio of 1 mg $FeCl_3$ /mg COD_0, the removal of color and COD was 88 and 66%, respectively. Meanwhile, only 72 and 44% of color and COD removal was achieved by PACL. The least sludge production was also obtained from coagulation-flocculation with $FeCl_3$ (154 mL/g), whereas PACL produce 252 mL/g of sludge.

Bashir et al. (2015) evaluated the efficiency of PACL and $Al_2(SO_4)_3$ for the pretreatment of tropical landfill leachate. The highest COD removal of 84.5% was achieved by $Al_2(SO_4)_3$ using optimum dosage of 9.4 g/L at pH 7. Whereas, only 56.8% of COD was able to be removed using 1.9 g/L PACL at pH 7.5. Although $Al_2(SO_4)_3$ showed better efficiency, PACL showed better ability to remove other physical parameter such as turbidity (99.2%), colour (97.3%) and TSS (99.2%). Amor et al. (2015) studied the removal of organic matter from the matured landfill leachate using $FeCl_3$ whereby the coagulation-flocculation process was conducted prior to Fenton and solar Fenton processes. The optimum condition of 2 g/L at pH 5 showed the removal of 63% of COD, 80% of turbidity and 74% of total polyphenols. Vedrenne et al. (2012) used $FeCl_3$ for the treatment of stabilized landfill leachate prior to Photo-Fenton. In the study, an addition of 0.3 g/L of $FeCl_3$ at pH 3 was able to remove 81.9% of total carbon (TC), 17.8% of COD, 27.5% of Pb, 7.7% of As, and 0.3% of Hg, respectively. 36.1% of NH_3N was also successfully removed from the leachate effluent.

Instead of conventional optimization method, the performance of coagulation–flocculation treatment was also investigated using response surface methodology (RSM). Liu et al. (2012) applied the RSM method to evaluate the efficiency of ferric-based coagulants, PFS, $FeCl_3$ and $Fe_2(SO_4)_3$ in landfill leachate. The quadratic models developed for responses indicated that the optimum conditions for leachate treatment were 8 g/L at pH 6.0 for PFS, 10 g/L at pH 8.0 for $FeCl_3$ and 12 g/L at pH 7.5 for $Fe_2(SO_4)_3$. In this study, $FeCl_3$ was found to be the most efficient coagulant showing 68.7% of COD removal. $Fe_2(SO_4)_3$ and PFS indicated inferior COD removal with only 55.9 and 56.4%, respectively. Another study using RSM optimization method for coagulation-flocculation was conducted by Moradi and Ghanbari (2014) using $FeCl_3$ as coagulant. The optimum condition for coagulation-flocculation process in this study was found at 1.5 g/L of $FeCl_3$ dosage at pH 7. The removal of COD, color and TSS were approximately 65, 79 and 95%, respectively. RSM optimization method was also used by Smaoui et al. (2015) to investigate the combination of $FeCl_3$ and cationic polyacrylamide flocculants. The optimal condition for COD removal was found at pH 3.36 with coagulant dosage of 0.87 and 26 mg/L of flocculants. These conditions were confirmed experimentally and allowed the removal of 80% of COD.

To conclude, it is inferred that coagulation-flocculation technique is effective for the removal of organic compounds, turbidity, TSS, color and heavy metals. From the previous literatures, a variety of coagulant can be used for treating landfill leachate such as $Al_2(SO_4)_3$, $FeCl_3$, $Fe_2(SO_4)_3$ and PACL. In this study, the coagulation-flocculation was used as a pretreatment before AOP. Since the characteristics of leachate is differing among the landfills, the coagulation-flocculation pretreatment needs to be re-evaluated to determine the optimum condition and dosage for the selected SLL.

2.5.4 Advanced Oxidation Process (AOPs)

AOPs are growing as preferable treatment technology for landfill leachate due to its excellent ability to remove refractory contaminants and to increase the leachate biodegradability (Rocha et al., 2011). AOPs is applied predominantly for the destruction of organic and inorganic pollutant by using powerful oxidizing agent. One of the most reactive oxidizing reagents for AOPs in leachate treatment is $\bullet$OH. It has high oxidation potential (2.8 -1.95 V) with non-selective behavior. $\bullet$OH quickly reacts with numerous species of organic matter with the rate constants of 10^8 - 10^{10} M^{-1} s^{-1} (Deng and Zhao, 2015). Hydrogen abstraction, electron transfer and radical combination are the basic reaction of $\bullet$OH radical in degrading the organic compounds as illustrated in **Equation 2-1**, **2-2** and **2-3** (Stasinakis, 2008). AOPs simultaneously destructs and transforms the recalcitrant organic pollutant into less-hazardous compounds thus provide an ultimate solution for leachate treatment (Deng and Zhao, 2015).

Hydrogen Abstraction:
$$R + \bullet OH \rightarrow R + H_2O \qquad \textbf{(2-1)}$$

Electron Transfer:
$$R^{n} + \bullet OH \rightarrow R^{n-1} + OH^{-} \qquad \textbf{(2-2)}$$

Radical Combination:
$$R + \bullet OH \rightarrow ROH \qquad \textbf{(2-3)}$$

$\bullet$OH can be generated by exposing H_2O_2 to the UV irradiation. H_2O_2 is the most common oxidants used to generate $\bullet$OH in AOPs treatment. In the process of UV/H_2O_2 oxidation, $\bullet$OH radicals are formed by hemolytic splitting of the oxygen–oxygen bond of H_2O_2 by UV light as illustrated in **Equation 2-4** (Wang et al., 2003).

$$H_2O_2 + hv \rightarrow 2\ \bullet OH \qquad \textbf{(2-4)}$$

$\bullet$OH also can be generated by using UV irradiation with the presence of catalyst in water. The most common catalyst in UV-based AOPs treatment is titanium dioxide (TiO_2). The reaction of OH^- and H_2O with positive valence band (HV^+_{vb}) and O_2 with electrons at the conduction band (e^-_{cb}) at the surface of TiO_2 facilitate the formation of $\bullet$OH as illustrated in **Equation 2-5, 2-6** and **2-7**.

$$HV^+_{vb} + OH^- \rightarrow \bullet OH \qquad \textbf{(2-5)}$$

$$HV^+_{vb} + H_2O \rightarrow \bullet OH + H^+ \qquad \textbf{(2-6)}$$

$$e^-_{cb} + O_2 \rightarrow O_2^{\bullet -} \qquad \textbf{(2-7)}$$

Instead of UV exposure, $\bullet$OH also can be produced by the activation of H_2O_2 using transition metal such as Fe^{2+} and Fe^{3+} (Deng and Englehardt, 2006). H_2O_2 activation by using Fe^{2+} is known as Fenton reaction, meanwhile activation of H_2O_2 via Fe^{3+} known as Fenton-like reaction. The mechanism of the formation of $\bullet$OH by Fenton and Fenton-like reaction are illustrated in **Equation 2-8** and **2-9**.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet OH_2 + H^+ \qquad \textbf{(2-8)}$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O \qquad \textbf{(2-9)}$$

Application of AOPs in the treatment of landfill leachate has been studied extensively in the past decade. In a recent study by Córdova et al. (2017), the efficiency of UV/H_2O_2 photochemical process on the removal of organic matter from biologically pre-treated landfill leachates was evaluated. The result found that pH 3 is the optimum condition for the UV/H_2O_2 process. In term of organic matter removal, 52% of COD was successfully removed using this technique. In another study, Hassan et al. (2017) reported an alternative way to remove bio-refractory organics and NH_3N from mature landfill leachate by combining biological and UV/TiO_2 processes. The result indicated that an average 82% of COD was abated. Various combination of AOPs also has been setup in order to get the highest removal of pollutant economically. Hu et al. (2011) compared the efficacy of several AOPs namely UV/Fenton, UV/H_2O_2, and Fenton reaction, to treat landfill leachate with the objective of removing COD. The results indicated that the UV/Fenton system showed the highest COD removal of 56.3% as compared to 46.7 and 39.2% using UV/H_2O_2 and Fenton, respectively. In another study, an alternative AOPs were investigated by Rocha et al. (2011) using heterogeneous (TiO_2/UV, TiO_2/H_2O_2/UV) and homogeneous (H_2O_2/UV, Fe^{2+}/H_2O_2/UV) photocatalytic processes. The results showed that the heterogeneous photocatalytic processes present a low efficiency in terms of mineralization of the leachate at alkaline pH, requiring longer reaction time, which are not economically attractive for commercial application of the process.

2.6 Fenton reaction for leachate treatment

Fenton treatment demonstrated a faster reaction rates and higher removal efficiency of organic compounds as compared to biological and physicochemical treatment (Deng and Englehardt, 2006). A review based on the applicability of various Fenton processes for the treatment of landfill leachate was conducted by Deng and Englehardt (2006). The review concluded that an initial pH between 2.0 and 4.5 favors the Fenton reaction in landfill leachate treatment. In addition, the ratio of H_2O_2/Fe(II) greatly influences treatment efficiency because it determines the degree of scavenging of $\bullet$OH. Moreover, aeration, final pH, temperature and UV irradiation also influence the efficiency of Fenton reaction in landfill leachate treatment.

Singh and Tang (2013) conducted a statistical analysis of optimum Fenton oxidation condition for landfill leachate treatment. The analysis was performed based on the optimum condition observed by peer reviewed publications for Fenton oxidation of raw, biological and coagulation treated leachates. This study concluded that the median pH of 3 for raw and coagulation treated leachates whereas the median pH of 4.2 for biologically treated leachate. The optimum ratio of H_2O_2/Fe(II) were 2.8, 0.9 and 2.4 (w/w) for raw leachate, biological and coagulation treated leachate, respectively. This review also suggested the median H_2O_2 and Fe(II) dosage of 1.2 H_2O_2/ initial COD and 0.9 Fe(II)/initial COD for landfill leachate treatment.

Gupta et al. (2014) investigated the applicability of Fenton treatment as a polishing step to treat the biologically treated leachates. The optimum pH condition was found in the range of 3-5. The results indicated that Fenton's reagent can act as a good compliment to biological treatment as it can remove leachate fractions which are widely considered to be bio-recalcitrant. Fenton reaction exhibited higher color removal (UV_{254}) by removing larger molecular weight humic substances in the landfill leachate. In a recent study by Amor et al. (2015), Fenton reaction was applied for the treatment of matured landfill leachate with and without pretreatment by coagulation-flocculation. The result indicated that 63% of COD removal was achieved without any pretreatments at optimum pH 3. However, longer reaction time (96 h) and higher dosage of H_2O_2 (113 mM) were required. The combination treatment with coagulation-flocculation successfully remove 89% of COD using lower dosage of H_2O_2 (96.8 Mm) in 3 h reaction time.

Recently, the application of RSM method assisted researcher to determine the accurate evaluation for Fenton reaction optimization. Amiri and Sabour (2014) investigated the multi response optimization of Fenton reaction using RSM for landfill leachate treatment. The modelling process was focused on overall COD removal. The optimum operational conditions were found to be at initial pH of 5.7, H_2O_2/Fe(II) ratio of 17.72 and Fe(II) concentration of 195 mM, which led to 69% COD removal. In this study, Fenton reaction has been selected to treat SLL after coagulation-flocculation pretreatment. The reaction has been proven as an excellent AOPs method for the removal of organic compound in many landfill leachate treatments.

2.7 Sulfate radical based AOP (SR-AOP)

Earlier, the concepts of AOPs were refer to the oxidation processes ∙OH in sufficient quantity can degrade the contaminant in the water. Later, the AOPs concept has been extended to other oxidative species which include SR. SR is a reactive oxidizing reagent with a high oxidation potential (E^o of 2.6 V) and reacts with organic compound with the rate of 10^6–10^9 $M^{-1}s^{-1}$ (Fagier et al., 2016). The feasibility of SR as alternatives reactive species to ∙OH in AOP treatment has been increasingly evaluated nowadays (Fagier et al., 2016; Ghanbari and Moradi, 2017; Khan et al., 2016). Unlike ∙OH, SR is more likely to react with refractory contaminants due to its selective oxidation reaction. ∙OH tends to attack organic compounds via hydrogen abstraction or addition reactions whereas SR tends to react with organic compounds through electron transfer (Zhou et al., 2015). The unselective behavior of ∙OH tends to attack any organic matter and consequently the ∙OH is quickly spent and the reaction is short-lived (20 ns) (Deng and Zhao, 2015). Meanwhile, the SR has been reported to have a longer radical lifetime (30-40 μs) and thus increased the probability to react with the non-biodegradable pollutant removal thus increased organic content removal (Zhou et al., 2015). In addition, SR oxidation is an independent of pH of the treatment effluent (Zhou et al., 2015). Enhanced removal of organic matter by SR oxidation has been reported in acidic, neutral and even at basic conditions (pH between 9 and 10) depending on the analyte and activator type (Matzek & Carter, 2016). In contrast, formation ∙OH radical is highly pH dependent. The oxidation potential (E^o) of ∙OH decrease with the increasing of pH (pH = 0, E^o = 2.8V; pH 14, E^o = 1.95V) (Deng and Englehardt, 2006).

Common sources of oxidants for SR generation are PS and PMS (Rastogi et al., 2009). Both oxidants have been widely used for domestic purposes such as bleaching, cleaning, and disinfection. PS and PMS has low oxidation potential with less efficiency in water and wastewater. However, once activated by heat, transition metal, elevated pH, ultraviolet (UV) or ultrasound irradiation, they are converted into SR which have high oxidation potential (Deng and Zhao, 2015).

A number of studies have investigated the heat activated SR for the degradation of various compounds in wastewater. Deng and Ezyske (2011) claimed that heat activated SR not only successfully removed the organic compound in the leachate but also mineralized the NH_3N. About 79% and 91% of COD were successfully removed from landfill leachate at pH 8.3 and 4. The NH_3N removal reached 100% at both of the pH condition. In another study, a thermally activated PS oxidation process was investigated by Olmez-Hanci et al. (2013) to treat aqueous bisphenol A (BPA) solution. It was found that increasing the treatment temperature (40–70 ºC) resulted in a significant enhancement of BPA degradation. Acidic to neutral pH condition was more favorable for BPA degradation than in alkaline condition. Other heat activated PS study was conducted by Fan et al. (2015) for the degradation of sulfamethoxazole in aqueous solution. The radical scavenging tests indicated that the predominant oxidizing species was SR with $\bullet OH$ playing a less important role. Despite heat, several studies have investigated the feasibility of SR activated by transition metals to generate SR. Transition metal ions can activate the decomposition of PS and PMS via a single electron transfer reaction, which is illustrated by **Equation 2-10** and **2-11**.

$$HSO_5^- + \text{Metal ion } (M^n) \rightarrow M^{n+1} + SO_4^{-\bullet} + OH^- \qquad \textbf{(2-10)}$$

$$S_2O_8^{2-} + \text{Metal ion } (M^n) \rightarrow M^{n+1} + SO_4^{-\bullet} + SO_4^{2-} \qquad \textbf{(2-11)}$$

Anipsitakis and Dionysiou, (2004) investigated nine transition metals for the activation of PS, PMS and H_2O_2 in the degradation of 2, 4-dichlorophenol. This study concluded that Co(II) and Ru(III) are the best metal catalysts for the activation of PMS, and Ag(I) was found to be the most efficient catalyst for activating PS. Nfodzo and Choi (2011) has evaluated the efficiency of PMS and PS activated by Fe(II), Co(II), Cu(II), and Ag(I) to degrade triclosan (TCS). The results revealed that the oxidants alone did not decomposed the TCS while SRs generated from the oxidant-metal combination was very effective to oxidize and mineralize TCS. PMS/Co(II), PMS/Cu(II), and PS/Ag(I) systems showed the highest reactivity with TCS.

The previous research extensively reported on the activation of SR using Co(II) for degradation of various compound in the wastewater. Sun et al. (2009) investigated the COD removal of landfill leachate using PMS/Co(II) and Fenton oxidation. Under optimal operational conditions, 57.5% and 56.9% removal of COD was achieved by PMS/Co(II) and Fenton treatment, respectively. The result obtained showed that the performance of PMS/Co(II) was comparable with Fenton. This study also indicated the possibility to apply PMS/Co(II) system in large scale system. In another study, Matta et al. (2010) investigated the degradation of carbamazepine using Fenton H_2O_2/Fe(II) and PMS/Co(II) oxidation. The results indicated that SR yielded a faster degradation of carbamazepine as compared to $\bullet$OH. These results also indicated that SR is more selective than $\bullet$OH for the oxidation of an organic pollutant. The performance of PMS/Co(II) also was assessed by Ling et al. (2010) in contrast to H_2O_2/Co(II) for degradation of basic blue 9 and acid red 183. This study showed that dye decomposition is much faster in PMS/Co(II) system than in H_2O_2/Co(II). In spite of the great performance of PMS/Co(II) treatment, Co(II) has been recognized as a possible human carcinogen by International Agency for Research on Cancer (IARC) (Guan et al., 2013). The secondary environmental pollution caused by the dissolved Co(II) ions in water would restrict the application of PMS/Co(II) to be applied in the real water treatment.

2.7.1 Fe(II) activated SR

Ferrous iron (Fe(II)) has been commonly selected as the alternative metal catalyst of SR production due to its low toxicity and cost effectiveness (Matzek and Carter, 2016). The degradation of various type of organic compounds using Fe(II) activated SR was investigated in recent years. Rastogi et al. (2009) investigated the degradation of PCBs in a sediment slurry using Fe(II) activated PMS. The outcome of the study indicated that 90% PCB removal was observed within 24 h. In another study by Xu and Li (2010), PS/Fe(II) system has been used for the oxidative degradation of azo dye, Orange G (OG) in aqueous solution. The experimental results showed that under optimum condition, the OG degradation in aqueous solutions was achieved by 99% within 30 min. The chemical activation with Fe(II) at ambient temperature was found to be more effective for the degradation of OG than that of increasing the temperature. The experiments also demonstrated that the PS/Fe(II) system can degrade OG in aqueous solutions to a higher degree than the Fenton's reagent. Wang and Chu, (2011) investigated the removal of xanthene dye Rhodamine B (RhB) in aqueous solution using static and stepwise addition of Fe(II) and PMS. The result showed that total RhB removal was obtained within 90 min under an optimal Fe(II)/PMS molar ratio of 1:1. The stepwise addition of Fe(II) and PMS can significantly improve the treatment performance by about 20%, and the retention time required can be greatly reduced comparing with the one-off dosing method.

The reaction between Fe(II) with PS or PMS oxidants generates SR that capable in degrading refractory organic contaminants. However, the slow transformation from ferric iron (Fe(III)) back to Fe(II) limits its widespread application. In a study conducted by Zou et al. (2013), hydroxylamine, a common reducing agent was added into Fe(II)/PMS process to accelerate the transformation of Fe(III) to Fe(II). With benzoic acid as probe compound, the addition of hydroxylamine into the treatment process accelerated the degradation of benzoic acid rapidly in the pH range of 2.0−6.0 by accelerating the key reactions, including the redox cycle of Fe(III)/Fe(II) and the generation of reactive oxidants. This study provides a promising idea based on SR-AOP process for the rapid degradation of refractory organic contaminants in water treatment.

Epold et al. (2015) compared the performance of Fe(II)-activated PS with Fenton and combined Fenton/PS systems for degrading the levofloxacin (LFX) in aqueous solutions. In general, all the technologies proved to be promising techniques for the treatment of wastewater containing LFX. However, the study indicated lower performance of Fe(II)-activated PS compare to combined Fenton/PS systems and Fenton alone. Fagier et al. (2016) studied the efficiency of Fe(II) activated PS and PMS coupled with coagulation–flocculation in the mineralization of organic matter of sugarcane vinasse. This study found that both Fe(II)/ PMS and Fe(II)/PS showed the highest TOC removal efficiency when the oxidation was carried out at pH 7. However, PS/Fe(II) showed lower performance of TOC removal (49%) compare to PMS/Fe(II) (70%) under selected optimum condition. A several of studies on the application of Fe(II) activated SR for degradation of individual compound in wastewater was reported by previous researchers (Rastogi et al., 2009; Xu and Li, 2010; Zou et al., 2013; Epold et al., 2015). However, the application of PS/Fe(II) and PMS/Fe(II) in the treatment on landfill leachate is very limited. Only one study was found so far and it was conducted by Liu et al. (2016) using the combination of Fe(II) activated SR with coagulation-flocculation pretreatment. Under optimum conditions of 0.3 Fe(II) /PS molar ratio, pH 3.0, and 60 ºC temperature, up to 75% and 95% of the COD and color removals were achieved. No violation of effluent standards for landfill leachate was occurred after being treated by the selected combined process.

2.7.2 UV activated Sulfate Radical

UV irradiation is another activation method of SR (Liu et al., 2013). Direct photolysis of PS and PMS resulting in the cleavage of the peroxide bond to produce SR and $\bullet$OH (Jaafarzadeh et al., 2016). The mechanism of SR generation from PS and PMS by UV was illustrated in **Equation 2-12** and **2-13**

$$S_2O_8^{2-} + \text{Energy input (UV)} \rightarrow SO_4^{-\bullet} + SO_4^{-\bullet} \quad \textbf{(2-12)}$$

$$HSO_5^{-} + \text{Energy input (UV)} \rightarrow SO_4^{-\bullet} + OH^{-} \quad \textbf{(2-13)}$$

Olmez-Hanci et al. (2011) investigated the potential degradation of dimethyl phthalate (DMP) by the photo-assisted PMS. The high oxidation potential of $\bullet$OH and SR generated by the activation of PMS using UV radiation was used to oxidize the aqueous DMP. It was observed that lowering the initial reaction pH slightly improved the degradation rate of DMP. On the contrary, TOC abatements were slightly enhanced with increasing initial reaction pH. An optimum PMS concentration of 40 mM resulted in the fastest and highest DMP degradation rates and efficiencies, respectively. At an initial concentration of 100 mg/L, more than 95% of DMP removal was obtained at 20 min of PMS/UV treatment conditions.

In another study, Olmez-Hanci and Arslan-Alaton (2013) conducted a study of UV activated PMS, PS and H_2O_2 in degradation of phenol. Complete phenol degradation was achieved under all examined reaction accompanied with complete TOC removals under optimized PMS (20 mM), H_2O_2 (30 mM) and PS (20 mM) concentrations. Liu et al. (2013) investigated UV activation of PMS to degrade atenolol (ATL) in water in which a linear positive correlation between the degradation rate of ATL and specific dose of PMS

(1–16M PMS/M ATL) was observed. Increasing solution pH from 3 to 9 promoted elimination of ATL due to the pH-dependent effect of PMS photo decomposition, while further pH increases from 9 to 11 caused slowing down of degradation because of apparent conversion of PMS from ∙OH to SR.

Deng et al. (2013) investigated the performance of carbamazepine (CBZ) degradation by UV (254 nm) radiation in the presence of PMS, H_2O_2 and PS. The degradation efficiency of the three UV-based processes was in the order of UV/PS > UV/H_2O_2 > UV/PMS. The maximum CBZ degradation occurred at pH 11, 3, 5 in UV/PMS, UV/H_2O_2 and UV/PS system, respectively. Comprehensively consideration of energy requirements, oxidant costs and affecting factors, UV/PS system was the most efficient and economic process for CBZ degradation and found to be the promising technology for water treatment. Another oxidant/UV study was conducted by Mahdi-Ahmed and Chiron (2014). This study investigates the elimination of ciprofloxacin residues (CIP) from treated domestic wastewater using UV/PMS, UV/PS and UV/H_2O_2. In distilled water, the order of efficiency in CIP removal was UV/PS >UV/PMS > UV/H_2O_2 while in wastewater, the most efficient process was UV/PMS followed by UV/PS and UV/H_2O_2. At the latest study by Sharma et al. (2015), the degradation of BPA was investigated using UV/PMS. At the initial pH of reaction mixture (5.15), the optimum dosage of PMS was found to be 0.66 mM, giving a BPA removal of 96.7% and a total organic carbon (TOC) removal of 72.5% after 360 min of UV radiation.

Based on the excellent previous finding of SR-AOP in treating various wastewater and contaminants, Fe(II)/PS, Fe(II)/PMS, UV/PS and UV/PMS were selected in combination with coagulation-flocculation pretreatment to degrade the organic compound in the SLL. The most efficient combination was used to develop the CFWTS.

2.8 Toxicity Analysis

Evaluation of the toxicity of landfill leachate are in great demand in order to ensure the safe discharge of treated leachate from leachate treatment facilities. Instead of physicochemical properties such as COD and NH_3N, the toxicity of leachate is gradually being incorporated into environmental legislation in some countries (Cho et al., 2009). Recently, the use of AOPs has increasingly be developed for the treatment of SLL. However, incomplete AOPs treatment of SLL may produce more complicated water matrices consisted of various transformation by-products. Therefore, toxicity tests have become useful tools for detecting the changes in treated leachate quality to complement the AOPs method (Cho et al., 2009).

The use of bioassays as screening tools to characterize the toxicity of contaminants in various water matrices like landfill leachates has become a popular and powerful tool in the field of environmental toxicology (Ghosh et al., 2017). The use of a single bioassay may underrate the potential toxicity for a contaminant or effluent to the ecosystem. Therefore, a set of bioassays, particularly involving organisms representing different trophic levels is more appropriate for complex effluents like leachates, as it enable toxicity assessment across different trophic organisms with varying modes of action and sensitivity (Ghosh et al., 2017). Abbas et al. (2018) reviewed the use of bioluminescence bacteria, *Vibrio fischeri* for toxicity analysis. This technique constitutes a simple and cost-effective method which has been frequently applied for the ecotoxicological screening and assessment of a wide range of potentially deleterious solid, liquid and gaseous substances. However, overestimation of toxicity potential exhibits a major constraint of this method. Barrios et al. (2017) conducted a correlation study between acute toxicity for *Vibrio fischeri* and *Daphnia magna* using the leachate produced from landfill simulator reactors. The results showed that the leachates produced inside the reactors are highly toxic, presenting EC_{50} less than 1% for *Daphnia magna* and EC_{50} less than 12%

for *Vibrio fischeri*. This result indicated that the micro crustaceans are more sensitive to these compounds, making them more suitable for ecotoxicological study.

Despite micro crustaceans, fish are eco-physiologically affected and their distribution prone to changes because of degraded water quality. The fish play a key role in community dynamics due to the place they occupy in the trophic chain (Salem et al., 2014). Among potential fish bio-indicator species for environmental stress, the zebrafish (*Danio rerio*) is the most extensively studied experimental model. Zebrafish has been classified as a model vertebrate for chemical (Hill et al., 2005) and aquatic toxicity studies (Moșneang et al., 2014). There are numerous critical pathways that regulate vertebrate development between humans and zebrafish are highly conserved (Hollert and Keiter, 2015). Qiu et al. (2016) conducted a toxicological evaluation of landfill leachate before and after the treatment process using zebrafish larvae, and embryos. The toxicity test results showed that the acute toxicity of landfill leachate has been reduced significantly where toxicity units (TU) decreased from 84.75 to 12.00 for zebrafish larvae and 82.64 to 10.55 for zebrafish embryos respectively.

In landfill leachate treatment, the toxicity test involving different organisms from aquatic and terrestrial ecosystems has been frequently evaluated. However, toxicity of treated leachate to plants is seldom reported (Kalčíková et al., 2015). Plants, as photosynthetic organisms, produce reactive oxygen species (ROS) during photosynthesis. Production of an undesirable amount of ROS has been proven after exposure by landfill leachate which results in growth inhibition, chlorophyll inhibition and oxidative stress (Sang et al., 2010). The use of plants toxicity leads to a better understanding of the effect of leachate to plants as well as identification of hazard of landfill leachates for primary producers in the ecosystem. In phytotoxicity study, seed germination tests have been used as short-term phytotoxicity tests to provide valuable information about root growth inhibition, plant enzymes activation, cell expansion and other parameters (Wang et al., 2002). The test is fast, simple, cost-effective and sensitive with minimal operational cost. All the advantages make the test ideally suitable as a rapid toxicity test and cost-effective tool to evaluate the toxicological risk of different pollutants. Ladies fingers (*Abelmoschus esculentus*) and mung beans (*Vigna radiata*) has been widely used for seed germination in various wastewater and effluent (David and Rajan, 2015). Thus, in addition to zebrafish toxicity, seed germination of ladies fingers and mung beans were evaluated for leachate and treated leachate in this study.

CHAPTER 3: METHODOLOGY

3.1 Sample Location

The leachate was collected from a sanitary landfill in Jeram, Selangor, Malaysia. The aerial view of this landfill is shown in Figure 3.1. The landfill was officially begun its operation on 1st January 2007. It has the capacity to handle 1,250 tonne of municipal solid waste per day for an estimated design lifespan of 16 years. The site has a footprint of approximately 8,000,000 m^3 air space or 650,000 m^2 ground space. The landfill is equipped with leachate treatment facilities which include the sequential batch reactor (SBR), dissolved air flotation (DAF) system, coagulation-flocculation system, sand filtration, and activated carbon filtration systems. Figure 3.1 shows the location of the sampling point (marked by the red-dashed line) where all leachate samples in this work were collected.

Figure 3.1: Aerial view of Jeram Sanitary Landfill (red-dashed line indicates the sampling point).

The stabilized landfill leachate (SLL) was collected directly from the first sedimentation pond before any treatment was applied. The physical parameters for the SLL (pH, turbidity, colour, conductivity, total dissolved solid and salinity) and biochemical oxygen demand (BOD_5) were analyzed immediately upon arrival at the laboratory.

3.2 Chemicals, Materials and Reagents

Sand, Ferric Chloride $FeCl_3$, sulphuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$), ammonium molybdate ($(NH_4)MoO_4$) and activated charcoal were purchased from Merck (Germany). PS and PMS were supplied by Acros Organics (USA). Sodium hydroxide (NaOH) was obtained from Fluka (Germany). Ammonium chloride (NH_4Cl), ammonium nitrate (NH_4NO_3), Aluminum Sulphate $Al_2(SO_4)_3$, mercury(II) iodide, potassium iodide, and sodium thiosulfate were purchased from Sigma Aldrich. PACL was obtained from R&M Marketing (Malaysia). Starch indicator was purchased from LabChem (USA). Potassium sodium tartrate ($KNaC_4H_4O_6$) was purchased from Univar (USA). All chemicals and reagents are analytical grade and used without further purification.

3.3 Landfill Leachate Characterization

3.3.1 Physical Parameter Determination

The physicochemical parameters of the SLL were determined according to standard methods published by APHA et al. (2012). pH, salinity and conductivity were measured using a Cyberscan series 600 portable meter (Eutech Instrument, Thermo Scientific). Turbidity and colour were measured using a Spectroquant colorimeter Move 100 (Merck). The biochemical oxygen demand (BOD_5) was determined using manometric method using Lovibond Oxidirect.

3.3.2 TOC Determination

TOC measurements were performed using a TOC analyzer (TOC-L, Shimadzu, Japan). The TOC concentration was calculated by subtracting the inorganic carbon (IC) concentration from the obtained total carbon (TC) concentration.

3.3.3 COD Determination

COD was measured through a small scale (2 mL) closed-tube digestion procedure with mercury suppression as described by Westwood (2007). The COD measurement was carried out in triplicate for each sample. The procedure was started with the addition of 2 mL leachate or treated leachate into a boiling tube. Then, 0.20 mL mercury(II) sulphate solution was added to the tube followed by 3.70 mL of mixed reagent. Mixed reagent was prepared by adding 1.53 g of potassium dichromate and 7.5 g silver sulphate into 1 L solution containing 250 mL deionized water and 750 mL concentrated H_2SO_4. The tube was closed and swirled vigorously before it is placed into the heating reactor. The tube was then heated for 120 min at 150 °C. After reaction, the tube was then removed and cooled to room temperature before analysis by UV-Vis spectrophotometer at wavelength 450 nm.

3.3.4 Determination of Metal

Metal analysis was conducted according to the standard acid digestion method 3050B provided by USEPA (1996). In brief, 100 mL of well-mixed leachate was transferred to a beaker and heated, without boiling, until the volume was reduced to 15 - 20 mL. Concentrated nitric acid (15 mL) was then added and the sample heated for another 30 min. Then, 15 mL of concentrated hydrochloric acid was added, and the sample was again heated for 30 min. The solution was then allowed to cool to room temperature and then filtered to remove insoluble materials. The digested sample was then diluted to the desired concentration. The samples were then analyzed for their metals content using the Inductive Coupled Plasma-Mass Spectrometry (ICP-MS, 7500 Agilent).

3.3.5 Determination of Residual H_2O_2

The concentration of residual H_2O_2 after Fenton treatment was determined using the iodometric method as described by Karci et al. (2012). In brief, a 50 mL solution of treated SLL was first transferred into a 250 mL Erlenmeyer flask. Then, 10 mL of potassium iodide (2% w/v), 2 drops of ammonium molybdate solution and 10 mL of H_2SO_4 (3.5 M) were added. Ammonium molybdate solution was prepared by dissolving 9 g of ammonium molybdate in 10 mL of 6N NH_4OH with the addition of 24 g of NH_4NO_3 in 100 mL of deionized water. The concentration of liberated iodine was determined by titrating the mixture with a standardized thiosulfate solution (0.001 – 0.1 M). Starch was used as an indicator.

3.3.6 Anion Determination

The anion concentration in leachates samples were determined using Ion Chromatograph (Dionex ICS-1100) with Na_2CO_3:$NaHCO_3$ eluent ratio of 8:1 using Dionex Impax^{TM} AS14A column at the flow rate of 1 mL/min.

3.3.7 NH_3N Determination

NH_3N concentration in the leachate was measured using the direct Nesslerization method (ASTM, 2008). Nessler's reagent was prepared by the addition of solution A (100 g of HgI_2 and 70 g KI in 50 mL of deionized water) into solution B (160 g NaOH dissolved in 50 mL deionized water). The mixture was then diluted to 1 L. A potassium sodium tartrate (Rochelle salt) solution was prepared by dissolving 50 g of salt using 100 mL of deionized water. The measurement procedure was commenced by the addition of 50 mL of sample into a conical flask followed by the addition of 1 mL of the Rochelle salt solution. Then, 1 mL of the Nessler's reagent was added into the same conical flask. After 5 min, the reaction mixture was analyzed using UV-Vis spectrometry at the wavelength of 425 nm. In the presence of ammonia, a gradual change in colour to yellow or brown can be observed. The concentration of NH_3N was calculated by comparing the UV-Vis spectra against a calibration curve constructed using NH_4Cl as reference.

3.4 Toxicity Analysis

3.4.1 Acute Toxicity Study

The acute toxicity of the treated SLL was evaluated using zebrafish *(Danio rerio)*. The test was performed according to the OECD (2004) standard method. Briefly, a group of 10 zebrafish with similar size was randomly selected and transferred into a 5 L test container. A control was maintained without the addition of water samples. All experiments were conducted for 48 and 96 h and no feeding was carried out for the duration of the experiment. The mortality of the fish for the control and exposed groups was recorded for LC_{50} determination. 96h LC_{50} values were converted to toxic unit values (TU) to be used as a measure of toxicity (**Equation 3-1**). The experiment was triplicated.

$$\text{Toxicity Unit (TU)} = \frac{100\%}{LC_{50}} \qquad \textbf{(3-1)}$$

3.4.2 Mung Beans and Lady Finger Germination Index

The phytotoxic effect after each selected treatment process was investigated based on the seed germination of mung beans (*Vigna radiata)* and ladies fingers (*Abelmoschus esculentus*). The procedure was modified from the method published by David and Rajan (2015). Germination experiments were carried out in sterilized petri dishes lined with double layers of filter paper. Twenty sterilized seeds were placed in the petri dishes that containing the SLL from each treatment process or, in the case of the control, tap water was used. The samples were incubated at 26 ± 2°C for germination. The germination % was recorded after 48 h and the relative toxicity was calculated using **Equation 3-2** and **3-3**.

$$\text{Germination percentage (GP)} = \frac{\text{Number of Seed Germination}}{\text{Number of Total Seed}} \times 100 \qquad \textbf{(3-2)}$$

$$\text{Relative Toxicity} = \frac{\text{(GP Control - GP Test)}}{\text{GP Control}} \times 100 \qquad \textbf{(3-3)}$$

3.5 Treatment Method

The treatment of SLL consisted of the combination of coagulation-flocculation pretreatment with two different types of AOPs ($\bullet$OH and SR based AOP). In $\bullet$OH-based AOP, the $\bullet$OH was generated using Fe(II) activated H_2O_2 or also known as Fenton reaction. In SR-based AOP, the SR was generated using PS and PMS activated by Fe(II) and UV light. The treatment was started with a series of batch study to determine the optimum condition for both coagulation-flocculation and AOPs. The result from the batch study was then used to determine the optimum condition for continuous flow water treatment system (CFWTS).

3.5.1 Coagulation-Flocculation pretreatment

Coagulation-flocculation treatment was performed using standard jar test apparatus (JLT6 Velp, Scientifica) equipped with six 1 L beakers at room temperature. The coagulation-flocculation pretreatment was conducted to obtained pre-treated leachate for subsequent AOPs process. The experiments were carried out using 500 mL of raw SLL with $FeCl_3$, $Al_2(SO_4)_3$ and PACL as a coagulant. In brief, the mixture was first vigorously stirred for 2 min at 200 rpm, followed by slow mixing for 30 min at 50 rpm. Then, stirring was halted and the floc was left to settle for 1 hour. In this study, the coagulation-flocculation process was carried out at pH of 5, 6, 7, and 8 with differing dosages of selected coagulants to obtain the optimized condition. Then, the pre-treated leachate was filtered through a sand filter to remove the remaining floc before the next treatment.

3.5.2 Fenton Oxidation Process in Stabilized Landfill Leachate treatment

All Fenton reactions were carried out in batch mode at room temperature. The experiment was started with the addition of 25 mL of the pre-treated SLL into a 30 mL glass vial. The pH of the leachate was first adjusted using H_2SO_4 and NaOH. Subsequently, H_2O_2 and Fe_2SO_4 were added and the mixtures were shaken using an orbital shaker at 150 rpm. The final leachate was re-adjusted to pH 7 by using NaOH before the physical and chemical parameters were determined. In this study, the parameters being investigated were reaction time, H_2O_2 to Fe(II) ratio, H_2O_2 dosage, and pH.

3.5.3 Application of SR-AOP in SLL treatment

3.5.3.1 Fe(II)/SR-AOP in SLL

All reactions were carried out in batch mode at room temperature. The experiment was started with the addition of 25 mL of the pre-treated SLL into a 30 mL glass vial. The pH of the leachate was first adjusted using H_2SO_4 and NaOH. Subsequently, the chemical oxidants (PS and PMS) and catalyst ($FeSO_4.7H_2O$) were added and the mixtures were shaken using an orbital shaker at 150 rpm. In this study, the effect of parameters which include reaction time, oxidants to Fe(II) ratio (PMS: Fe(II) and PS: Fe(II)), oxidants dosage, and pH were evaluated.

3.5.3.2 UV/SR-AOP in SLL treatment

All reactions were carried out in batch mode at room temperature. The experiment was started with the addition of 100 mL of the pre-treated SLL into a 250 mL jacketed beaker. In this study, an ultraviolet lamp (Tank master 13, Atlantic Ultraviolet Corporation (USA)) was immersed into the pre-treated SLL. Subsequently, the chemical oxidants (PS and PMS) were added and the mixtures were shaken using a magnetic stirrer at 150 rpm. In this study, the effect of parameters which include reaction time, oxidants dosage, and pH were evaluated.

3.5.3.3 Removal of H_2O_2 by Activated Carbon Adsorption

Residual H_2O_2 from Fenton treatment was removed using an activated charcoal adsorption column. The dimension of glass column was inner diameter of 2.2 cm and a height of 30 cm. The Fenton reaction treated samples were passed through the activated carbon column consisting of 6 and 9 g of activated charcoal at the flow rate of 5 mL/min.

3.5.3.4 Cation exchange column after SR-AOP treatment

In this study, Amberlite (IRA-402) ion exchange was utilized for the sulfate ion removal. The uptake capacity of residual sulfate ion was initially tested using a fixed amount of Amberlite resin with 1 L of treated SLL. The flow rate was set at 7 and 12 mL/min and the dimension of the glass column was 1 cm inner diameter and 5 cm height. Every 7 and 12 mL/min, the treated SLL was taken to determine the uptake capacity of sulfate ion until its reach the saturated condition. Based on this initial experiment, the amount of Amberlite resin for residual sulfate ion removal in CFWTS was calculated.

3.5.4 CFWTS for SLL treatment

The CFWTS consisted of three stages of treatment. The first stage was the coagulation-flocculation pretreatment with a sand filtration system. The second stage was the Ammonia stripping-UV/PS treatment and the last stage was the Amberlite ion Exchange column system. During the first stage, two coagulation-flocculation tank equipped with two overhead stirrers were used. The tanks were designed to occupy 8 L of SLL. The dimension of the tank was 20 cm inner diameter and 35 cm in height. This system was also equipped with an electronic ball valve at the bottom of the first coagulation-flocculation tank to control the transfer of SLL into the second tank. Then, the SLL was pumped through a sand filtration column into the second stage of treatment by using a peristaltic pump. The column dimension was 5 cm inner diameter and 60 cm height. At the second stage, the SLL was continuously recirculated between an ammonia stripping and UV tank through another peristaltic pump. The dimension of ammonia stripping tank was 10×10×30 cm. The tank was also equipped with an air pump to produce air bubbles. The UV tank used in this study was Atlantic Sanitron UV purifiers with the capacity of 2.7 L/cycle. A solenoid valve was installed at the bottom of UV tank to control the transfer of SLL into the final stage. The SLL was then pumped through the Amberlite ion exchange column using a peristaltic pump. The dimension of the column was 4.5 cm inner diameter and 40 cm in height. The schematic diagram of CFWTS was illustrated in Figure 3.2. The electronic system in CFWTS was controlled by an Arduino microcontroller. At first, a set of instruction was setup using an open-source Arduino Software (IDE). Then, the instruction was uploaded into the Arduino board. The system was designed to be fully automated and continuously operated from the first treatment of coagulation-flocculation until the final treatment of Amberlite cation exchange column. The circuit system was illustrated in Figure 3.3.

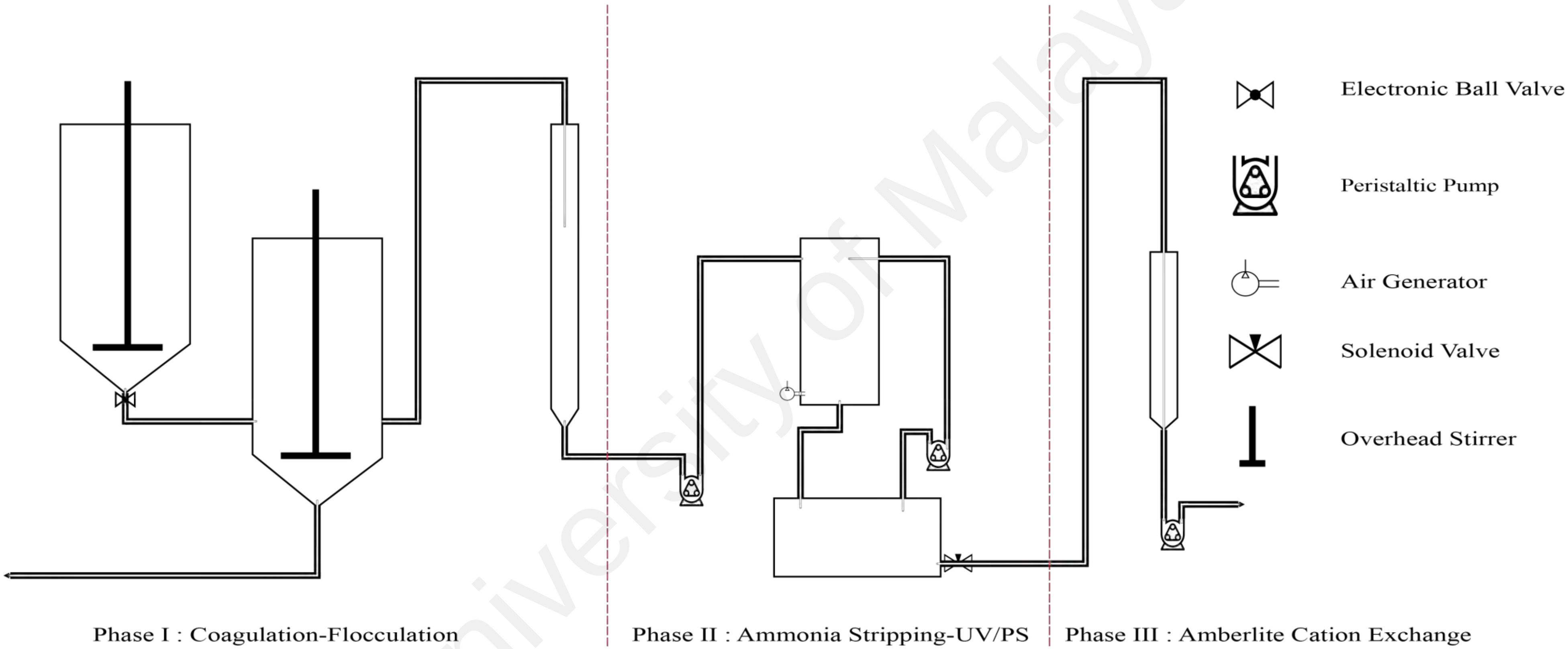
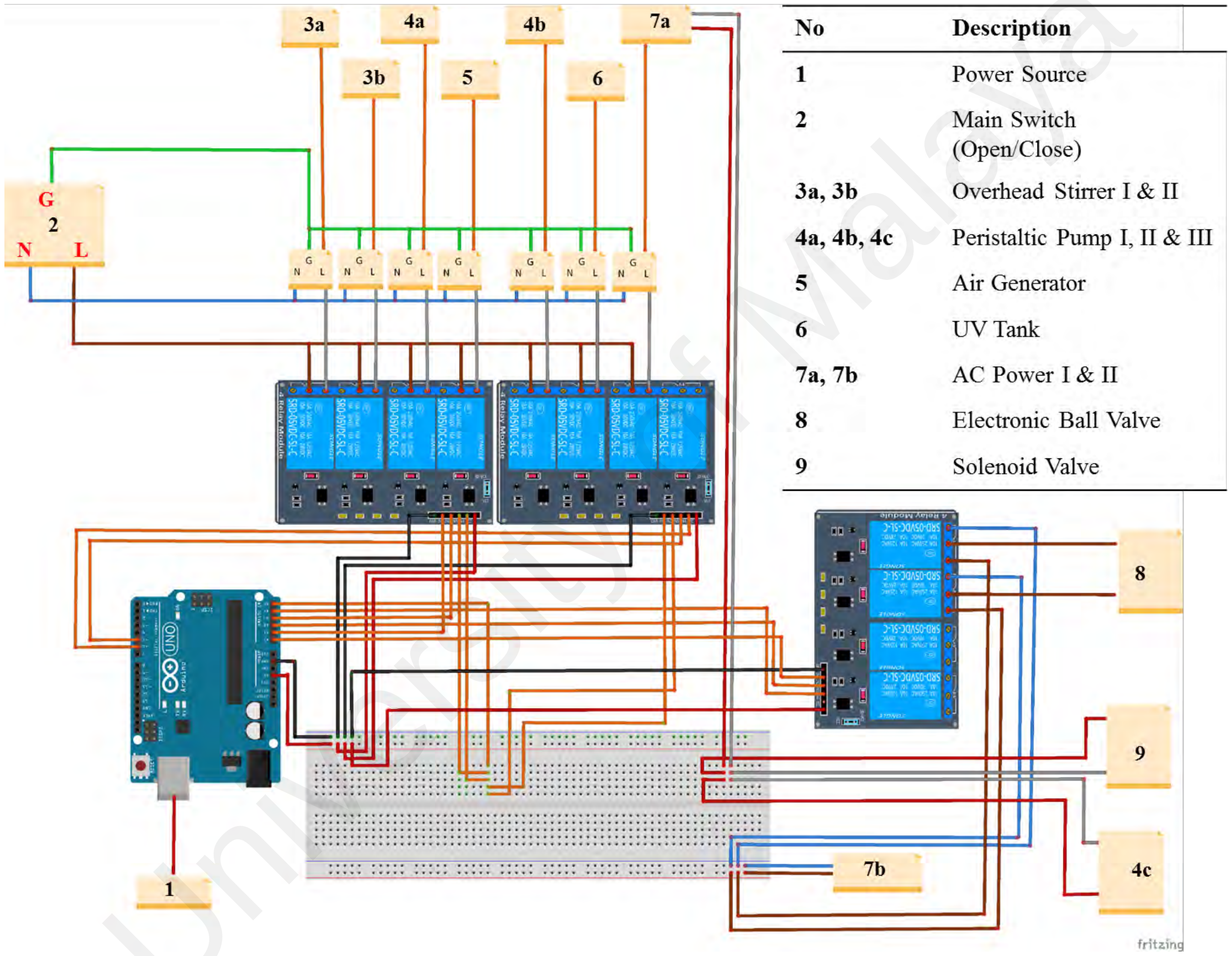


Figure 3.2: Schematic diagram of continuous flow wastewater treatment system (CFWTS) consists of three phases namely; Phase 1: Coagulation-Flocculation, Phase 2: Ammonia Stripping-UV/PS and Phase 3: Amberlite Cation Exchange.



No	Description
1	Power Source
2	Main Switch (Open/Close)
3a, 3b	Overhead Stirrer I & II
4a, 4b, 4c	Peristaltic Pump I, II & III
5	Air Generator
6	UV Tank
7a, 7b	AC Power I & II
8	Electronic Ball Valve
9	Solenoid Valve

Figure 3.3: Schematic drawing of continuous flow wastewater treatment system (CFWTS) circuit system.

3.5.4.1 Coagulation-Flocculation and Sand Filtration Method

5 L of leachate was added into the coagulation-flocculation reactor followed by addition of $FeCl_3$ so that the the $FeCl_3$: COD ratio is 1: 1.3. The pH of the raw leachate was adjusted to pH 6 before $FeCl_3$ addition. The mixture was stirred vigorously at 150 rpm for 10 min. Then, the stirring was slowed down to 70 rpm for another 30 min. The mixture was allowed to settle for 1 hour. Sand filtration was used after coagulation-flocculation treatment to remove residual floc in the pre-treated leachate. The column was made of 500 g of sand and the pre-treated leachate was pumped through the column into Ammonia stripping/UV-PS tank.

3.5.4.2 Ammonia Stripping-UV/PS Method

Initially, the pH of pre-treated leachate was adjusted to 11.5. An air pump was connected to gas dispersion tube (pyrex) to generate tiny air bubbles in the ammonia stripping tank. 12 mM of PS was added into the tank. Then, the pre-treated SLL was cycled between the ammonia stripping tank and UV tank (2.7 L Atlantic Sanitron UV Purifier) using a peristaltic pump. Three flow rates were used namely 15 mL/min, 50 mL/min, and 100 mL/min for flow rate optimization study. For every flow rate used, the reaction was allowed to proceed for 24 hours. The reduction in pH was recorded for every hour.

3.5.4.3 Cation Exchange Column method

Residual sulfate from SR-AOP treatment was removed using an Amberlite (IRA-402) ion exchange column. The SR-AOP treated samples were passed through column consisting of 200 g of Amberlite at the flow rate of 12 mL/min.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Stabilized Landfill Leachate (SLL) Characterization

The chemical characteristics of the collected leachate were presented in Table 4.1. Typical SLL is characterized by a relatively moderate concentration of COD (5000 – 20,000 mg/L), high concentration of NH_3N (3000 – 5000 mg/L), slightly basic (~7.5) and low biodegradability (BOD/COD < 0.1) (Foo and Hameed, 2009).

Table 4.1: Chemical characteristics of SLL.

Parameters	Values
pH	7.95 ± 0.08
Turbidity (FAU)	620 ± 10
COD (mg/L)	5123 ± 281
BOD (mg/L)	351 ± 36
TOC (mg/L)	1389 ± 227
NH_3N (mg/L)	2700 ± 200
TDS (mg/L)	10 ± 2
Conductivity (µS/cm)	21 ± 2
Salinity	13 ± 2
BOD/COD	0.07
TOC/COD	0.27

The selected landfill leachate showed the COD of 5123 mg/L, NH_3N concentration of 2700 mg/L, BOD/COD of 0.07 and pH of 7.95. Therefore, the collected leachate can be categorized as SLL. Huo et al. (2008) reported that only the leachates with BOD/COD ratio of more than 0.25 are suitable to be treated by biological treatment. As a result, physicochemical treatment is often applied for the treatment of SLL rather than the biological treatment. Therefore, in this study, the collected SLL was first treated using coagulation-flocculation. Then, the efficiency of Fenton and SR-AOP reaction in the mineralization of pre-treated SLL was evaluated.

4.2 Removal of organic matter from SLL using Coagulation-Flocculation-Fenton coupled with activated carbon adsorption

4.2.1 Coagulation- Flocculation Pretreatment

Coagulation–flocculation is a relatively simple and controllable technique which is widely used in the pretreatment of SLL (Liu et al., 2012). It is an essential stage to reduce total suspended solids, organic content, and color to improve the efficiency of the subsequent treatment processes (Amor et al., 2015). Coagulation involves the destabilization of the colloidal suspension and consequently giving rise to particles aggregation (Smaoui et al., 2015). The particles destabilization can be accomplished by the addition of coagulants. In this study, the effectiveness of three coagulants namely, $FeCl_3$, $Al_2(SO_4)_3$ and PACL, in the removal of TOC of the SLL was evaluated at different pHs and coagulant dosages.

The results indicated that the concentration of TOC of SLL was significantly reduced after coagulation-flocculation. Coagulant dosage, pH, and the type of coagulant were found to influence the efficiency of this pretreatment method (Figure 4.1). The TOC removal efficiency was found to increase from pH 5 to 6 for all selected coagulants. The highest TOC removal efficiency was achieved at pH 6. At pH 6, the percentage of TOC removal was 71, 60 and 55% for $FeCl_3$, PACL and $Al_2(SO_4)_3$, respectively. The efficiency of coagulation-flocculation in the TOC removal was found to decrease with pH after pH 6. In landfill leachate, nearly all colloidal particles are negatively charged at pH around 5-9 (Duan and Gregory, 2003). The colloidal particles are often stable and resist to aggregate due to the electrical repulsion of the surface negative charge (Li et al., 2010). The addition of cations from coagulant interacts strongly with the negatively charge colloid in the leachate and causing the suspended solid to destabilize and coagulate.

The effectiveness of coagulation-flocculation in the TOC removal is depending on the pH of the leachate. At different pH, the coagulant forms different types of hydrolyzed species. For example, Fe^{3+} of $FeCl_3$ transforms into polynuclear cation under acidic condition (**Equation 4-1**) meanwhile it also reacts with hydroxide ion (OH^-) to form $Fe(OH)_3$ or $Fe(OH)_4^-$ at basic condition (**Equations 4-2** and **4-3**). The same scenario occurs for Al^{3+} of $Al_2(SO_4)_3$. By increasing the pH, the hydrolyzed species of Al^{3+} transform from the species with high number of positive charges to the species with lower number of positive charge (Li et al., 2010). For PACL, Al_{13} species is more readily available at wider pH range due to its high stability (Duan and Gregory, 2003). Under appropriate conditions, Al_{13} species forms rapidly and remaining stable in aqueous solutions for long periods (Duan and Gregory, 2003). In this study, the highest TOC removal was mostly achieved at pH 6 (Figure 4.1) for all selected coagulants. Therefore, it can be concluded that slightly acidic condition favors the coagulation-flocculation process due to the formation of polynuclear cation that neutralizes the negatively charged colloid in the SLL.

$$xFe^{3+} + yH_2O \rightarrow Fe(OH)_y^{(3x-y)} + yH^+ \qquad \textbf{(4-1)}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad \textbf{(4-2)}$$

$$Fe^{3+} + 4OH^- \rightarrow Fe(OH)_4^- \qquad \textbf{(4-3)}$$

Instead of pH, coagulant dosage was also found to influence the TOC removal efficiency. In general, the percentage of TOC removal was found to increase with increasing coagulant dosage from 3 to 7 g/L (Figure 4.1). This observation can be explained by charge neutralization phenomena. At appropriate dosage, suitable amount of cations can neutralize the negatively charged colloid in the SLL and promotes the destabilization of the colloidal system during flocculation. When the dosage of coagulant is overdose, the colloid will be stabilized as a result of charge repulsion due to the presence of excess positive charge ion of the coagulant and thus diminishing the effectiveness of coagulation-flocculation in the removal of TOC (Li et al., 2010; Amor et al., 2015). Among the tested coagulants, $FeCl_3$ was found to be the most efficient coagulant for TOC removal at the lowest dosage. This finding is in agreement with the previous studies (Duan and Gregory, 2003; Ntampou et al., 2006; Li et al., 2010; Amor et al., 2015). The lower efficiency of PACL as coagulant might be due to the depolymerazation of Al_{13} species by natural organic matter (Masion et al., 2000).

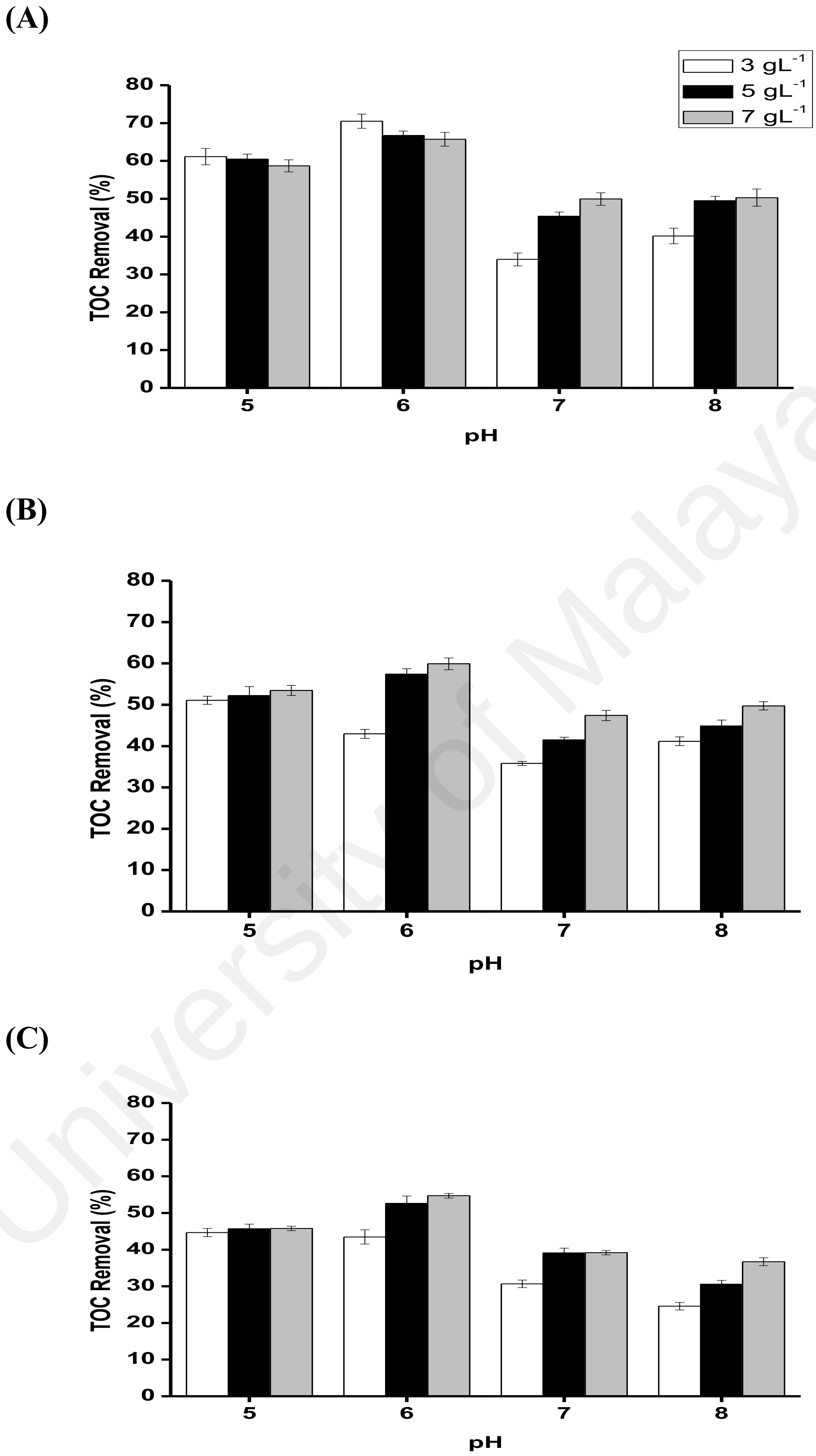


Figure 4.1: Effect of pH and coagulant dosage on TOC removal: (A) $FeCl_3$, (B) PACL and (C) $Al_2(SO_4)_3$. Note: White, black and grey histogram represent 3, 5 and 7 g/L respectively.

To achieve the highest efficiency of TOC removal with the lowest dosage, $FeCl_3$ was chosen as the coagulant for the SLL pretreatment. The effect of the $FeCl_3$ dosages were evaluated in detail (2-7 g/L) to determine the optimal dosage for TOC removal. The effect of $FeCl_3$ dosage on the removal of TOC is shown in Figure 4.2. The result indicated that 67% of TOC removal was achieved at 2 g/L of $FeCl_3$. The highest TOC removal of 71% was observed at 3 g/L of $FeCl_3$. The TOC removal was found to decrease from 71 to 65% when the dosage of $FeCl_3$ was increased from 3 to 7 g/L. Consequently, 3 g/L of $FeCl_3$ was selected to pretreat the SLL at pH 6. The pre-treated SLL was treated with Fenton reaction after sand filtration.

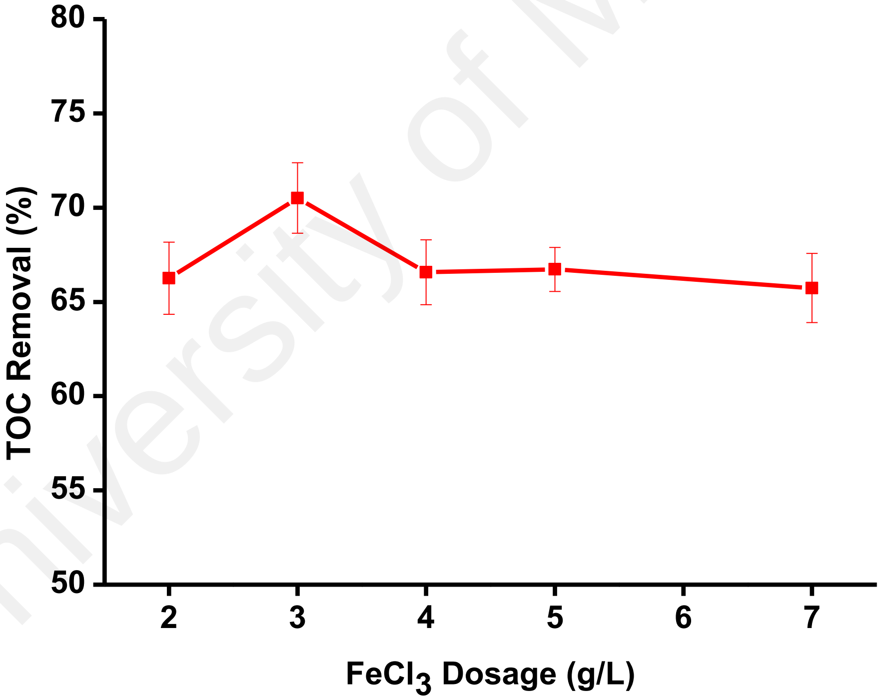


Figure 4.2: Effect of $FeCl_3$ dosage in TOC removal at pH 6.

4.2.2 Fenton Oxidation process

Operating condition of Fenton process in the treatment of SLL was optimized by varying the reaction time, H_2O_2 to Fe^{2+} ratio (H_2O_2:Fe^{2+}), H_2O_2 dosage and pH. This experiment was started with the investigation on the variation of TOC removal with reaction time (Figure 4.3). The result indicated that the TOC removal was increased significantly to 51% for the first 1 h of reaction using 240 mM H_2O_2 and 12 mM of $FeSO_4$. No significant TOC removal was observed after 1 h. When the reaction time was increased from 1 to 72 h, the TOC removal was only increased by 3%. Therefore, 1 h of reaction time was selected for further study.

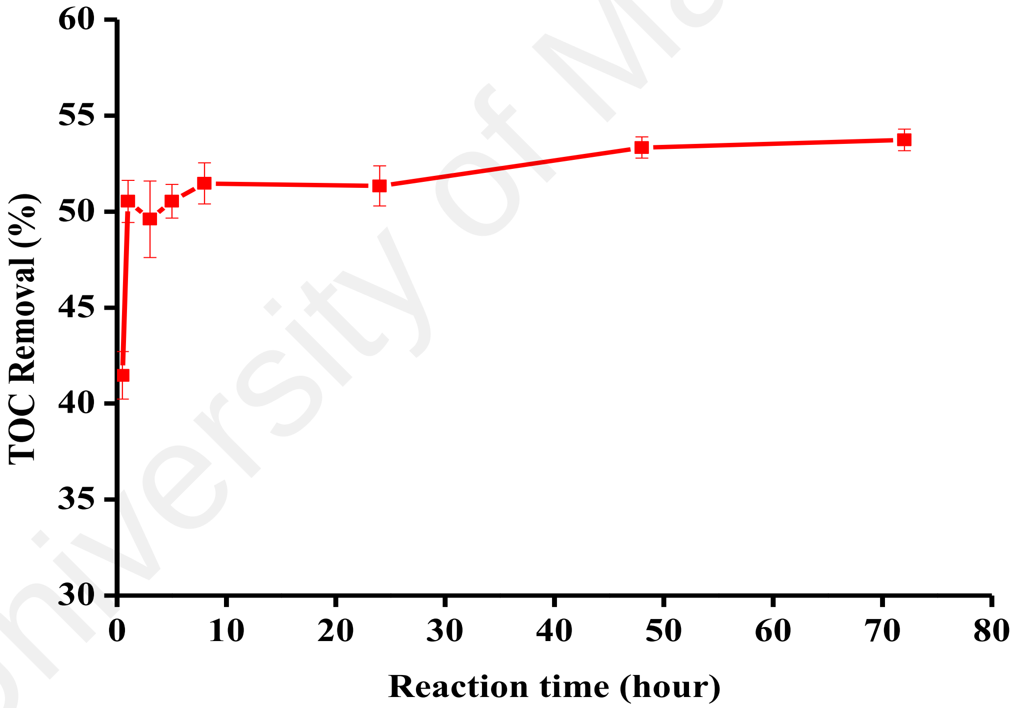


Figure 4.3: Effect of reaction time on TOC removal (dosage of H_2O_2 = 240 mM, pH of SLL = 3, H_2O_2:Fe^{2+} ratio= 20:1).

H_2O_2:Fe^{2+} is an important parameter for Fenton reaction to produce sufficient amount of •OH for water treatment. Fe^{2+} act as catalyst to generate •OH from H_2O_2 as shown by **Equation 2-9** (Section 2.54**)**. The effect of H_2O_2: Fe^{2+} on TOC removal was examined by varying the concentration of Fe^{2+} from 4 to 120 mM with H_2O_2 concentration of 120 mM. The H_2O_2 concentration was selected based on the previous study conducted by Amor et al. (2015). The experiment was performed at pH 3 and the concentration of TOC was monitored at 1 h of reaction time. The result indicated that only 12% of TOC removal was achieved when the Fenton reaction was carried out without the addition of Fe^{2+} (Figure 4.4).

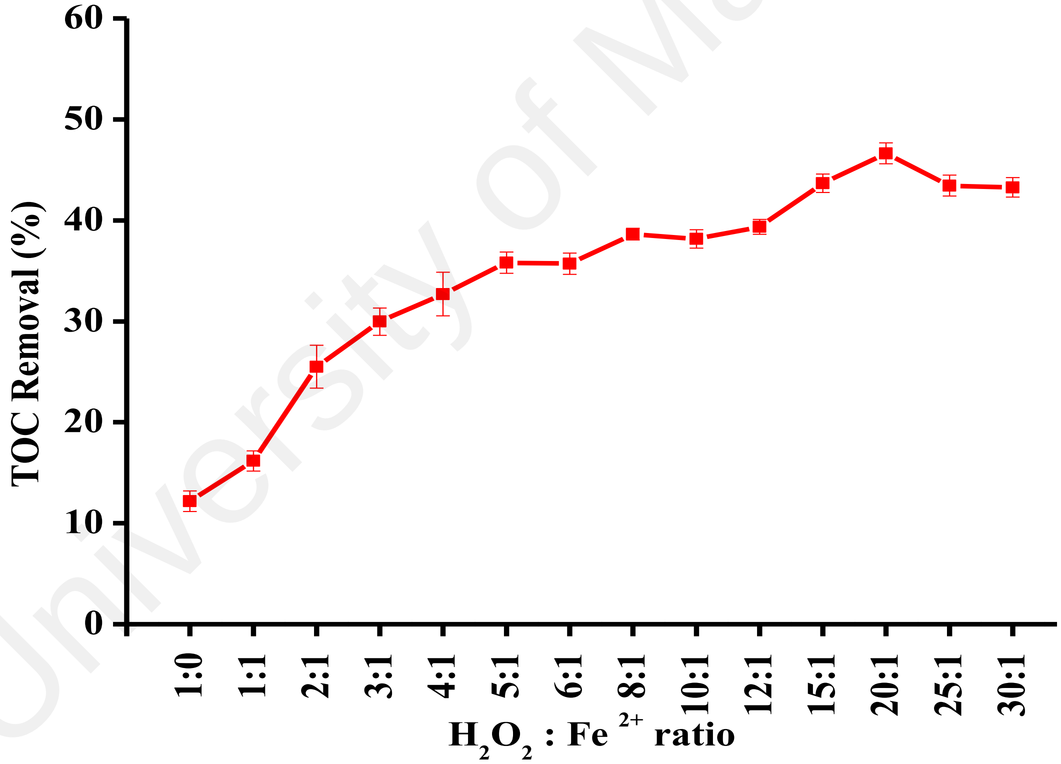


Figure 4.4: Effect of H_2O_2:Fe^{2+} ratio on TOC removal (dosage of H_2O_2 = 240 mM, pH of SLL = 3, reaction time = 1h).

The reduction of TOC might due to the presence of the Fe^{3+} in SLL from the coagulation-flocculation treatment. Both Fe^{2+} and Fe^{3+} are reported as catalysts in Fenton and Fenton-like reaction to generate •OH from H_2O_2 (Deng and Englehardt, 2006). The TOC removal was found to increase from 16 to 47% when H_2O_2: Fe^{2+} was increased from 1:1 to 20:1 and Fenton reaction achieved its highest TOC removal at H_2O_2: Fe^{2+} of 20:1. This result showed that the decreased of Fe^{2+} enhanced the TOC removal. It was due to the excess amount of Fe^{2+} ion that consumed the •OH (Equation 4-4). When the H_2O_2: Fe^{2+} increased from 20:1 to 30:1, the efficiency of Fenton reaction in the TOC removal was found to decrease from 47 to 43%. This was due to the insufficient amount of Fe^{2+} to catalyze the Fenton reaction and consequently reduced the amount of •OH (Deng and Englehardt, 2006; Babuponnusami and Muthukumar, 2014).

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-} \qquad \textbf{(4-4)}$$

To assess the effect of H_2O_2 dosage on the TOC removal, the H_2O_2:Fe^{2+} was fixed at 20:1. The concentration of H_2O_2 was varied from 30 to 960 mM (Figure 4.5). TOC removal efficiency was found to increase rapidly from 16 to 52% with increasing H_2O_2 dosage from 30 to 240 mM. This result was caused by the increased of the amount of •OH when the concentration of H_2O_2 was increased (Babuponnusami and Muthukumar, 2014). The TOC removal was retarded when the H_2O_2 dosage was increased from 240 and 960 mM. In general, the increasing of H_2O_2 concentration enhanced the TOC removal efficiency (Babuponnusami and Muthukumar, 2014). However, higher amount of H_2O_2 was also found to scavenge the •OH as shown by **Equation 4-5**.

$$H_2O_2 + \bullet OH \rightarrow H_2O + \bullet H_2O \qquad \textbf{(4-5)}$$

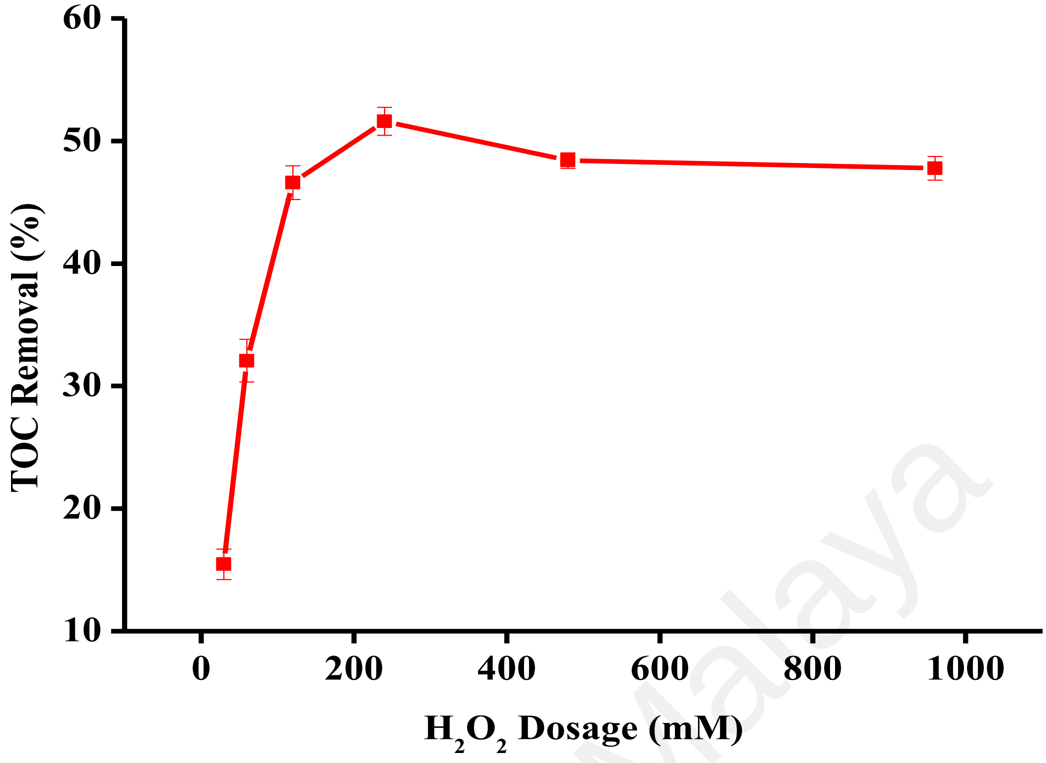


Figure 4.5: Effect of H_2O_2 dosage on TOC removal (pH of SLL = 3, reaction time = 1h, H_2O_2:Fe^{2+} ratio = 20:1).

The effect of pH on the efficiency of TOC removal was evaluated at pH 2 to 8. The results indicated that the pH can significantly influence the efficiency of Fenton reaction in TOC removal. As shown in Figure 4.6, TOC removal achieved its highest efficiency of 51% at pH 3. Above pH 3, the TOC removal was found to decrease with increasing pH. At higher pH, self-decomposition of H_2O_2 and precipitation of Fe^{2+} as ferrous hydroxide reduced the amount of •OH (Tang and Huang, 1996). Meanwhile, at pH 2 the TOC removal was also found to be lower than pH 3. At this low pH region, the reduction of the efficiency of the Fenton reaction was due to the scavenging effect of •OH by H^+ ion (Tang and Huang, 1996). In this study, pH 3 was selected as the optimum pH condition and this result was in agreement with other studies (Zhang et al., 2005; Deng, 2007; Hermosilla et al., 2009; Amor et al., 2015).

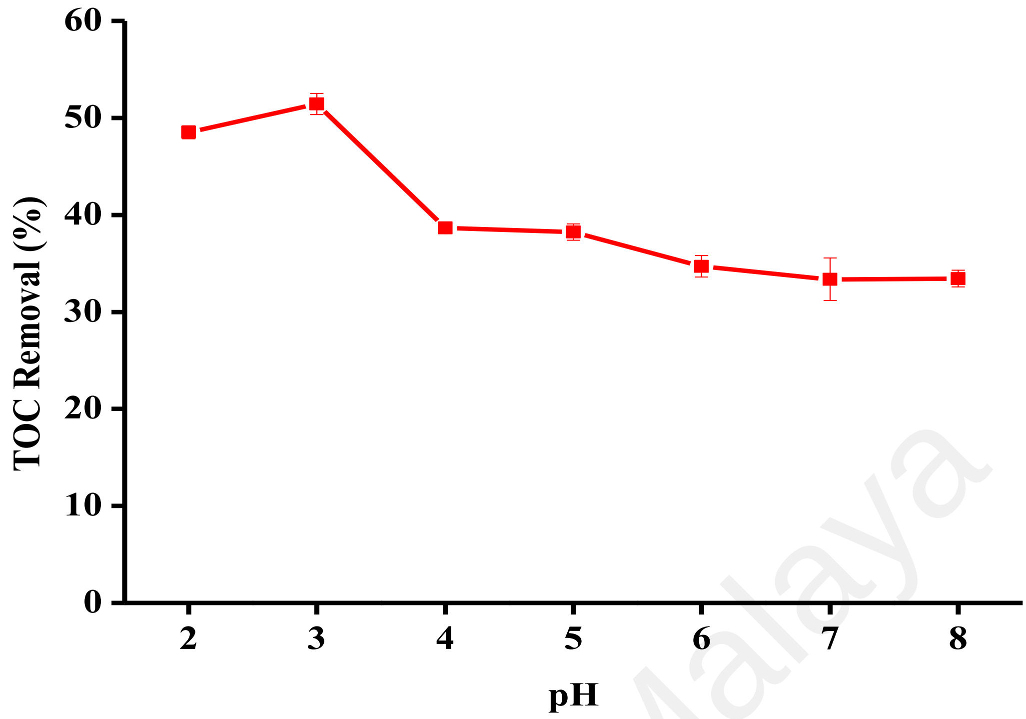


Figure 4.6: Effect of pH on TOC removal (reaction time = 1h, H_2O_2:Fe^{2+} ratio = 20:1, dosage of H_2O_2 = 240 mM).

4.2.3 Zebrafish Acute Toxicity

Zebrafish is a very useful vertebrate in toxicology modelling because of their small size, rapid development, and fundamental similarity to other vertebrates including humans (Hollert and Keiter, 2015). SLL from optimized condition of each stage was used for this purposed. The 96h LC_{50} of SLL and treated SLL on Zebrafish are summarized in Figure 4.7. 96h LC_{50} refers to the lethal concentration which causes the death of 50% of a group of test animals in 96 h (OECD, 2004). The LC_{50} values were presented in % (v/v). Zero mortality was observed in the control group and thereby removing the possibilities of experimental interference due to starvation. It was observed that the LC_{50} of untreated SLL were 1.4% ± 0.2 (v/v). After coagulation-flocculation, the LC_{50} was found to increase to 24.5% ± 0.3 (v/v). This result indicated that the pre-treated SLL was less toxic than raw SLL.

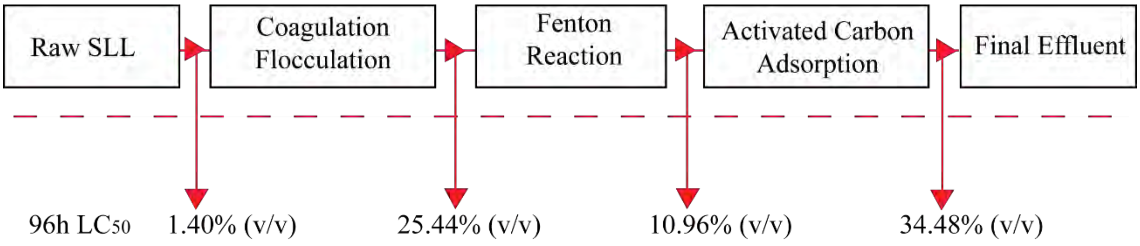


Figure 4.7: LC_{50} of each treatment process.

In contrast, after Fenton reaction, the toxicity of the treated SLL was found to be higher than the pre-treated SLL. The LC_{50} for the Fenton reaction treated SLL was 10.96% ± 0.3 (v/v). The toxicity of the Fenton reaction might be due to the presence of remaining H_2O_2 after Fenton treatment. The residual concentration of H_2O_2 after Fenton treatment was 229.5 mg/L. It was reported that H_2O_2 residue causes relaxation and constriction of blood vessels, and also the possible cell damage to the fish and aquatic organisms (Faraci, 2006). Therefore, this result suggested that excess H_2O_2 should be removed from the effluent before discharging it into the environment. In industrial wastewater treatment, additional chemicals such as sodium thiosulfate and sodium sulphite are frequently added to reduce the H_2O_2 residual (Liu et al., 2003; Olmez-Hanci et al., 2014).

To further verify the toxicity due to the presence of H_2O_2, activated charcoal was used to remove the H_2O_2 residual. The treated leachate from Fenton reaction was passed through an activated carbon column at 5 mL/min to remove the residual H_2O_2 in the SLL effluent. As shown by Figure 4.8, the percentage removal of H_2O_2 by activated charcoal was higher than 90%. At the first 0.12 L, 98% of H_2O_2 removal was achieved for 6 and 9 g of powdered activated charcoal. Slight decreased in efficiency was observed when the volume exceeded 0.12 L. At 0.5 L, the percentage removal of H_2O_2 was maintained at more than 90%. The LC_{50} of the treated SLL after activated charcoal adsorption was 34.5 %. This result showed that the final treated SLL was far less toxic than the pre-treated and Fenton reaction (Figure 4.7).

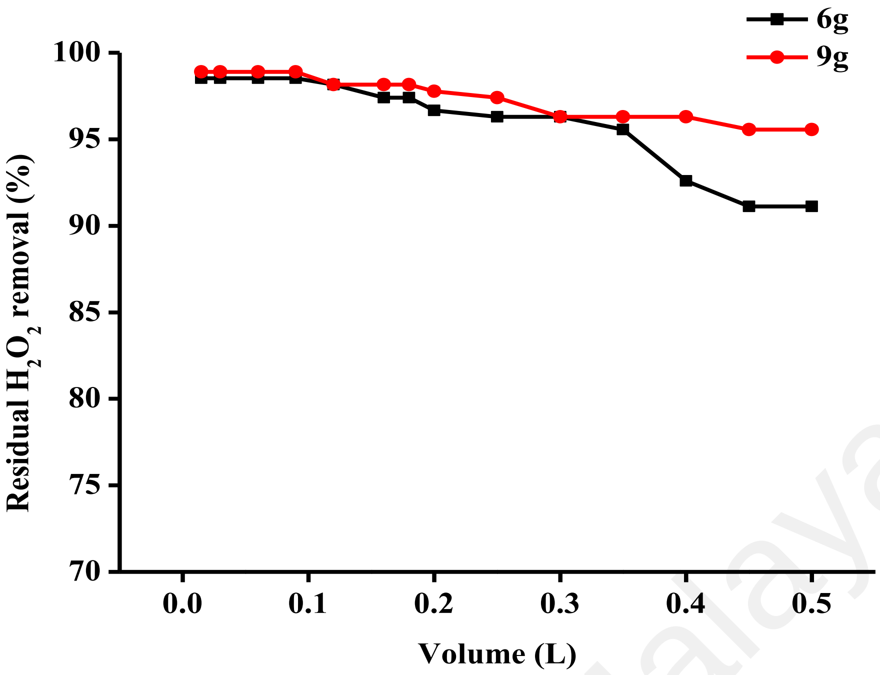


Figure 4.8: Effect of H_2O_2 removal as a function of volume.

4.2.4 Performance of Coagulation-Flocculation-Fenton coupled with activated carbon adsorption

In order to assess the performance of the coagulation-flocculation-Fenton coupled with activated carbon adsorption, the experiment was conducted using the optimized condition of SLL from each stage of treatment. The TOC, COD and turbidity of the treated SLL were measured, and the results are shown in Table 4.2. It was observed that 71% of TOC, 65% of COD and 90% of turbidity of SLL were successfully removed during coagulation-flocculation. However, the COD concentration (1295 mg/L) of SLL after coagulation-flocculation far exceeded the discharge standard stipulated in Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009 which is 400 mg/L. Subsequently, Fenton reaction further enhanced the removal of TOC and COD to 165 and 582 mg/L, respectively. The reduction of TOC and COD was found to be 50 and 55% from the coagulation-flocculation pretreatment. Additionally, the adsorption by activated charcoal was also found to remove the TOC and COD by 30 and

38%, respectively. Alvarez-Vazquez et al. (2004) reviewed that the COD removal by conventional multistage biological treatment is generally less than 60%. In comparison with conventional biological treatment of SLL, the selected combination technique in this study provides better organic content removal (90% COD removal) and produced lower toxic effluent. According to the Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulation 2009, the concentration of COD for the final leachate effluent is set at <400 mg/L. In this study, the COD concentration for the final effluent was 361 mg/L. Therefore, it can be concluded that the produced effluent meets the local discharge limit.

Table 4.2 : The performance of coagulation-flocculation-Fenton coupled with activated carbon.

Treatment	**Parameters, (% removal)**		
	TOC mg/L	COD mg/L	Turbidity (FAU)
Raw SLL	1135	3700	520
Coagulation-Flocculation	331 *(71)*	1295 *(65)*	78 *(85)*
Fenton Reaction	165 *(50)*	582 *(55)*	- *(100)*
Activated Carbon Adsorption	116 *(30)*	361 *(38)*	-
Total percentage removal	*90*	*90*	*100*

4.3 SLL Treatment by Coagulation-Flocculation coupled with SR-AOP

4.3.1 Coagulation-Flocculation Pretreatment

As shown in section 4.1, $FeCl_3$ was found to be the most effective coagulant for the treatment of landfill leachate. This result was also in agreement with previous reported literature that indicates the effectiveness of $FeCl_3$ as compared to other coagulants (Maleki et al., 2009; Li et al., 2010; Oloibiri et al., 2015). Therefore, $FeCl_3$ was used in coagulation-flocculation pretreatment to produce pre-treated leachate for SR-AOP study. However, this study was performed on the new batch of SLL. The SLL was found to foam heavily during coagulation-flocculation. To reduce the foaming, the SLL was diluted before the pretreatment.

The effect of initial COD to $FeCl_3$ ratio has not been optimized in earlier study. The COD concentration in the leachate is always fluctuates and differ based on the location, season etc. The COD:$FeCl_3$ ratio optimization was important in order to directly apply the correct dosage of coagulant based on the COD concentration of leachate effluent. Since $FeCl_3$ has been proven to be efficient coagulant, the effectiveness of $FeCl_3$ for the COD removal was re-evaluated at different COD:$FeCl_3$ ratio at pH 6. As shown in Figure 4.9, the coagulation-flocculation significantly removed the COD from the SLL. The result also showed that the percentage of COD removal was strongly depending on COD:$FeCl_3$. In general, the percentage of COD removal was found to increase from 64 to 75% when the COD:$FeCl_3$ was increased from 1:1.1 to 1:2.2. The percentage removal of COD was found to decrease to 74 and 73% when the COD:$FeCl_3$ was further increased to 1:2.5 and 1:3, respectively. The addition of a suitable ratio of COD:$FeCl_3$ generates an optimum amount of cation (Fe^{3+}) to neutralize the negatively charged colloids and enhanced the coagulation process (Li et al., 2010). When the amount of $FeCl_3$ was in excess (COD:$FeCl_3$ of more than 2.2), the colloid was stabilized again as a result of charge repulsion due to present of excess positively charged ions. In order to reduce the chemical consumption, COD:$FeCl_3$ ratio of 1:1.3 was selected for further study. COD:$FeCl_3$ of 1:1.3 produced the percentage of COD removal of 72% which was 4.0% lower than the COD:$FeCl_3$ of 1:2.2.

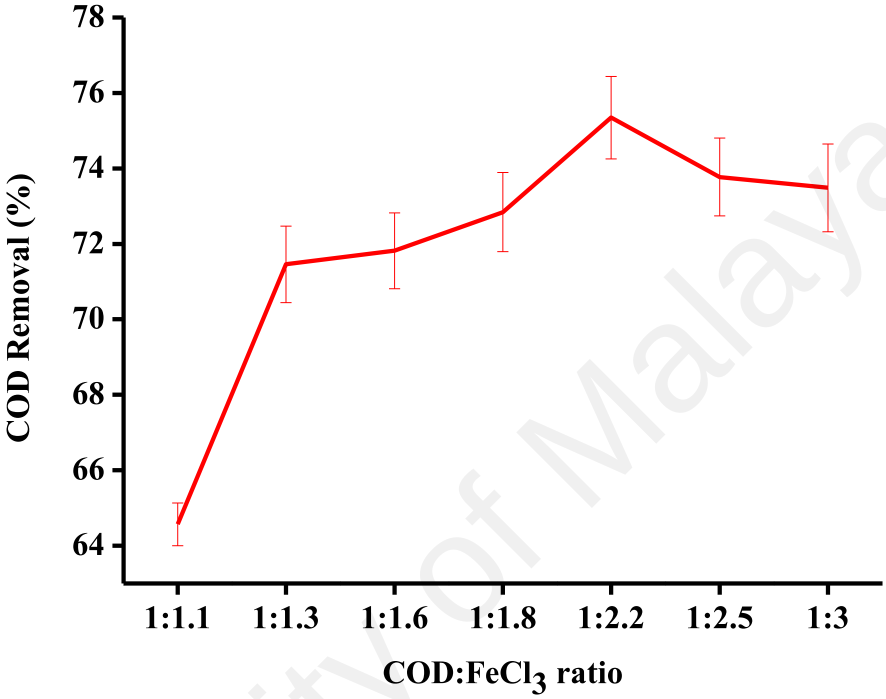


Figure 4.9: Effect of COD: $FeCl_3$ ratio on COD removal (pH= 6).

Table 4.3 shows the main chemical characteristics of the raw and pretreated SLL used in this study. The results indicated that almost 100% and 94% of turbidity and colour were successfully removed through coagulation-flocculation. The organic concentration was also significantly reduced after coagulation-flocculation. 75 and 70% reduction of COD and TOC was achieved after the pretreatment. COD concentration of the pretreated SLL complied with The Malaysian discharge standard of 400 mg/L. However, it was found that COD concentration was still not complying with maximum discharge standard (MDS) in many countries. Kurniawan et al. (2006) reported that the maximum discharge standard (MDS) of landfill leachate in USA, Germany, France, Hong Kong and South Korea were 200 mg/L of COD. In this study, the COD concentration after coagulation-flocculation was 276 mg/L.

Table 4.3: Chemical characteristic of SLL and pre-treated SLL.

Parameter	SLL	Pre-treated SLL	% Removal
COD (mg/L)	1117	276	75
TOC (mg/L)	356	107	70
Turbidity (FAU)	301	< 25	100
Colour (Pt/Co)	5098	311	94

4.3.2 Fe(II)/SR-AOP optimization

In this study, SR was generated using two different types of oxidants namely PS ($S_2O_8^{2-}$) and PMS (HSO_5^-). These oxidants showed high solubility and stability in water at different pHs (Zhou et al., 2015; Fagier et al., 2016). Therefore, it can be an added advantage to leachate treatment since the leachate may turn acidic after coagulation-flocculation. In this study, Fe (II) was used as a catalyst to activate the SR because it is low toxic and more environmentally friendly compared to other metal catalyst such as cobalt (Rastogi et al., 2009). The SR formation from both PS and PMS activated by Fe(II) are illustrated by the **Equation 4-6** and **4-7**:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-\bullet} + SO_4^{2-} + Fe^{3+} \quad k = 2.0 \times 10\ M^{-1}s^{-1} \qquad \textbf{(4-6)}$$

$$HSO_5^{-} + Fe^{2+} \rightarrow SO_4^{-\bullet} + OH^{-} + Fe^{3+} \quad k = 3.0 \times 10^4\ M^{-1}s^{-1} \qquad \textbf{(4-7)}$$

The effect of the operating condition of SR-AOP on the reduction of COD concentration was studied by varying PS:Fe(II) and PMS:Fe(II), pH, the dosage of oxidants and reaction time. The concentration of Fe(II) was varied from 1 to 24 mM to investigate the effect of Fe(II) concentration on the reduction of COD. The concentration of oxidants (PS and PMS) was fixed at 12 mM. The result from these experiments was presented as percentage reduction of COD versus PS:Fe(II) and PMS:Fe(II) (Figure 4.10). The control experiment was first setup without the addition of Fe(II) to investigate the possibility of PS and PMS in reducing the concentration of COD of pre-treated SLL. It was found that less than 3% of COD was reduced without additional of Fe(II) in the both treatment systems. The increasing Fe(II) concentration was found to enhance the percentage reduction of COD for both PS and PMS systems. As shown in Figure 4.10, percent COD reduction was found to increase with increasing PS:Fe(II) and PMS:Fe(II) from 1:0.5 to 1:2. This result was attributed to the formation of the higher amount of SR and consequently, increased the COD reduction efficiency (Rastogi et al., 2009). On the other hand, when the PS:Fe(II) and PMS:Fe(II) were increased to 1:3, no significant increment of COD reduction was observed. This result was due to the consumption of SR by the excess amount of Fe(II) as indicated in **Equation 4-8** (Matzek and Carter, 2016). The rate of scavenging reaction of SR by Fe(II) is much higher than the rate of SR production (**Equation 4-6** and **4-7**). Therefore, an excess amount of Fe(II) can limit the SR formation (Fagier et al., 2016). In this study, the highest COD reduction was achieved at the ratio of 1:2 with 22 and 20% of COD reduction by Fe(II)/PMS and Fe(II)/PS, respectively.

$$SO_4^{-\bullet} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \quad k = 4.9 \times 10^{9}\ M^{-1}s^{-1} \qquad \textbf{(4-8)}$$

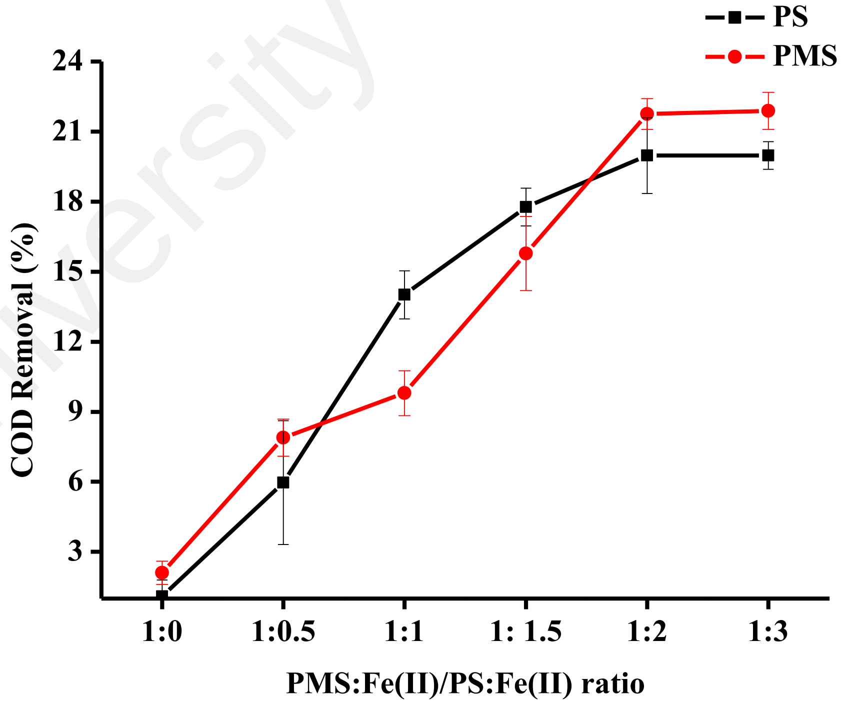


Figure 4.10: The effect of Oxidant: Fe(II) ratio on COD removal from pre-treated leachate (Dosage of oxidants = 12mM, Reaction time = 1 h, pH = 5).

The effect of pH on the COD reduction efficiency was evaluated from pH 3 to 7. The percentage of COD reduction was found to vary from 20 to 22% for PMS and PS treatment systems, respectively (Figure 4.11). This result indicated that pH does not have the significant influence on the COD reduction. The result was contradicting with some of the previous studies that indicated the degradation of organic pollutants achieved its highest efficiency at acidic conditions through acid-catalysis formation of SR (Zhang et al., 2015). This phenomenon is probably due to the complexation of Fe(II) with soluble organic substances in landfill leachate. Complexation can stabilize the Fe(II) from been precipitated and consequently enhanced the COD removal (Wu et al., 2014). Therefore, it could be an added advantage for this method to be coupled with coagulation-flocculation which often lowering down the pH of the pre-treated landfill leachate.

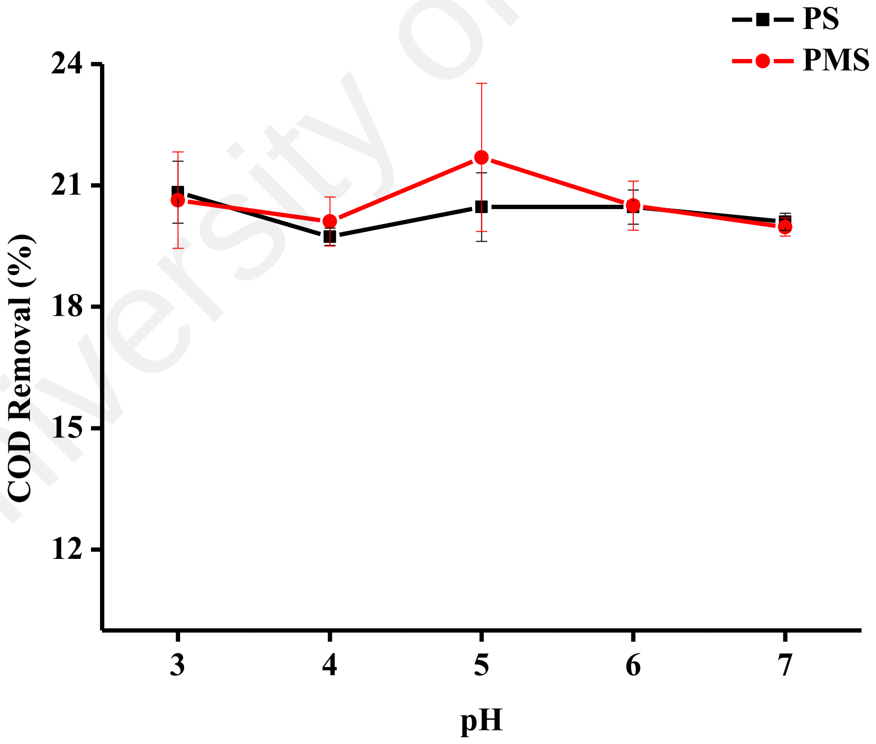


Figure 4.11: The effect of initial pH on COD removal from pre-treated leachate (Dosage of oxidants = 12mM, Reaction time = 1 h, Oxidant: Fe(II) ratio = 1:2).

The effect of PS and PMS concentration on COD reduction was investigated using PMS:Fe(II) and PS:Fe(II) of 1:2 and 1 h reaction time. The concentration of oxidants (PMS and PS) was varied from 5 mM to 20 mM (Figure 4.12). COD reduction efficiency was found to increase with increasing oxidant dosage from 5 to 15 mM. The percentage of COD reduction was increased from 19 to 24% and from 16 to 23% for PMS/Fe(II) and PS/Fe(II), respectively. The increased of percent COD reduction was due to higher production of SR which favoured the oxidation process (Olmez-Hanci and Arslan-Alaton, 2013). However, the percentage of COD reduction in the both treatment systems was found to decrease after the oxidant dosage of 20 mM.

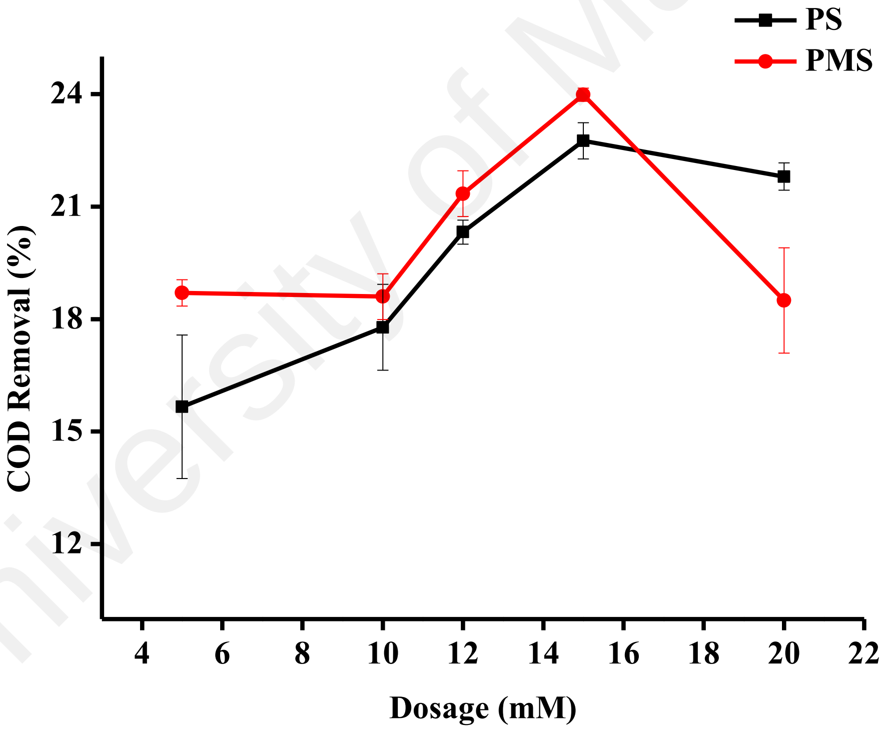


Figure 4.12: The effect of oxidants dosage on COD removal from pre-treated leachate (pH 5, reaction time = 1 h, oxidant: Fe(II) ratio = 1:2).

This result was attributed to the scavenging reaction of SR by the excess amount of PS and PMS as indicated in **Equation 4-9** and **4-10**. The rate of scavenging reaction was much higher than the rate of SR production. In addition, peroxysulfate ($SO_5^{\bullet-}$) (E° = 1.1V) and persulfate radical that ($S_2O_8^{\bullet-}$) (E° = 2.1V) generated from the reaction are weaker oxidants in comparison with SR (E° = 2.5-3.1 V), thus higher PS and PMS dosage could lower the COD reduction efficiency (Jaafarzadeh et al., 2016). Furthermore, SR may self-react and inhibit the COD reduction efficiency (**Equations 4-11**) (Olmez-Hanci et al., 2013). In this study, 15 mM was selected for optimum dosage for both PS and PMS.

$$S_2O_8^{2-} + SO_4^{-\bullet} \rightarrow S_2O_8^{-\bullet} + SO_4^{2-} \quad k = 6.1 \times 10^5\ M^{-1}S^{-1} \qquad \textbf{(4-9)}$$

$$HSO_5^{-} + SO_4^{-\bullet} \rightarrow SO_5^{-\bullet} + HSO_4^{-} \quad k = 1 \times 10^5\ M^{-1}S^{-1} \qquad \textbf{(4-10)}$$

$$SO_4^{-\bullet} + SO_4^{-\bullet} \rightarrow S_2O_8^{2-} \quad k = 4 \times 10^8\ M^{-1}S^{-1} \qquad \textbf{(4-11)}$$

The concentration of COD was measured after 0.5, 1, 2, 3 and 5 h of reaction to evaluate the effect of reaction times on the percent COD reduction (Figure 4.13). The result indicated that the COD degradation was increased significantly for the first 3 h for both PS/Fe(II) and PMS/Fe(II) systems. The percentage of COD reduction for PS/Fe(II) and PMS/Fe(II) at 3 h of reaction time were 34 and 35%. When the reaction times increased from 3 to 5 h, the percent COD reduction was found to increase slowly to 35% for both PS/Fe(II) and PMS/Fe(II), respectively. Hence, 3 h of reaction time was sufficient to achieve the highest efficiency in COD reduction of pre-treated SLL. At all reaction times, PMS/(FeII) showed slightly higher COD removal as compared to PS/Fe(II). This condition might be due to the high reactivity of PMS as compared to PS in generating SR under Fe(II) activating methods. As shown in the rate constant of the **Equation 4-6** and **4-7,** PMS is about 1000 times reactive than PS.

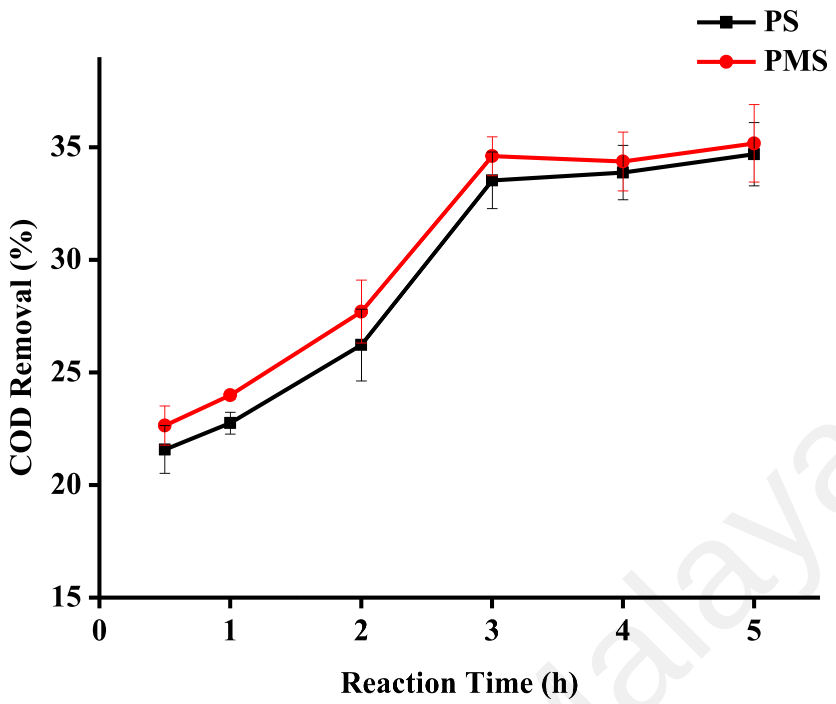


Figure 4.13: The effect of reaction time on COD removal from pre-treated leachate (pH 5, Oxidants dosage = 15 mM, Oxidant: Fe(II) ratio = 1:2).

4.3.3 UV/SR-AOP Optimization

During UV/SR-AOP, the UV light imparts energy to the PS anion resulting in the cleavage of the peroxide bond to generate two moles of SR (**Equation 2-12 section 2.7**). Meanwhile, photolysis of PMS generates one mole of SR and one mole of •OH (**Equation 2-13 section 2.7**) (Mahdi-Ahmed and Chiron, 2014; Jaafarzadeh et al., 2017). For comparison, activation of PMS and PS using transition metals (M) only generates one mole of SR radical (**Equation 2-10 and 2-11 section 2.7**) (Ghanbari and Moradi, 2017).

SR is an electrophile, and it can react with organic compounds via electron transfer mechanism. This reaction could start with the formation of sulfate adduct at the unsaturated bond of organic compounds and subsequently, forms the reactive carbocation for further reaction (He et al., 2014). SR reacts with organic compounds through electron abstraction at the carboxylate anion and eliminates it as CO_2. SR is also found to react with organic compounds through hydrogen abstraction (H-abstraction) (He et al., 2014).

During water treatment, SR reacts with organic compounds directly and propagates to secondary reactions which progressively decompose the organic compounds (Matzek and Carter, 2016).

The treatment of pre-treated SLL with UV/SR-AOP was started with the addition of PS and PMS without the presence of UV irradiation to study the effectiveness of PS and PMS in reducing the COD of SLL. Zhang et al. (2018) reported that the residual iron from the coagulation-flocculation process could activate the PS and PMS to form SR. In this study, the total iron concentration of SLL after coagulation-flocculation was 7.1 mg/L, which was higher than raw leachate (2.4 mg/L). The result showed less than 5% of COD removal was achieved by both PS and PMS without UV irradiation (Figure 4.14). Hence, PS and PMS alone are not able to reduce the COD of SLL efficiently.

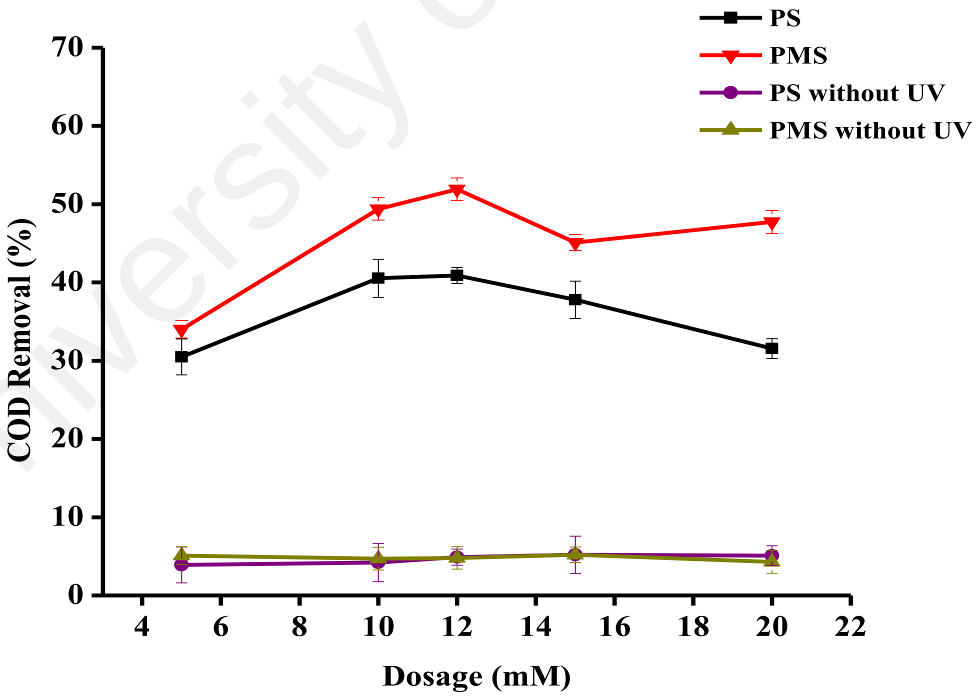


Figure 4.14: Effect of PMS and PS dosage (without pH adjustment, reaction time = 1 h) on COD removal from pre-treated leachate.

The effect of operating parameters of UV/SR-AOP on COD removal was studied by varying the dosage of PS and PMS, initial pH of the pre-treated SLL, and reaction time. Figure 4.14 illustrates the effect of PS and PMS dosage on COD removal efficiency. For PS, the percentage of COD removal was found to increase from 30 to 41% with increasing PS dosage from 5 to 12 mM. The similar trend was also observed for the PMS but with a slightly higher of COD removal efficiency as compared to PS. Both PS and PMS achieved its highest COD removal efficiency at the dosage of 12 mM. However, the percentage of COD removal was found to decrease when the dosage of PS and PMS was further increased to 20 mM. The increased of COD removal from 5 to 12 mM of PS and PMS was due to the increase in the amount of SR formation with increasing concentration of PS and PMS (**Equation 2-12** and **2-13 Section 2.72**) (Shah et al., 2015). In general, the higher amount of SR degraded higher amount of organic compounds and consequently contributed to higher COD removal (Fagier et al., 2016). However, when the concentration of PS and PMS exceeded 12 mM, the process of COD removal was retarded due to the scavenging reaction of excess SR as illustrated by **Equation 4-11**. Therefore, the excess amount of PMS and PS could reduce the amount of available SR for the degradation of organic compounds. Moreover, the excessive amount of PS and PMS also has been reported to form less reactive persulfate radical (E^o = 2.1 V) and peroxysulfate ion (E^o = 1.1 V) as illustrated in **Equation 4-9** and **4-10** (Mahdi-Ahmed and Chiron, 2014; Wang and Liang, 2014; Ghanbari et al., 2016). In this study, 12 mM was selected for optimum dosage for both UV/PS and UV/PMS

Figure 4.15 shows the effect of initial pH of SLL on COD removal. Several researchers have reported that PS and PMS showed the optimum performance in pollutant treatment at acidic condition (Liu et al., 2013; Zhang et al., 2015; Khan et al., 2016). This is due to the redox potentials of SR which is higher under acidic condition rather than the alkaline condition (Anipsitakis and Dionysiou, 2003; Ghanbari et al., 2016). In addition, the acid-catalysis is also found to assist the formation of SR through the reactions as described in **Equation 4-12** and **4-13** (Zhang et al., 2015).

$$H^{+} + S_2O_8^{2-} \rightarrow HS_2O_8^{-} \qquad \textbf{(4-12)}$$

$$HS_2O_8^{-} \rightarrow SO_4^{2-} + SO_4^{-\bullet} + H^{+} \qquad \textbf{(4-13)}$$

In this study, the effect of initial pH on COD removal was investigated in the range of pH 3–7. The results showed that the COD removal efficiency was almost remained unchanged when the initial pH of SLL was increased from 3 to 7. Deng et al. (2013) and Liu et al. (2013) also reported the similar observation when SR-AOP was applied to treat the selected pharmaceuticals. This phenomenon can be explained by the decreasing trend of pH during SR-AOP and the stability of SR. In UV/SR-AOP, photolysis of PS and PMS was first occurred to produce SR and SR can be converted to $\bullet$OH under alkaline conditions (Lau et al., 2007; Deng et al., 2013). Under acidic conditions, SR is the predominant species. In this study, pH of the SLL was found to decrease significantly to 2.5–2.7 irrespective of the selected initial pH value during UV/SR-AOP. Under this condition, conversion of SR to pH-sensitive $\bullet$OH are less likely to happen. Therefore, SR played the major role in degrading the organic matter in SLL, and it allows the COD removal efficiency to remain almost constant. Since the pH of the pre-treated SLL after coagulation-flocculation treatment was 5.2, further pH adjustment was not required.

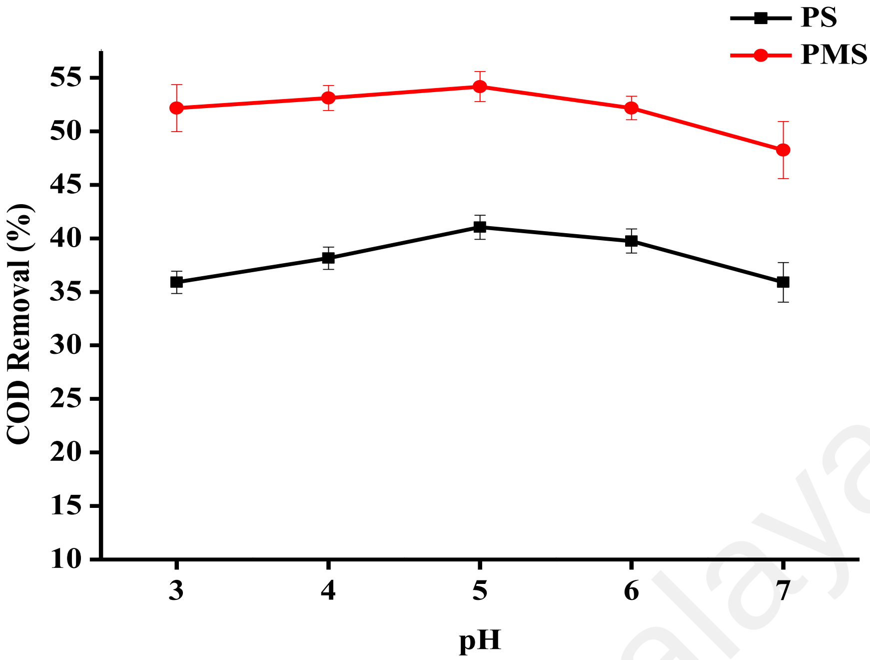


Figure 4.15: Effect of initial pH of pre-treated SLL (Oxidants dosage 12 mM, reaction time = 1 h) on COD removal.

For the effect of reaction time, the COD removal was found to increase significantly for the first 2 h for both UV/PMS and UV/PS treatment (Figure 4.16). When the reaction time increased from 2 to 8 h, the COD removal was increased slowly from 53 to 64 and 63 to 73% for UV/PS and UV/PMS, respectively. The result also indicated that no significant improvement in the COD removal efficiency after 3 h of reaction time. Similar to Fe(II) activation, PMS showed higher COD removal as compared to PS especially during the first 2 h of reaction time. PS is known to be more stable against chemical decomposition than PMS (Ao and Liu, 2017). In UV activation method, less reactive PS may not be fully photolyzed and yield less amount of SR. In addition, recent study by Ahmed and Chiron (2014) indicated that UV/PMS has demonstrated better kinetic performance as compared to UV/PS in real wastewater (Ahmad and Chiron 2014). This finding was in agreement with Ao and Liu (2017) that showed the rate of Sulfamethoxazole degradation was much faster when UV/PMS was used as treatment method as compared with UV/PS.

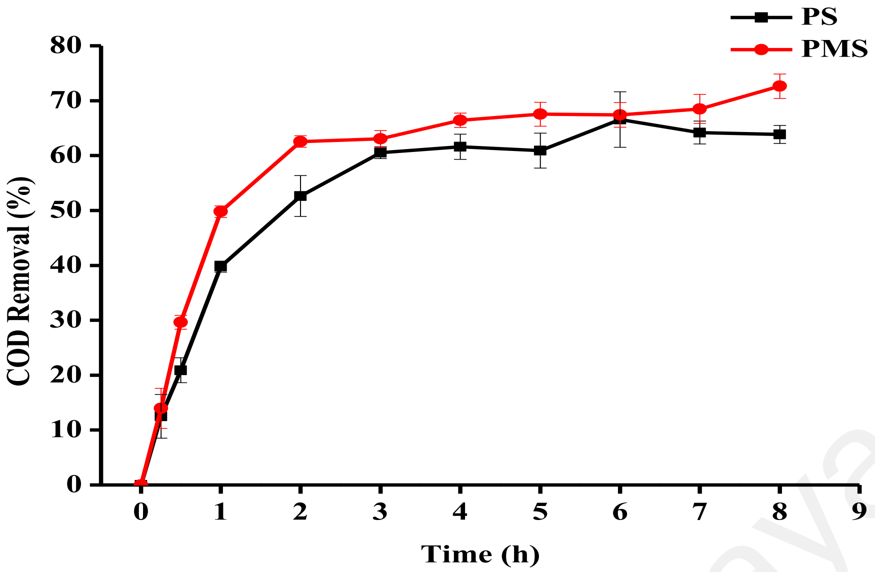


Figure 4.16: Effect of reaction time (PS and PMS dosage =12 mM, without pH adjustment) on COD removal.

4.3.4 The performance of Coagulation-flocculation coupled with Fe(II) and UV-SR-AOP

The performance of the coagulation-flocculation coupled with Fe(II)/SR-AOP and UV/SR-AOP in the treatment of SLL was re-evaluated using the optimized conditions. The COD, TOC, turbidity, and colour of the treated SLL were measured, and the results are tabulated in Table 4.4. It was observed that 94 and 100% of colour and turbidity were successfully removed using coagulation-flocculation. In term of organic content, 77 and 73% of COD and TOC removal were achieved using coagulation-flocculation. It was observed that the removal of COD using SR-AOP treatment have insignificant different performance either by PMS or PS oxidant at the optimum reaction time using the same activation method. Almost 84 and 85% of COD removal were achieved by the combination of coagulation-flocculation treatment coupled with Fe(II)/PS and Fe(II)/PMS system, respectively. The COD concentration of final treated SLL after Fe(II)/PS and Fe(II)/PMS were 170.3 and 180.2 mg/L.

The combination of coagulation-flocculation with UV/SR-AOP was found to further increase the COD removal to around 92 and 91% for UV/PMS and UV/PS, respectively.

The COD concentration of final treated SLL by UV/PMS and UV/PS were 95 and 102 mg/L. In addition, UV/PMS and UV/PS had succeded in removing 89 and 88% of TOC respectively. UV/SR-AOP showed better performance as compared to Fe(II)/SR-AOP treatment system in removing organic pollutants. This is due to the photolysis of PS and PMS by UV irradiation generated two mole of radical meanwhile the activation by Fe(II) only generate one mole of SR (Ghanbari and Moradi, 2017). In addition, UV/SR-AOP system did not produce any sludge after SR reaction as compared to Fe(II)/SR-AOP which produced higher amount of sludge. However, the combination of coagulation-flocculation with both of the treatment approach (Fe(II)/SR-AOP and UV/SR-AOP) could reduce the COD concentration of SLL to the concentration which is lower than the MDS. The final effluent for all the combination treatment were complying with the maximum discharge standard of 200 mg/L COD.

Table 4.4: Summary of Fe(II) and UV/SR-AOP treatment.

Treatment	**Parameters (% removal)**			
	COD (× 10^2 mg/L)	TOC (× 10^2 mg/L)	Turbidity (× 10^2 FAU)	Colour (×10^2 Pt/Co)
Raw SLL	11.2 ± 0.2	3.47 ± 0.06	3.0 ± 0.1	51 ± 2
Coagulation-Flocculation	2.6 ± 0.1 (77)	0.95 ± 0.04 (73)	ND (100)	3 ± 1(94)
Fe(II)/PMS	1.7 ± 0.2 *(85)*	0.65 ± 0.02 *(82)*	-	ND *(100)*
Fe(II)/PS	1.8 ± 0.3 *(84)*	0.70 ± 0.03 *(80)*	-	ND (100)
UV/PMS	0.95 ± 0.08 *(92)*	0.39 ± 0.08 (89)	-	ND (100)
UV/PS	1.02 ± 0.09 *(91)*	0.40 ± 0.03 (88)	-	ND (100)

*ND = Not Detected

4.3.5 Acute toxicity study

The 96 h LC_{50} of SLL and treated SLL on Zebrafish are summarized in Table 4.5. Based on the literature review, toxicity of water that treated with SR based AOPs is seldom reported. In order to determine the acute toxicity during each treatment, the 96 h LC_{50} were converted to toxic unit values (TU) and then used for comparison purpose. It was observed that the TU of raw leachate was 10.14. After coagulation-flocculation, the TU was found to decrease to 1.74. This result indicated that the acute toxicity is reduced by around 6 times after coagulation-flocculation pretreatment. However, the TU were found to increase slightly to 3.13 and 1.84 after Fe(II)/PMS and Fe(II)/PS treatment respectively. The TU for UV/PMS treatment also slightly increase to 1.80. Only UV/PS treatment system maintain the TU at the same level with coagulation-flocculation which is 1.74.

Table 4.5: Acute toxicities of leachate samples to Zebrafish.

Treatment	96h LC_{50}	Toxicity Unit (TU)
Raw Leachate	9.9 ± 0.2	10.1 ± 0.2
Coagulation-Flocculation	57.4 ± 0.7	1.74 ± 0.02
Fe(II)/PS	54.3 ± 0.8	1.84 ± 0.03
Fe(II)/PMS	32.0 ± 0.5	3.13 ± 0.02
UV/PS	57.4 ± 0.5	1.74 ± 0.01
UV/PMS	55.3 ± 0.9	1.80 ± 0.03
Fe(II)/PS/PAC	55.2 ± 0.5	1.81 ± 0.05
Fe(II)/PMS/PAC	30.4 ± 0.9	3.29 ± 0.02
UV/PS/PAC	57.2 ± 0.8	1.75 ± 0.02
UV/PMS/PAC	59.3 ± 0.7	1.68 ± 0.02

A series of experiment was carried out to identify the species that cause the toxicity of the treated SLL. The analysis of the concentration of PS and PMS of the treated SLL was first conducted using the iodometric method (Kolthoff et al., 1953). The treated SLL was then passed through the powder activated carbon (PAC) column to remove the remaining PS and PMS. After PAC treatment, around 98% of PS and PMS were removed. In addition, PAC also removed part of the remaining organic matter containing in the treated SLL. The toxicity of the neutralized treated leachate with and without PAC treatment was evaluated. The 96 h LC_{50} and TU of all effluents was almost remained unchanged (Table 4.5). This result showed that the remaining oxidants do not cause the toxicity of the Fe(II)/PS, Fe(II)/PMS UV/PS, and UV/PMS treated SLL. Therefore, the ion that could not be removed by PAC was suggested to be responsible for the toxicity. Analysis by ion chromatography indicated that the sulfate ion concentration in treated SLL was found to increase significantly after Fe(II) and UV/SR-AOP treatment (Figure 4.17).

As high as 5923 mg/L of sulfate ion was generated from Fe(II)/PMS treatment. Meanwhile 4331 mg/L of sulfate ion was formed using Fe(II)/PS. The UV/SR-AOP system produce much lower amount of sulfate ion residue due to lower dosage of PS and PMS usage. The concentration of sulfate in UV/PMS treated leachate is 1481 mg/L meanwhile 1015 mg/L of sulfate was found in UV/PS system. Despite activation method, sulfate ion concentration was found to be higher in SLL that treated with PMS as compared to PS even though the same molar concentration of oxidants were used. At the same COD removal efficacy, PS indicate better potential application in leachate treatment due to the formation of a lesser amount of residual sulfate ion as compared to PMS treatment. More reactive PMS is expected to generate the higher amount of SR, which ended up as sulfate ion at the selected reaction time.

High sulfate ion concentration has been found to pose the problem to osmotic balance for some aquatic organisms (Iowa DNR, 2009). Therefore, sulfate ion is proposed as the species that responsible to increase the toxicity of the Fe(II) and UV/SR-AOP treated SLL. So far, no permissible concentration for sulfate ion in drinking water is proposed. However, there is an increasing likelihood of complaints arising from a noticeable taste as the sulfate ion concentration in water is higher than 500 mg/L (WHO, 2004). Thus, it is more feasible to use PS than PMS as SR oxidant for leachate treatment due to the lower toxicity of the produced effluent. However, the method for sulfate ion removals such as reverse osmosis, ion exchange or chemical precipitation should be considered to utilize SR-AOP system in real leachate treatment. As a result, sulfate ion was removed via Amberlite Ion Exchange in the following experiment.

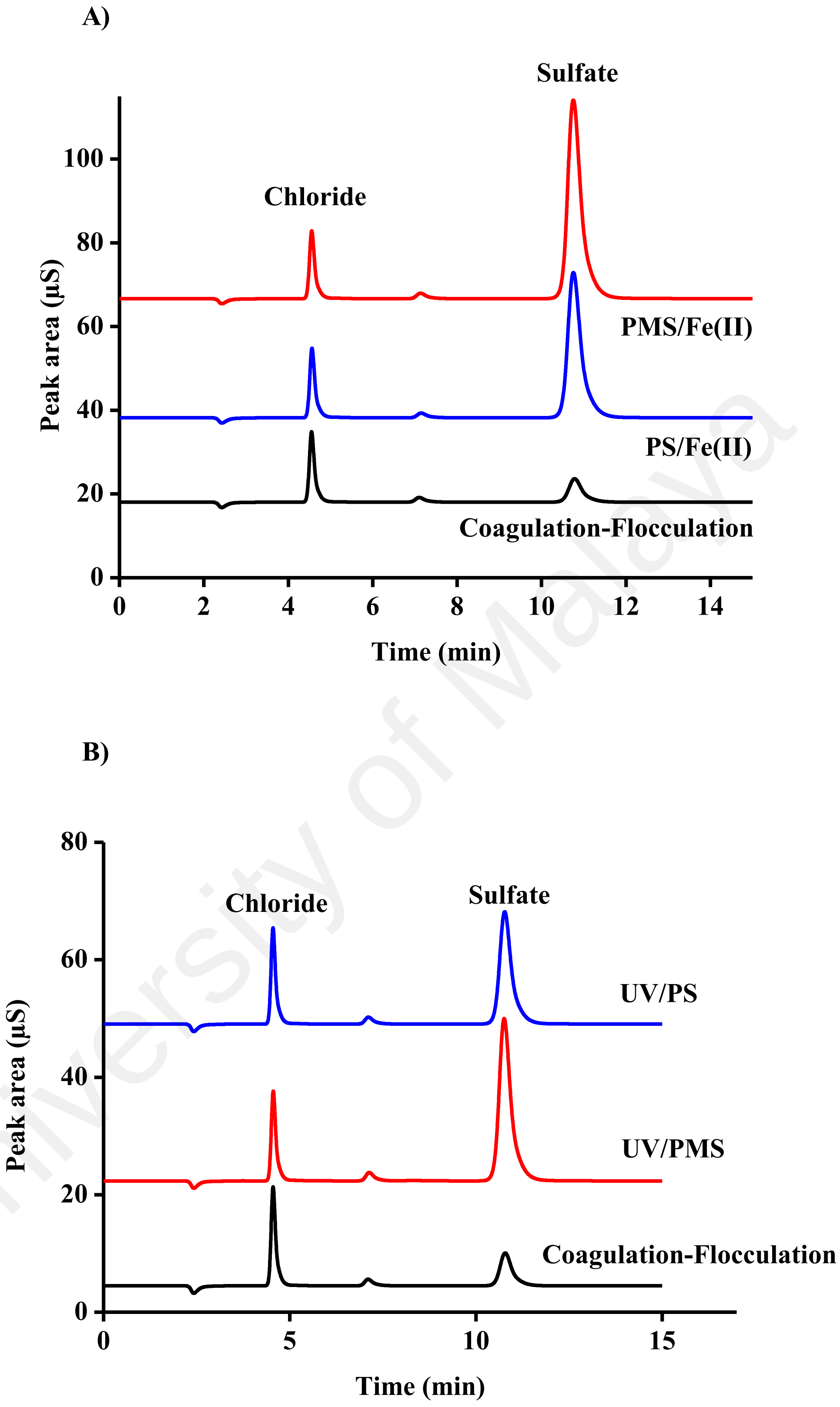


Figure 4.17 Ion chromatography analysis of treated SLL A) Fe(II)/SR-AOP B) UV/SR-AOP.

4.4 CFWTS

The CWFTS was developed based on the optimization of batch study. The purpose of this experiment was to study the possibility to convert the developed batch experiment into continuous flow treatment system that deal with larger amount of leachate. The developed CFWTS system consisted of the combination of (1) coagulation-flocculation treatment, (2) Ammonia stripping-UV/PS treatment and (3) cation exchange column. The system is able to treat 5 L of SLL in one process. The final CFWTS diagram was illustrated in Figure 4.18

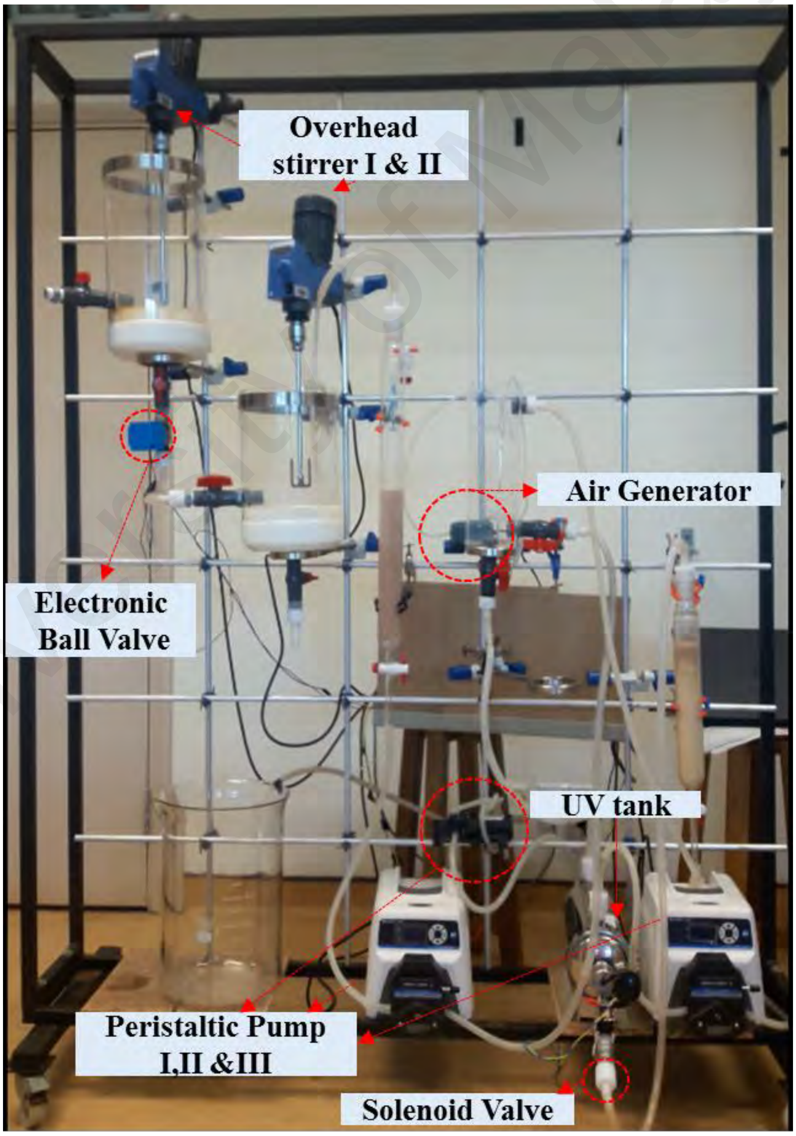


Figure 4.18: CFWTS Diagram.

4.4.1 CFWTS Control System

Open-source microelectronics such as Arduino microcontroller have become increasingly useful in the various field of treatment due to their low cost and integrated development interfaces (Grinias et al., 2016). Arduino microcontroller boards can be coupled to both in-house and portable instrumentation for user control, data acquisition, and analysis. In this study, in house Arduino-based circuit was developed to control CFWTS. The code of instruction was generated using an open-source Arduino Software (IDE 1.8.5). Then, the instructions were upload into the Arduino UNO board. This Arduino microcontroller system performed the time-based control for each of treatment process such as the opening of the valve (Solenoid and Electronic Ball Valve), stirring time of overhead stirrer, the peristaltic pump operation, UV tank and air pump (Figure 4.18). The coding for the Arduino UNO is presented in Appendix A.

4.4.2 CFWTS optimization

In the CFWTS, the coagulation-flocculation tank was designed to treat 5 L of SLL. The speed and time of overhead stirrer was adjusted to 150 rpm (10 min) for rapid mixing and 70 rpm (30 min) for slow mixing. The time for coagulation-flocculation was slightly increased due to the higher amount of SLL. The outcome of the study was consistent with the Jar test batch experiment where almost 74% has been removed from the raw SLL. This result indicated that the increasing volume of SLL did not affect significantly on the COD removal efficiency. The repeatable COD removal was achieved using optimum conditions of 1:1.13 $FeCl_3$: COD ratio at pH 6. The COD concentration after coagulation-flocculation was 274 mg/L. The sludge produced from the treatment was easily removed from the bottom of coagulation-flocculation tank while the treated SLL was pumped through a sand filtration column and then into ammonia stripping-UV/PS tank using a peristaltic pump.

In the ammonia stripping-UV/PS treatment tank, SLL effluent was circulated between ammonia stripping tank and UV reactor using another peristaltic pump. The dosage of PS was fixed at 12 mM based on preliminary optimization from UV/PS batch experiment. However, the initial pH condition, reaction time and the flow rate were re-evaluated. Figure 4.19a illustrates the COD and NH_3N removal using CFWTS without pH adjustment. The result indicated that significant COD were removed after the first 10 h exposure. Almost 74% of COD successfully removed from the treated SLL. The COD concentration was reduced from 257 mg/L in coagulation-flocculation tank to 68 mg/L after ammonia stripping-UV/PS treatment. After 24 h exposure, the percentage of COD removal was slightly increased to 87%. The COD removal was consistent with the earlier UV/PS batch experiment although require longer retention time due to higher amount of treated SLL and different UV system. However, the initial pH condition after coagulation-flocculation treatment (pH 5.5) did not favors the removal of NH_3N. After 24 h exposure, the NH_3N removal was less than 5%. The NH_3N concentration was reduced from 551 mg/L in coagulation-flocculation tank to only 545 mg/L after ammonia stripping-UV/PS treatment. This result might due to the acidic pH condition of treated SLL that prevent the conversion of NH_4^+ to ammonia gas. The NH_4^+ volatilization required a high pH to release the ammonia gas to the air (Liao et al., 1995). In common ammonia stripping, the pH of the effluent was increased to 11.5 (Liao et al., 1995). In order to simultaneously remove COD and NH_3N, another experiment was setup by adjusting the pH of the pre-treated SLL to 11.5 (Figure 4.19b). The result indicated that, the increased of pH to 11.5 was not significantly affect the COD removal efficiency. Although the reaction time for SLL treatment with pH adjustment was not as fast as the reaction without pH adjustment, the different of COD removal between the two conditions was less than 8% after 10 h of treatment. After 24 h, the COD removal between these two conditions was only 2% in different. The changes of pH condition to 11.5 clearly increased the NH_3N removal significantly for the first 5 h of exposure. The percentage of NH_3N removal after 5 h was 70%. After 24 h, the removal of NH_3N slowly increased to only 71% due to the reduction of pH of SLL to acidic condition.

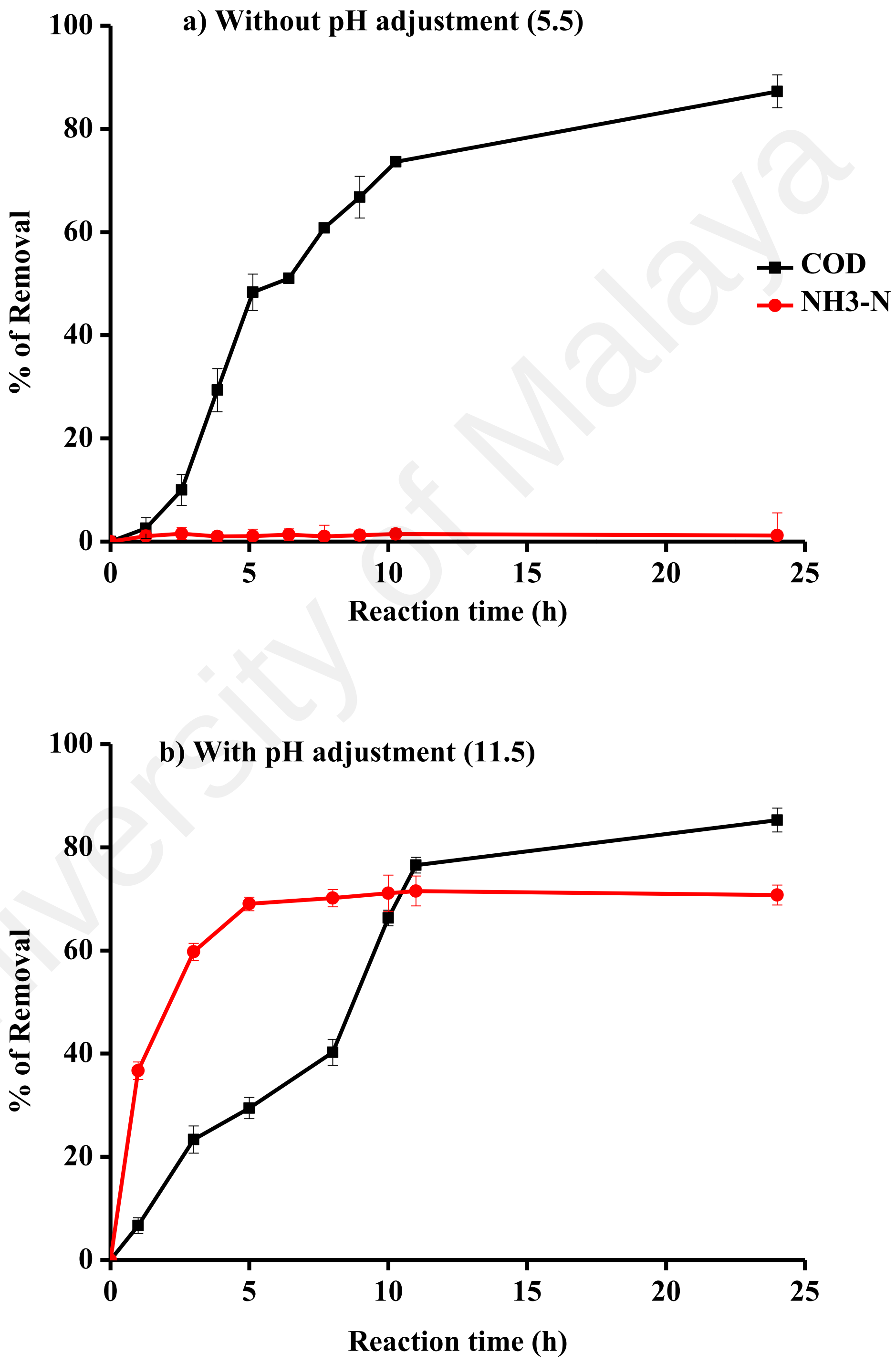


Figure 4.19: Effect of pH condition on COD and NH_3N removal (Flow rate = 50 mL/min, PS dosage = 12 mM).

The effect of flow rate on the ammonia stripping-UV/PS treatment system was investigated based on two parameters of interest; COD and NH_3N concentration. The COD was rapidly removed from the SLL at first 10 h of exposure for all the tested flow rate (Figure 4.20). The range of COD removal were 56 to 66%. Although the removal of COD after 10 h was still increased, the removal was occurred in a slower rate. A higher flow rate of 50 mL/min and 100 mL/min demonstrated a higher amount of COD removal as compared to 15 mL/min flow rate. This condition might due to the rapid cycle of ammonia stripping-UV/PS system that facilitate the additional UV exposure for SR generation. The SLL was repeatedly recirculated between the two reactors thus enabling the continuous activation of SR. In this study, 50 mL/min flow rate was found to be the optimum flow rate for COD removal since it's showed the highest COD reduction at all reaction time.

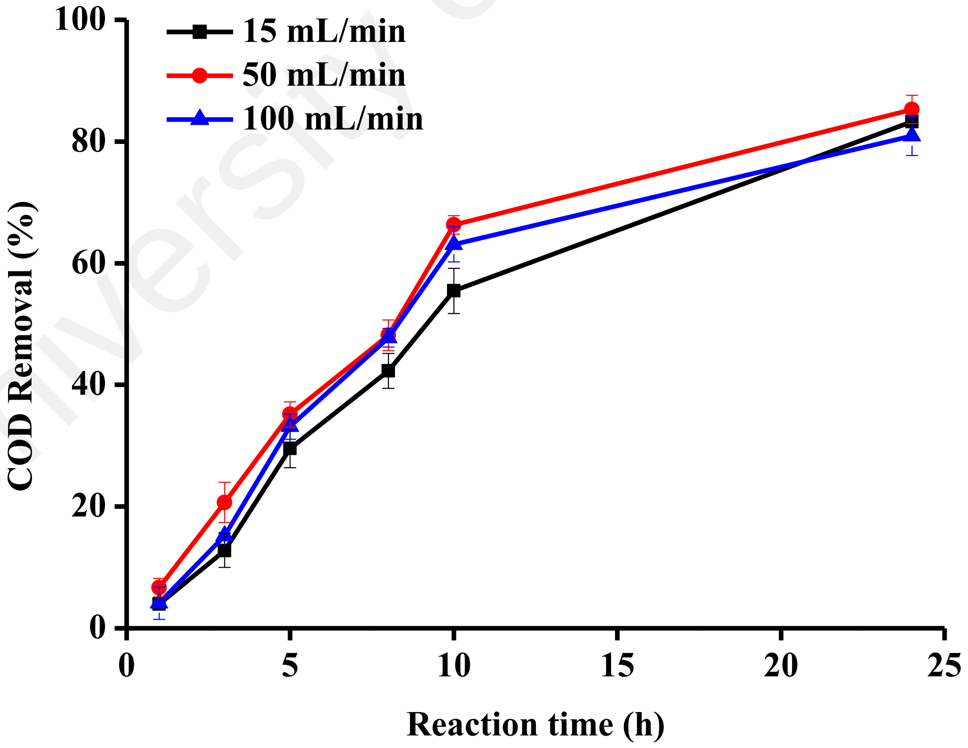


Figure 4.20: Effect of flow rate on COD removal (Dosage = 12 mM, initial pH = 11.5).

Figure 4.21 illustrate the NH_3N removal and reduction of pH as a function of reaction time. The results showed that the NH_3N was rapidly removed from the treated SLL at first 5 h of exposure for all the tested flow rate. After 5 h, the percentage of NH_3N removal was observed to be at constant level. This phenomenon can be explained by the decreasing trend of pH during the oxidation process. Once the UV irradiation started, the pH of the SLL effluent slowly dropped from alkaline into acidic condition. The acidification of the SLL effluent was due to the occurrence of acidic photoproduct of PS in SLL effluent such as bisulfate (HSO_4^-) as illustrated in **Equation 4-14** and **4-15** (Lau et al., 2007). In addition, the decreased of pH might also be due to the elimination of ammonia. After 5 h exposure, the pH of the SLL dropped to pH 9.13. The longer time of exposure, the more acidic of SLL effluent was generated. Since the conversion of NH_4^+ to ammonia gas only favors in alkaline condition, any reaction longer than 5 h will not remove any NH_3N from the SLL.

$$SO_4^{\bullet-} + H_2O \rightarrow HSO_4^- + \bullet OH \qquad \textbf{(Equation 4-14)}$$

$$HSO_4^- \rightarrow H^+ + SO_4^{2-} \qquad \textbf{(Equation 4-15)}$$

In contrast to COD, the NH_3N removal was rapidly remove by a lower flow rate. After 24 h exposure, the highest percentage of NH_3N removal (71%) was found at 15 mL/min. The reduction of pH is much faster in higher flow rate. In lower flow rate, the pH slowly reduces to acidic in SLL hence giving more times for further NH_3N removal. 50 mL/min flow rate and 9 h reaction time were selected as the optimum condition for CFWTS. This condition has been selected by considering the removal of both important parameter (COD and NH_3N) and also the final pH of the treated SLL. After 9 h reaction time using a 50 mL/min flow rate, the final pH of the effluent was in neutral range, thus adjustment of pH was not required.

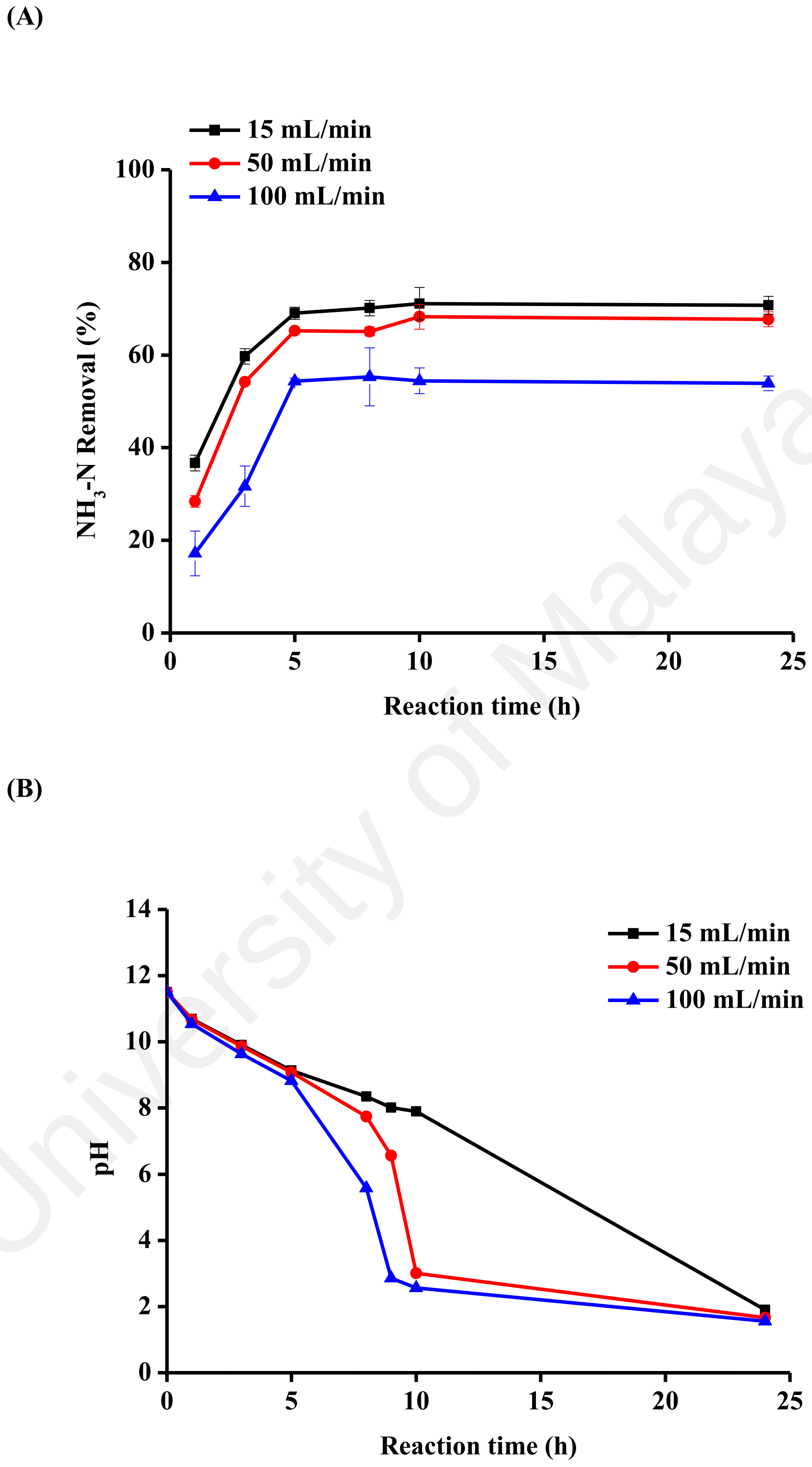


Figure 4.21: Effect of flow rate on: (A) NH_3N removal and (B) pH (Dosage =12 mM, Initial pH = 11.5).

The application of SR-AOP treatment produced considerable amount of residual sulfate ion in the final effluent as proven in section 4.3.5. Sulfate ion was found to be toxic to certain organism especially the zebrafish. Thus, the method for residual sulfate removal was necessary before discharging the SR-AOP treated SLL into the environment. In this study, cation exchange column was selected to remove sulfate ion. Commercial Amberlite (IRA-402) resin was utilized for this purpose. A preliminary batch experiment was conducted to determine the uptake capacity of sulfate ion removal using 5 g of Amberlite resin using 12 mL/min (Figure 4.22).

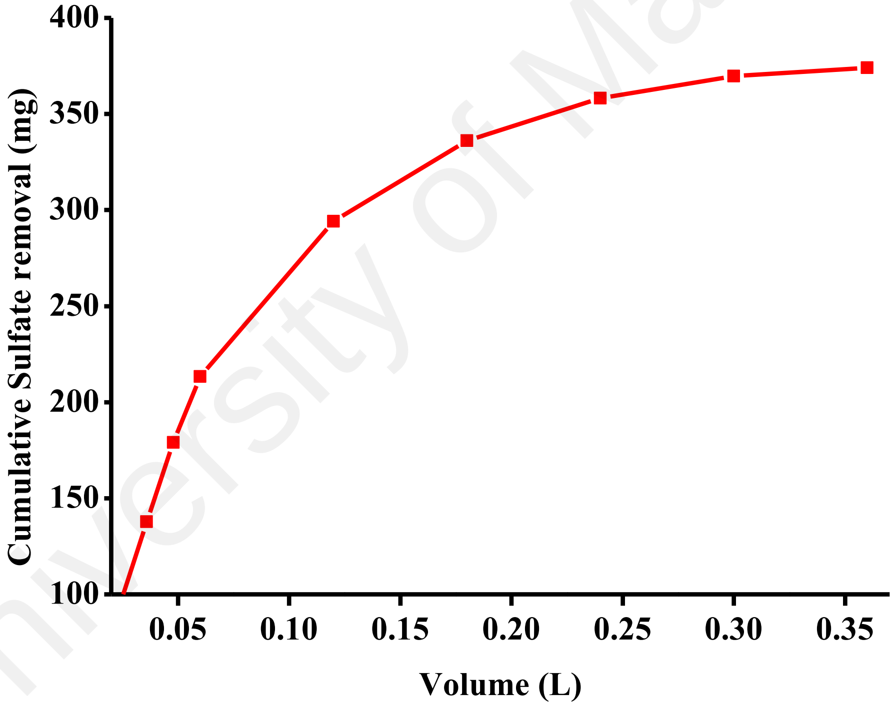


Figure 4.22: Performance of 5 g of Amberlite cation using 12 mL/min flow rate.

The result in the batch study showed that more than 374 mg of cumulative sulfate ion has been removed after 0.42 L of SR-AOP treated SLL that pass through the 5 g of Amberlite ion exchange. Based on the calculation, 1 g of Amberlite resin could remove 75 mg of sulfate ion. The final SLL effluent contains 4178 mg/L of sulfate ion. For 4 L of SR-AOP treated SLL, ± 200 g of Amberlite resin was needed to remove all the residual sulfate ion.

Amberlite IRA402 resin is a type 1 strongly basic, clear gel, cation exchange resin. It has a crosslinked polystyrene structure that is designed to give an optimum balance of capacity and regeneration efficiency in water treatment applications. In the CFWTS, the SLL effluent after ammonia stripping-UV/PS treatment system was pumped into 200 g of Amberlite cation exchange column using 12 mL/min for residual sulfate ion removal. The analysis of residual sulfate ion in the final SLL effluent was conducted using an ion chromatography and there is no residual sulfate ion was detected in the final effluent.

4.4.3 The performance of CFWTS

4.4.3.1 Efficacy of CWTS on metals removal

Metals are known to be toxic to the biochemical mechanisms and prone to bio-accumulate in the ecosystem (Darus et al., 2012; Ishak et al., 2017). A number of studies have shown the tendency of metals in water to accumulate in human body either by ingestion or via dermal contact absorption and also other aquatic organism (Figueira et al., 2011). Thus, the removal of metals from the SLL into certain concentration was necessary to avoid possible effect to human health and the environment.

Table 4.6 showed the concentration of metals in the SLL before and after treatment. In the raw SLL, 6 metal (Cr, Fe, Ar, Cd, Hg and Pb) was found to exceed the Environmental Quality Act (Control of Pollution from solid waste Transfer Station and Landfill) Regulation 2009. However, after coagulation-flocculation treatment, all the metals in the SLL effluent were complying with the standard requirement. Thus, no further specific treatment for metals was required. In addition, the additional UV/PS treatment further removed the residual of metal in the SLL effluent by sludge sedimentation.

Table 4.6: Metals concentration before and after treatment.

Heavy metals	**Raw ($\mu g/L \times 10^2$)**	**CF ($\mu g/L \times 10^2$)**	**UV/PS ($\mu g/L \times 10^2$)**	***Discharge Standard ($\mu g/L \times 10^2$)**
Al	14 ± 1	0.43 ± 0.07	0.22 ± 0.01	-
Cr	3.0 ± 0.1	0.08 ± 0.02	0.07 ± 0.01	2
Mn	1.91 ± 0.09	0.27 ± 0.08	0.20 ± 0.04	2
Fe	113 ± 7	71 ± 4	1.5 ± 0.4	50
Ni	1.20 ± 0.06	0.08 ± 0.03	0.01 ± 0.01	2
Cu	0.34 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	2
Zn	2.3 ± 0.1	0.26 ± 0.04	0.25 ± 0.01	20
As	6.5 ± 0.4	0.11 ± 0.02	0.06 ± 0.01	0.5
Cd	0.10 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.1
Hg	0.87 ± 0.03	0.15 ± 0.01	0.14 ± 0.05	0.05
Pb	1.40 ± 0.03	0.20 ± 0.02	0.17 ± 0.02	1

*Environmental Quality Act (Control of Pollution from solid waste Transfer Station and Landfill) Regulation 2009

4.4.3.2 The performance of optimized CFWTS on various parameter of interest

Table 4.7 illustrates the concentration and percentage removal of COD, TOC, colour, turbidity and NH_3N before and after CFWTS. Almost 91% and 90% of COD and TOC removal were achieved by the developed CFWTS. The COD and TOC concentration of final treated SLL were 92 and 30 mg/L, respectively. The COD concentration was complying with the maximum discharge standard of 200 mg/L COD (Kurniawan et al., 2006). The other parameter also achieved satisfactory removal efficiency except for NH_3N. Although the removal of NH_3N was more than 68%, the final concentration was still higher than the Malaysian environmental quality standard which is 5 mg/L.

Table 4.7: Efficacy of CFWTS on COD, TOC, color, turbidity and NH_3N removal.

Parameter	**Raw Leachate**	**Coagulation Flocculation**	**UV/PS**	**Cation Exchange**
COD (× 10^2 mg/L)	10.39 ± 1.5	2.7 ± 0.2	1.02 ± 0.07	0.92 ± 0.06
% removal		74	90	91
TOC (× 10^2 mg/L)	3.10 ± 0.12	0.87 ± 0.09	0.35 ± 0.03	0.30 ±0.0 4
% removal		72	89	90
NH_3-N (× 10^2 mg/L)	5.49 ± 0.15	5.21 ± 0.13	1.80 ± 0.05	1.79 ± 0.12
% removal		5	67	68
Color (× 10^2 Pt/Co)	51 ± 2	3.11 ± 0.01	ND	-
% removal		94	100	-
Turbidity (× 10^2 FAU)	2.8 ± 0.1	ND	-	-
% removal		100	-	-

*ND = Not detected

4.4.4 Toxicity

So far, no proper standard has been setup for toxicity of effluent before discharge into the environment. Most of the standards are developed based on the physicochemical parameter such as TOC, COD, BOD_5, heavy metals, NH_3N, etc. High concentration of organic pollutant removal efficiency may not always reflex the toxicity reduction. In addition, the treatment may contribute to the increase of toxicity due to the miscellaneous chemical interaction in the effluent. Thus, it is important to evaluate the toxicity of the SLL effluent in each treatment as additional information to physicochemical data.

In this study, three types of toxicity study were conducted based on acute toxicity by zebrafish and phytotoxic by mung beans and lady finger. Table 4.8 illustrate the acute toxicity of zebrafish in SLL before and after treatment. The TU of SLL was decreased from 10.14 in the raw SLL to 1.64 after CFWTS treatment. The decreased was almost 6 times from the original SLL effluent. For phytotoxicity study, the relative toxicity was calculated based on the seed germination index. It was found that, the relative toxicity (TU) for both of the plant were reduced from 85% in the raw SLL to 8% for mung beans and 2% for lady finger after the CFWTS treatment (Table 4.9). It was found that the finding was consistent with acute toxicity test which indicated improvement of toxicity before and after treatment.

Table 4.8: LC_{50} of Zebrafish in CFWTS

Treatment	**48h LC_{50}**	**96h LC_{50}**	**Toxicity Unit (TU)**
Raw SLL	11.03 ± 0.2	9.86 ± 0.7	10.14 ± 0.02
CFWTS	62.6 ± 0.2	60.9 ±0.6	1.64 ± 0.02

Table 4.9: Relative toxicity and of SLL toward Lady Finger and Mung beans

Treatment	**Germination Index (Relative toxicity)**	
	Lady Finger	Mung Beans
Raw SLL	15 (85 ±5)	15 (85 ± 5)
Coagulation-Flocculation	88 (12 ± 3)	92 (5 ± 3)
UV/PS	83 (17 ± 3)	83 (17± 3)
Amberlite ion Exchange	92 (8 ± 3)	98 (2 ± 3)

CHAPTER 5: CONCLUSION AND FUTURE RECOMMENDATION

5.1 Conclusion

In this study, the efficiency combination of coagulation-flocculation with two different types of AOPs (•OH and SR based AOP) for the treatment of SLL were successfully evaluated. In coagulation-flocculation pretreatment, the efficiency of three different types of coagulants namely $FeCl_3$, $Al_2(SO_4)_3$ and PACL in the removal of COD were investigated. In AOPs study, the •OH was generated using Fe(II) activated H_2O_2 or also known as Fenton reaction meanwhile SR was generated using PS and PMS activated by Fe(II) and UV light. The treatment was started with a series of batch study to determine the optimum condition for both coagulation-flocculation and AOPs. The optimum result from the batch study was then used to develop CFWTS. In coagulation-flocculation, the result indicated that the removal of organic compound (TOC and COD) was more favorable when the pretreatment was performed in the slightly acidic condition (pH 6). Among the selected coagulants, $FeCl_3$ is the most efficient coagulant. However, it was found that COD concentration after pretreatment was still not complying with MDS of many countries indicating the requirement of further treatment. The pre-treated SLL was subjected to Fenton and SR-AOP oxidation after coagulation-flocculation.

In Fenton treatment, nearly 50% of TOC removal was achieved when the reaction was carried out at pH 3, H_2O_2:Fe^{2+} ratio of 20:1, H_2O_2 dosage of 240 mM and 1 h of reaction time. By coupling the coagulation-flocculation with the Fenton reaction, the removal of TOC, COD and turbidity of SLL were 85, 84 and 100%, respectively. The toxicity study performed using zebrafish revealed that 96 h LC_{50} for raw SLL was 1.40% (v/v). After coagulation-flocculation, the LC_{50} of the pre-treated SLL was increased to 25.4%. However, after the Fenton reaction, the LC_{50} of the treated SLL was found to decrease to 11.0% due to the presence of H_2O_2 residue. In this study, H_2O_2 residue was removed using powdered activated charcoal. This method increased the LC_{50} of treated effluent to 34.5% and the removal of TOC and COD was further increased to 90%.

In Fe(II) activated SR-AOP, almost 30 to 35% of COD removal was achieved when the reaction was carried out at pH 4.5, PS and PMS:Fe^{2+} ratio of 1:2, PS and PMS dosage of 15 mM and 3 h of reaction time. By using the optimal condition, nearly 83 and 84% of COD were reduced by the combination of coagulation-flocculation pretreatment coupled with PMS/Fe(II) and PS/Fe(II) treatments respectively. Other parameter such as color and turbidity were 100% removed from the SLL by both treatments. Acute toxicity analysis by zebrafish showed the slightly increased of toxicity from TU of 1.74 after coagulation-flocculation to 1.84 and 3.13 after Fe(II)/PS and Fe(II)/PMS treatment. In UV-activated SR-AOP, 60 to 63% of COD removal was achieved when the reaction was carried out at pH 4.5, PS and PMS dosage of 12 mM and 3 h of reaction time. This treatment was two-times more efficient as compared to Fe(II) activated SR-AOP. The overall COD removal by combination of coagulation-flocculation coupled with UV/PS and UV/PMS system were approximately 91 and 92%, respectively. The COD concentration of final treated SLL was 95 and 102 mg/L for UV/PMS and UV/PS. This result showed that the combination of coagulation-flocculation with UV/SRAOP could reduce the COD concentration of SLL to the concentration which is lower than the MDS. Acute toxicity analysis by zebrafish showed a slightly increased of toxicity after UV/PMS system meanwhile a static toxicity was found in UV/PS system. The increase of toxicity was due to the presence of residual sulfate ion after SR-AOP treatment.

Since UV-SRAOP showed higher efficiency in COD removal as compared to Fe(II)-SRAOP, UV-based treatment was selected for the development of CFWTS. Additionally, PS was selected as the oxidant due to lower residual sulfate ion production. In CFWTS, the COD removal was consistent with the previous UV/PS batch experiment. However, it required longer retention time due to a higher volume of treated SLL. Since the changes of pH did not significantly affect the COD removal, the initial pH was adjusted to 11.5 for simultaneous removal of NH_3N. In this study, 91% COD and 68% of NH_3N were successfully removed from SLL. In order to utilize this alternative method into the real water treatment system, the method for removal of sulfate ion needs to be emphasized. In this study, the residual sulfate formation that contributed to the toxicity of SLL was removed using Amberlite cation exchange resin and the analysis showed the absence of residual sulfate in the final SLL effluent. These findings indicated that UV/PS based CFWTS could be an alternative method to be applied in a full-scale leachate treatment system.

5.2 Future work suggestions

In this study, the UV/PS treatment based on the CFWTS was developed for the treatment of SLL. The optimum conditions have been optimized. The possibility of the treatment to be used in full scale water treatment need to be evaluated. However, the type and intensity of the UV light are not investigated in detail in this study. The different type of UV system might influence the efficiency of pollutant removal in SLL. The intensity of UV light might affect the reaction time of the treatment. In addition, the actual cost of energy and chemicals that consume in the treatment are not calculated in this study. In order to apply this treatment for the big scale, the actual calculation should be considered.

The UV/PS treatment based on the CFWTS also can be used to treat different type of wastewater. Since SLL is the most complex wastewater, this system might be efficient for other type of wastewater. Furthermore, their modular feature allows it to be retrofitted to existing systems and for future different water treatment system to be installed in conjunction.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

Journal Articles

1. Ishak, A. R., Hamid, F. S., Mohamad, S., & Tay, K. S. (2018). Stabilized landfill leachate treatment by coagulation-flocculation coupled with UV-based sulfate radical oxidation process. *Waste Management*, 76, 575-581.
2. Ishak, A. R., Hamid, F. S., Mohamad, S., & Tay, K. S. (2017). Removal of organic matter from stabilized landfill leachate using Coagulation-Flocculation-Fenton coupled with activated charcoal adsorption. *Waste Management & Research*, 35(7), 739-746.

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1. Ishak, A. R., Mohamad, S., Soo, T. K., & Hamid, F. S. (2016). Leachate and surface water characterization and heavy metal health risk on cockles in Kuala Selangor. *Procedia-Social and Behavioral Sciences*, *222*, 263-271 (Oral Presenter)
2. Ishak, A. R., Mohamad, S., & Tay, K. S. (2016). The treatment on Stabilized landfill leachate by combine coagulation flocculation and UV-SRAOP. *International Symposium on Pure & Applied Chemistry (ISPAC)*, Borneo Convention Centre, Sarawak (Oral Presenter)
3. Ishak, A. R., Mohamad, S., & Tay, K. S. (2016). The treatment on landfill leachate by combine coagulation flocculation and Fenton treatment. UM#111 Chemistry Symposium 2016 (Poster Presentation)