COMPARISON AND OPTIMIZATION OF OZONE – BASED ADVANCED OXIDATION PROCESSES IN THE TREATMENT OF STABILIZED LANDFILL LEACHATE

By

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LIST OF ABBREVIATION

AP	Adequate precision
ANOVA	Analysis of variance
AOPs	Advanced oxidation process
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CV	Coefficient of variance
DoE	Design of experiment
EC	Electrical conductivity
MSW	Municipal solid waste
NH_3-N	Ammonical nitrogen
$OH^{\cdot}$	Hydroxyl radical
PBLS	Pulau Burong Landfill Site
pH	Hydrogen ions
R^2	Coefficient of determination
R^2_{Adj}	Adjusted Coefficient of determination
RSM	Response surface methodology
SD	Standard deviation
SS	Suspended solids

PERBANDINGAN DAN PENGOPTIMUMAN PROSES-PROSES PENGOKSIDAAN LANJUTAN BERASASKAN OZON DALAM OLAHAN LARUT LESAPAN STABIL

ABSTRAK

Pencemaran larut lesapan merupakan salah satu masalah utama di tapak pelupusan. Antara parameter yang paling bermasalah bagi larut lesapan stabil adalah COD, ammonia, dan warna. Teknologi olahan yang boleh digunakan adalah berbeza berdasarkan jenis larut lesapan yang terhasil. Walaupun selepas olahan, ciri-ciri efluennya masih sukar untuk mematuhi standard pelepasan. Pengozonan merupakan salah satu proses kimia yang boleh digunakan dalam olahan larut lesapan kambus tanah. Walau bagaimanapun, prestasi pengozonan adalah rendah apabila digunakan secara bersendirian; keberkesanannya dapat dipertingkatkan melalui proses pengoksidaan lanjutan. Sehingga kini, penggunaan reagen Fenton dan persulfate secara berasingan bagi meningkatkan process pengozonan dalam satu reaktor ozon masih belum terbukti. Justeru itu, kajian ini dijalankan untuk menilai dan membandingkan prestasi tiga proses olahan, iaitu ozon, ozon/Fenton dan ozon/persulfate di dalam mengolah larut lesapan stabil yang dijalankan secara berasingan mengikut keadaan ujikaji yang berbeza. Satu reka bentuk komposit tengah *"Cental Composite Design"* (CCD) dengan kaedah tindak balas permukaan *"Response Surface Methodology"* (RSM) telah digunakan untuk menilai hubungan di antara pembolehubah operasi. Berdasarkan analisis statistik, model kuadratik bagi empat tindak balas (COD, NH_3-N, warna, dan penggunaan ozon (OC)) telah terbukti menunjukkan kesan ketara dengan nilai kebarangkalian yang sangat rendah (<0.0001). Bagi ketiga-tiga reka bentuk pengoptimuman tersebut, keputusan yang diramal adalah hampir menyamai keputusan ujikaji di makmal. Selain itu, kajian ini juga dijalankan untuk mengkaji kesan ketiga-tiga proses olahan terhadap biodegradasi dan ciri-ciri terlarut dalam larut lesapan stabil. Nisbah kebolehbiodegradasi (BOD_5/COD) dalam larut lesapan stabil telah meningkat daripada 0.034 kepada masing-masing 0.05, 0.14 dan 0.29 menggunakan O_3, O_3/fenton dan and O_3/persulfat. Peratus $COD_{(bi)}$ terbiodegradasi (24%), $COD_{(ubi)}$ tidak terbiodegradasi (76%), $COD_{(s)}$ terlarut (59%), $COD_{(bsi)}$ terbiodegradasi boleh larut (38%), $COD_{(ubsi)}$ tidak terbiodegradasi boleh larut (62%) dan zarah COD (PCOD) (41%) di dalam larut lesapan stabil turut dikaji. Peratus $COD_{(bi)}$ telah meningkat kepada 28%, 36% dan 30% setelah O_3, $O_3/H_2O_2/Fe^{2+}$ dan $O_3/S_2O_8^{2-}$ digunakan. Manakala, $COD_{(S)}$ meningkat kepada 59% selepas penggunaan O_3 dan 72% setelah kedua-dua AOPs berasaskan ozon dimasukkan. Peratus $COD_{(bsi)}$ juga turut meningkat kepada masing-masing 38%, 51% dan 55% selepas O_3, $O_3/H_2O_2/Fe^{2+}$ dan $O_3/S_2O_8^{2-}$ digunakan. Manakala peratus PCOD telah berkurangan daripada 41% kepada 35% selepas penggunaan O_3 dan 28% selepas kedua-dua AOPs berasaskan ozon dimasukkan. Memandangkan keberkesanan O_3 dalam proses olahan larut lesapan stabil adalah lemah, maka disarankan agar ozon hanya digunakan sebagai proses pra atau pasca olahan. Ozon/Fenton lebih cekap dalam penyingkiran COD dan warna, manakala, Ozone/persulfat merupakan kaedah berkesan untuk mempertingkatkan biodegradasi. Selain itu, proses ozone/persulfat adalah lebih berkesan dalam menyingkirkan ammonia di samping juga berkesan dalam penyingkiran COD dan warna daripada larut lesapan stabil. Data yang sesuai dalam pemajuan loji olahan larut lesapan stabil menggunakan Ozon/persulfat juga dicadangkan. Efluen akhir proses Ozon/Fenton mematuhi tahap pelepasan standard untuk COD dan warna, manakala Ozon/persulfat merupakan kaedahyang berkesan dalam meningkatkan kebolehrosotan organik.

COMPARISON AND OPTIMIZATION OF OZONE – BASED ADVANCED OXIDATION PROCESSES IN THE TREATMENT OF STABILIZED LANDFILL LEACHATE

ABSTRACT

Leachate pollution is one of the main problems in landfilling. Among the most problematic parameters in stabilized leachate are COD, ammonia, and color. The treatment technology that can be used may differ based on the type of leachate produced. Even after treatment, the effluent characteristics are always hard to comply with the discharge standard. Ozonation is one of the chemical processes that can be used in the treatment of landfill leachate. However, its performance when use alone is low; its effectiveness can be improved using advanced oxidants. To date, application of Fenton and persulfate reagents separately to improve ozonation process in one ozone reactor was not well established. The study aimed to evaluate and compare the performance of the three treatment processes, namely ozone, ozone/Fenton and ozone/persulfate in treating stabilized leachate separately at different experimental conditions. A central composite design (CCD) with response surface methodology (RSM) was applied to evaluate the relationships between operating variables. Based on statistical analysis, quadratic models for the four responses (COD, NH_3–N, Color, and ozone consumption (OC)) proved to be significant with very low probability values (<0.0001). For the three optimization designs; the predicted results fitted well with the results of the laboratory experiment. This study also investigated the effects of the three treatment processes on the biodegradable and soluble characteristics of stabilized leachate. The biodegradability (BOD_5/COD ratio) in stabilized leachate was 0.034, and it's improved to 0.05, 0.14 and 0.29 by applying O_3, O_3/fenton and O_3/persulfate, respectively. Fractions of biodegradable $COD_{(bi)}$ (24%), non-biodegradable $COD_{(ubi)}$ (76%), soluble $COD_{(s)}$ (59%), biodegradable soluble $COD_{(bsi)}$ (38%), non-biodegradable soluble $COD_{(ubsi)}$ (62%), and particulate COD (PCOD) (41%) in stabilized leachate were also investigated. The fraction of $COD_{(bi)}$ increased to 28, 36 and 30% after applying O_3, $O_3/H_2O_2/Fe^{+2}$ and $O_3/S_2O_8^{2-}$, respectively. $COD_{(S)}$ increased to 59% after O_3, 72% after both ozone-based AOPs. $COD_{(bsi)}$ increased to 38, 51 and 55% after O_3, $O_3/H_2O_2/Fe^{+2}$ and $O_3/S_2O_8^{2-}$, respectively, whereas the PCOD reduced from 41 to 35 after O_3 and 28% after both ozone-based AOPs. Accordingly, the performance of O_3 in stabilized leachate treatment is poor and suggests utilizing as pre or posting treatment process. Ozone/fenton process has higher performance in COD and color removal, while, ozone/persulfate is an efficient method for enhanced biodegradability. Furthermore, ozone/persulfate process has higher performance in ammonia removal as well as it has good removal efficiency of COD and color from stabilized leachate. Suitable data for establishing fully stabilized leachate treatment plant using ozone/Fenton and ozone/persulfate was suggested. The final effluent of ozone/Fenton process complied with the discharge standard for COD and colour, while ozone/persulfate is an efficient method for enhancing the biodegradability of organics.

CHAPTER 1

INTRODUCTION

1.1 Background

Growing population and industrial development have increased waste generated by urban areas and otherwise. In most countries, sanitary landfilling is the most common way of eliminating municipal solid waste (MSW) (Renou et al., 2008). MSW is waste from domestic, commercial, and industrial activities in urban areas (Bartone 1990). Sanitary landfilling is the most economical and environment-friendly method for disposing municipal and industrial solid waste (Tengrui et al., 2007).

Malaysia generates about 6.2 million tons of solid waste per year, which equals approximately 25,000 tons per day. This amount is expected to increase to more than 31,000 tons per day by 2020 because of increasing population and per capita waste generation (Yahya 2012). Food, paper, and plastic constitute 80% of the overall weight of Malaysian waste (Manaf et al., 2009). The average amount of MSW generated in Malaysia is 0.5 kg/capita/day to 0.8 kg/person/day, and that in major cities is as high as 1.7 kg/capita/day (Kathirvale et al., 2003). Despite the many advantages of landfilling, the resulting highly polluted leachate has been a cause of significant concern, especially because landfilling is the most common technique of solid waste disposal (Ghafari et al., 2005).

Leachate is formed when water mainly from rain infiltrates deposited waste. As the liquid moves through the landfill, many organic and inorganic compounds, such as ammonia and heavy metals, are transported into the leachate. The leachate then moves to the surface or base of the landfill cell and may pollute the surface and groundwater, which may affect human health and aquatic environment. Many factors affect the quality and quantity of leachate, such as seasonal weather variation, landfilling technique, waste type and composition, and landfill structure (Mohajeri, 2010). Leachate pollution in Malaysia is very serious, and the high generation of landfill leachate in tropical areas such as Malaysia is mainly attributed to the high amount of rainfall (Lema et al., 1988).

1.2. Problem statement

Landfill leachate is liquid that has seeped through solid waste in a landfill and extracted dissolved or suspended materials in the process. The environmental impact of leachate depends on leachate strength, proper leachate collection, and the efficiency of leachate treatment. Leachate contains high amounts of organic compounds, ammonia, and heavy metals and sometimes contaminates ground and surface water (Christensen et al., 2001). Landfill leachate usually contains a complex variety of materials and organic compounds, such as humic substances, fatty acids, heavy metals, and many other hazardous chemicals (Schrab et al., 1993).

Leachate in classical wastewater treatment plants is rarely treated because of its nature and high levels of pollutants (i.e., high chemical oxygen demand [COD] and ammonia content and low biodegradability). Researchers worldwide are still searching for a total solution to the leachate problem. Multiple-stage treatments are still required to remove leachate pollution thoroughly. No single method can effectively remove all pollutants simultaneously. Treatment by a conventional water treatment system (i.e., a combination of sedimentation, biological treatment, filtration, and carbon adsorption) cannot remove salts or organics, such as harmful recalcitrant compounds. Such a system has difficulty treating recalcitrant organics, such as COD, and associated pollutants, such as colour and ammonia, because these pollutants are stable and difficult to degrade. The rest of the parameters are easier to treat. Landfill leachate is a soluble organic and mineral compound formed when water infiltrates refuse layers, extracts a series of contaminants, and instigates a complex interplay between hydrological and biogeochemical reactions that acts as a mass transfer mechanism, which in turn produces sufficiently high moisture content to initiate liquid flow (Aziz et al., 2004). The quantity of this leachate is generally small compared with that of other wastewater, but its contents are extremely hazardous.

COD, colour, and ammonia are significant problems in leachate treatment. COD, colour, and NH_3–N are among the main parameters included in the standard discharge limits for pollutants in landfill leachate in Malaysia. The presence of high levels of these parameters in landfill leachate over a long period of time is one of the most important problems routinely faced by landfill operators. For example, the average values of COD and colour in the Pulau Burung Landfill Site (PBLS) are 2,321 mg/L and 5,094 Pt-Co, respectively (Bashir et al., 2011). The acceptable discharge limit according to Malaysian Environmental Quality Regulations 2009 (control of pollution from solid waste transfer station and landfill) is 400 mg/L for COD and 100 Pt-Co for colour. Such a high quantity of unprocessed organics depletes dissolved oxygen in a process called eutrophication. Moreover, NH_3–N is extremely toxic to aquatic organisms (Bashir et al. 2010a). The average values of NH_3–N in landfill leachate in Kulim, Pulau Burung, and Kuala Sepetang are 562, 1,627, and 564 mg/L, respectively. The acceptable discharge limit according to the Environmental Quality Regulations is 5 mg/L.

Stabilized leachate, indicated by a low biochemical oxygen demand (BOD_5)/COD ratio (i.e., low biodegradability) and seen in many landfills in Malaysia, is particularly difficult to treat biologically (Mohajeri et al., 2010a, 2010b; Bashir, et al., 2010a,b). Therefore, additional physico-chemical processes are necessary for the pre-treatment and post-treatment of leachate (Tauchert et al., 2006).

In this regard, dedicated treatment facilities are required before leachate can be discharged to the environment. Various site-specific treatment techniques can be used to treat hazardous wastewater depending on leachate characteristics, operation and capital costs, and regulations. Leachate treatment schemes likely include biological, physical, and chemical processes; their combination and specific modification are greatly influenced by the characteristics of leachate produced (Goi et al., 2009; Baig and Liechti, 2001). Advanced oxidation processes (AOPs) have received considerable attention as alternative methods for reducing the organic load of wastewater. These methods transform non-biodegradable pollutants into nontoxic substances (Catalkaya and Kargi, 2007).

Ozone is utilized in chemical processes used in the water industry. Fenton's reagent has seen recent application in the wastewater industry. Fenton and ozone have been applied separately to leachate treatment, especially to remove recalcitrant organics, and may be attractive means for treating landfill leachate because of the high oxidative power of ozone (Tizaoui et al., 2006; Lucas et al., 2007; Tizaoui et al., 2007). Some ozone techniques have been used to remove COD and colour from landfill leachate (e.g., ozone alone, ozone in AOPs [O_3/H_2O_2,/O_3/UV], and ozone and Fenton separately for pre-treatment and post-treatment) (Gau and Chang, 1996; Geenens et al., 2001; Haapea et al., 2002; Kamenev et al., 2002; Fang et al., 2005; Goi et al., 2009; Cortez et al., 2011a, 2011b). The performance of both O_3/H_2O_2,/O_3/UV in removing difficult parameters from stabilized leachate (i.e., COD, ammonia, and colour) as well as improving biodegradability is limited.

Fenton and Persulfate reagents recently received attraction in removing organics from wastewater and landfill leachate, however, the performance of both reagents in stabilized leachate treatment is still limited. Persulfate oxidation works by releasing sulfate radicals that have powerful effects on the oxidation of organics (Watts, 2011; Renaud and Sibi, 2001). Generation of sulfate radicals during persulfate oxidation can be significantly enhanced by catalysts, namely, heat, UV radiation, high pH, and iron ions (Gao et al., 2012; Shiying et al., 2009; Rostagy et al. 2009). Consequently, the effectiveness of employing ozone in initiating sulfate radicals during persulfate oxidation in one ozone reactor has never been investigated. The performance of O_3/persulfate under different operating conditions (i.e., pH, reaction time, ozone, and persulfate dosage) remains unknown.

The performance of cooperation of ozone and tow Fenton's and persulfate reagents in improving ozonation process in one reactor has not been investigated.

Design criteria are not sufficiently established as well. Removal efficiency under different operating conditions (i.e., pH, organic loading, ozone, Fenton and persulfate dosage) remains unestablished. Changes in the biodegradability of leachate after oxidation have also not been reported.

The interactions and statistically relationships of the independent factors for each three ozonation processes and optimization of the operational conditions using response surface methodology (RSM) and central composition design (CCD) have not been well studied. RSM is a useful and helpful tool for the optimization of wastewater treatment processes. RSM gives a large amount of knowledge from a small number of experimental runs. However, traditional methods are time consuming and a large number of experimental runs are required to describe the behavior of the process. The interaction effect of the independent parameters on the response can be observed and investigated via RSM.

The effects of the three design applications (ozone alone, ozone/Fenton, and ozone/persulfate) on the biodegradability and solubility (e.g., biodegradable COD, non-biodegradable COD , soluble COD , biodegradable soluble COD , non-biodegradable soluble COD , and particulate COD) of stabilized leachate have not been documented. Knowledge about organic behavior after exposure to ozone, ozone/Fenton, and ozone/persulfate has also not been well established.

Ozone – based AOP has been used to improve oxidation potential during one-stage ozonation and reduce the long reaction time associated with combined treatment. Ozone/AOPs efficiently treat stabilized leachate. This study was conducted because these methods are not properly established for landfill leachate treatment. This research is novel because current knowledge only focuses on the conventional biological process, which has limitations in removal performance.

This study focuses on treating leachate from the semi-aerobic stabilized PBLS as one kind of landfill in Malaysia. Leachate from PBLS is characterized by high organic and ammonia concentration and very low biodegradability and is not subjected to biological process. Studies on COD, colour, and NH_3–N removal from semi-aerobic stabilized leachate and on enhancing biodegradability by using ozone/AOPs remain limited.

1.3. Objectives:

This research aims to establish new technology and knowledge in stabilized leachate treatment by using ozone – based advanced oxidation processes (ozone, ozone/Fenton, and ozone/persulfate) to reduce treatment time and improve the efficiency of treatment by increasing oxidation potential of ozone. The specific objectives of this study include the following:

1) To compare and optimize the effectiveness of ozone, ozone/Fenton, and ozone/persulfate oxidation separately in removing COD, colour, and ammonia from stabilized leachate under different experimental conditions.
2) To evaluate the influence of the three oxidation processes on the biodegradability and COD fractions of stabilized leachate.
3) To establish the optimized design data for a leachate treatment plant by using the best among the three ozone-based advanced oxidation processes.

1.4 Scope of the study

Many useful applications can occur in the ozone oxidation process. Ozone oxidation can maintain its dominance through the use of proper operating conditions, such as ozone dosage, initial pH, initial COD concentration, and reaction time.

Samples from PBLS, Malaysia, were used. The experiments were performed on a laboratory-scale ozone reactor supported by an ozone generator and analyzer. Preliminary experiments were carried out to select important variables for the three oxidation processes (ozone, ozone/Fenton, and ozone/persulfate). Statistically designed experiments were then conducted separately by using CCD under RSM, thereby obtaining optimal operational conditions.

The study focuses on optimizing the removal of major leachate pollutant parameters, namely, COD, colour, and ammonia. Following the optimal operational condition for each process, the effect on biodegradability and the behavior of organic fractions are discussed.

1.5 Organization of the thesis

This thesis consists of the following five chapters:

Chapter 1 Introduction: An introduction and definition about the municipal solid waste and landfill leachate is presented. Problem statements that provide the basis and rational to identify the research directions is given in this chapter.

Also the main aim and specific objectives of the present study are elaborated in detailed together with the scope of the study to be covered.

Chapter 2 Literature review: A comprehensive review of landfill leachate problems, leachate treatment processes are presented. Physic-chemical treatment techniques, ozone and AOPs are particularly discussed in detail.

Chapter 3 Materials and methods: This chapter presents the site location and characteristics, sampling, experimental procedures, materials and instruments, chemicals and reagents used and analytical methods of parameters. This chapter also describes the statistical methods used to determine operational variables process optimization using RSM.

Chapter 4 Results and discussion: The first section in this chapter describes the characteristics of leachate. The second section illustrates the performance of the three oxidation processes (ozone, ozone/Fenton, and ozone/persulfate) in removing COD, colour, and ammonia by using classical experimental methods. The third section reports the optimization performance of the three processes based on RSM and CCD and describes the modeling and statistical data analysis. The fourth section describes the performance of the optimal operational conditions in enhancing biodegradability and the effects on COD fractions. Finally, the ozone, ozone/Fenton, and ozone/persulfate processes are compared. Furthermore, design data for a leachate treatment plant by using ozone/Fenton and ozone/persulfate reactions are presented.

Chapter 5 Conclusions and Recommendations: In this chapter, the conclusions of the findings in the current study are presented. Furthermore, the recommendations based on the study findings are presented for future studies.

CHAPTER 2

LITERATURE REVIEW

This chapter consists of five sections. The first section provides a general overview of MSW sources, definitions, management practices, landfill descriptions, and types. The second section gives an overview of landfill leachate characteristics. The third section summarizes different leachate treatments, including physico-chemical treatment processes, and the fourth focuses on applications of ozone in leachate treatment. The fifth section reviews different leachate treatment processes using RSM compared with conventional optimization treatments.

2.1 Municipal solid waste

Continuous population growth and industry development have increased solid waste generation. A sanitary landfill is the most economical and environment-friendly method for disposing municipal and industrial solid waste (Tengrui et al., 2007). Gershman et al. (1986) defined municipal solid waste (MSW) as rubbish from residences, institutions, and commercial establishments and non-hazardous light industrial refuse. McBean et al. (1995) defined MSW as residential solid waste produced from the house, and outdoor activities of a single or multi-family house. Dixon and Jones (2005) defined MSW as a mixture of waste primarily originating from residential and commercial establishments. The Malaysian Solid Waste and Public Cleansing

Management Act of 2007 (Act 672) defines MSW as any substance requiring disposal because it is broken, worn out, contaminated, or physically spoiled. Table 2.1 presents example of general characteristics of two well-known sanitary landfills in Malaysia.

Table 2.1: Characteristic of solid waste in Pulau Burung and Kulim Landfills

Waste characteristics	**Pulau Burung (amount, %)**	**Kulim (amount, %)**
Food	40	45
Plastic	22	24
Paper	10.5	7
Metals	2.5	6
Glass	3.25	3
textile	3.5	-
Others	18.25	15
Total	100	100

Source: Azizi et al., (2010)

2.1.1 Category of municipal landfill solid waste

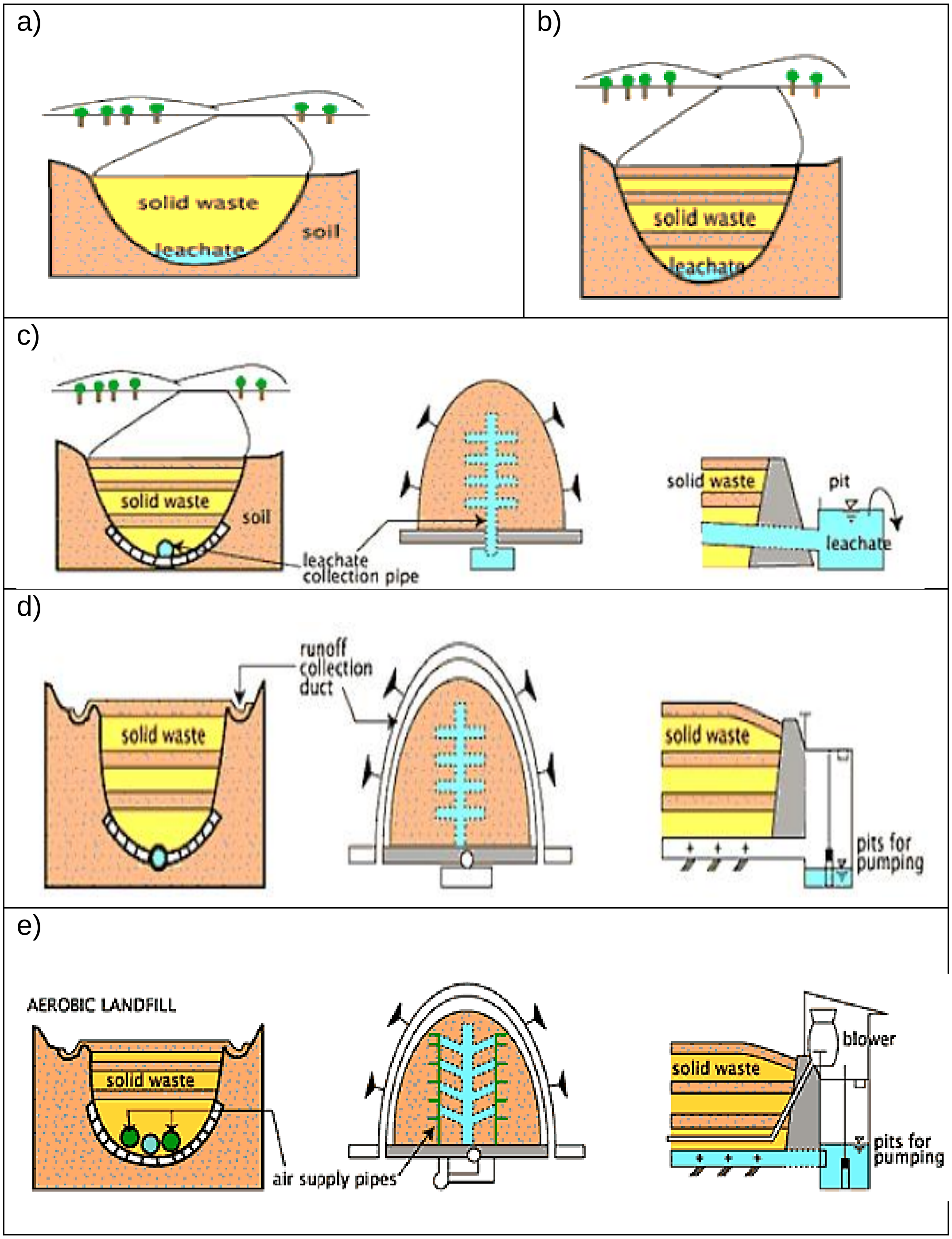
Landfill sites are generally classified into five: anaerobic, aerobic, anaerobic sanitary, improved anaerobic sanitary, and semi-aerobic. The use of these different landfills is generally based on environmental concerns and economic factors.

a) **In an anaerobic landfill,** solid wastes are decomposed by a conventional municipal method (Matsufuji, 1990). However, this type of landfill poses many major environmental and health concerns because it produces toxic leachate. Hudgins and Harper (1999) reported that anaerobic landfills contain high concentrations of organic compounds and pathogens. The waste mass also slowly degrades, posing long-term risks (Figure 2.1a).

b) **In an anaerobic sanitary landfill,** solid waste is sandwiched by soil. The conditions of solid waste here are the same as in anaerobic landfills (Figure 2.1b).

c) **In an improved anaerobic landfill,** the leachate collection system is installed at the bottom of the site. Other features are the same as in an anaerobic sanitary landfill. The conditions are still anaerobic, but moisture content is much lower than that in anaerobic sanitary landfills (Figure 2.1c).

d) **Semi-aerobic landfills** are designed with an underlying piping system that allows air to flow inside and outside the solid waste. This design enlarges the aerobic zone inside the landfill, creates active aerobic consortia, and increases the rate of waste decomposition (Figure 2.1d).



Source: Shimaoka et al, (2000)

Figure 2.1: Classification of landfill category structures**:** (a): Anaerobic landfill, (b), Anaerobic sanitary landfill, (c): Improved anaerobic sanitary landfill, (d): Semi-aerobic landfill with natural ventilation and leachate collection, (e): Aerobic landfill with forced aeration

a) Technology used in **aerobic landfills** has been evaluated over the last few years. The aerobic landfill system adds air and re-circulates leachate to maintain air humidity and to provide nutrients to microorganisms in order to reduce methane gas, volatile organic compounds, and odor emissions and thereby eliminate site leachate treatment. The aerobic landfill process enhances the biodegradation of waste and speeds up the stabilization of the landfill (Figure 2.1e).

2.1.2 Semi-Aerobic landfill (Fukuoka Method)

The semi-aerobic landfill is the most desirable landfill design for Malaysia (MHLG, 2006). On July 15, 2011, the semi-aerobic landfill was approved as a new Clean Development Mechanism in Malaysia (Tashiro, 2011). This type of landfill was first tested at the Shin-Kamata landfill in Fukuoka, Japan in 1975 (Chong et al., 2005).

The Fukuoka method is specially designed for temperate climate and has been adopted in Japan and in tropical countries, such as Malaysia, Indonesia, China, Sri Lanka, and Iran, since the 1980s. A schematic diagram of semi-aerobic (Fukuoka) landfills is shown in Figure 2.2. The mechanism of the semi-aerobic landfill system allows oxygen flows into the waste mass through leachate collection pipes by passive ventilation to accelerate aerobic microbial decomposition in the waste. One of the main advantages of this landfill system is that discharged leachate and gas are continuously used in the leachate collection and gas ventilation system, thereby improving leachate quality.

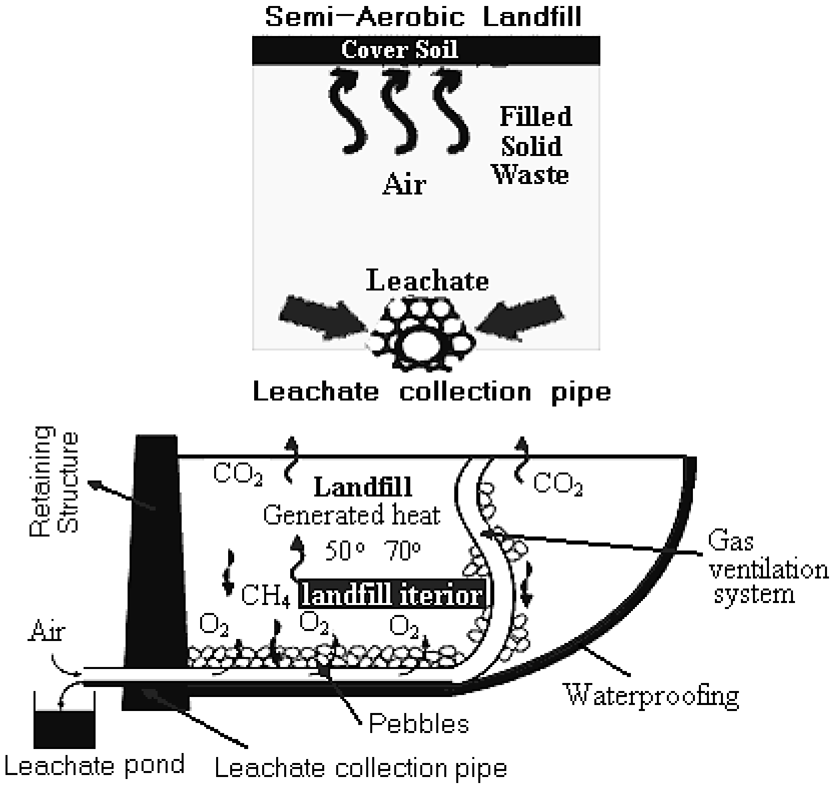


Figure 2.2: Schematic diagram of semi-aerobic landfill
(Japan International Cooperation Agency, JICA, 2005)

2.1.3 Principles of decomposition of solid waste

A complex series of reactions occurs at the landfill when wastes are buried: physical, chemical, and biological decomposition reactions. Decomposition progress rates of solid waste largely depend on waste characteristics. Physical decomposition occurs during the operational management of solid waste landfill and includes segregation, mechanical size, and volume reduction. Chemical decomposition involves combustion, pyrolysis, and gasification. Biological decomposition includes aerobic and anaerobic degradation. Biodegradation generates highly contaminated hazardous leachate and gases (Matsufuji, 2007).

Biodegradation increases BOD levels in leachate and reduces the pH level, and then gasification generates gas from organic acids, thereby reducing BOD levels and increasing pH (Matsufuji, 2007). Decomposition in landfills is divided into five phases: initial adjustment (Phase I), transition (Phase II), acidification (Phase III), methane fermentation (Phase IV), and maturation (Phase V) (Tchobanoglous, 1993).

Phase I: Initial adjustment phase

During this phase, aerobic conditions occur where organic biodegradable materials undergo microbial decomposition facilitated by air trapped within the landfill. Leachate generated from this phase is characterized by entrained particulate matter and small amounts of organic substances from aerobic degradation (McBean et al., 1995).

Phase II: Transition phase

In this phase, Biological decomposition of waste occurs. Transformation from aerobic to anaerobic environment occurs as the oxygen in waste cell decreases with more carbon dioxide being produced.

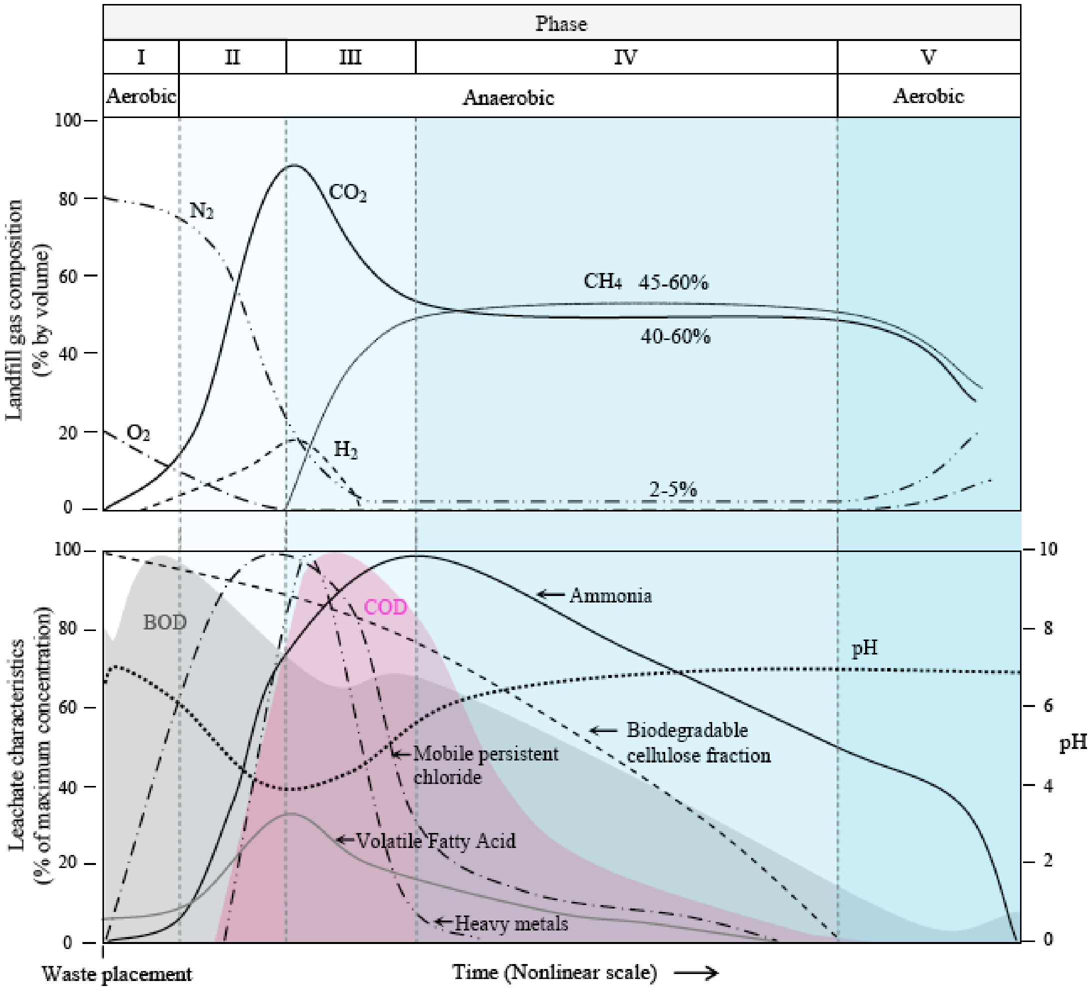


Figure 2.3: Leachate characteristics during decomposition process

(Source: Tchobanoglous, 1993)

During the initial aerobic phase, oxygen present in landfill is rapidly consumed, resulting in the production of CO_2 and the leachate temperatures can be increases. The aerobic phase in a landfill lasts only a few days because oxygen is not replenished once the waste is covered and the pH in this early stage becomes neutral. When the condition turns anaerobic, the hydrolytic, fermentative, and acetogenic bacteria becomes dominant, resulting in an accumulation of carboxylic acids. Consequently, chemical oxygen demand (COD) and pH in the leachate are reduced by the end of this phase as more volatile organic acids and CO_2 are produced (Kjelsen et al., 2002).

Phase III: Acid phase

This phase is also known as the acetogenic phase and is governed by acidogenic bacteria (acid formers). In this phase, oxygen in the landfill is consumed by aerobic bacteria. Development of organic acids and dissolved CO_2 reduces leachate pH to 5 or lower (Salem et al., 2008). Therefore, the heavy metals become soluble, and essential nutrients are removed from the leachate because of the decreasing pH. Ammonium and metal concentrations also rise, and complex molecules are degraded.

Phase IV: Methane fermentation phase

In this phase, methanogen conditions are established after several months or years, and leachate becomes neutral or slightly alkaline. Methanogenic bacteria consume acids and produce methane and carbon dioxide. Under stabilized methanogenic conditions, landfill gas is composed of approximately 55% to 60% methane and 40% to 45% carbon dioxide, with trace amounts of other gases (He et al., 2004). The pH in this phase increases to neutral values of 7 or 8.

Phase V: Maturation phase

In this phase, nutrients and substrates become limited, and biological decomposition is less active. Aerobic conditions may return after conversion of biodegradable waste to carbon dioxide and methane gas. Landfill gas is depleted, and then the leachate stabilizes. Leachate often contains humic and fulvic acids, which are difficult to biodegrade. The slow degradation of these resistant organic materials may continue with the production of humic-like substances.

2.2 Landfill Leachate

One of the most critical disadvantages of landfill disposal methods is the generation of highly polluted liquid (i.e., landfill leachate). Landfill leachate is the liquid that seeps through solid waste in a landfill (Christensen et al., 2001). Renou et al. (2008) defined leachate as the highly contaminated liquid generated from the degradation of the organic fraction of wastes combined with percolating rainwater.

The age of the landfill site is one of the most important factors for the stability of leachate, namely, stabilized leachate, which is relatively less biodegradable (BOD_5/COD ratio < 0.1) and contains lower COD concentration compared with young leachate (Schiopu et al., 2101; Rivas et al., 2004).

2.2.1 Leachate characteristics and quality

According to Tatsi et al. (2003) and Renou et al. (2008), landfill leachate is characterized by two major factors: quantity (volumetric flow rate) and quality (chemical composition). Many factors affect the quality and quantity of leachate, including seasonal weather variation, landfilling technique, waste type and composition, and landfill structure (Mohajeri, 2010; El-Fadel et al., 2002). Unfortunately, landfill leachate is rapidly generated in tropical countries, such as Malaysia, because rainfall generally exceeds the evaporation rate during the rainy season (Lema et al., 1988).

Landfill leachate usually contains various materials and organic compounds, such as humic substances, fatty acids, heavy metals, and many other hazardous chemicals. Regardless of concentration changes based on a complex set of interrelated factors, landfill leachate can be classified into four major groups of pollutants according to their complexity: dissolved organic matter, inorganic macro-components, heavy metals, and xenobiotic organic compounds (Widziewicz et al., 2012; Emenike et al., 2012; Worrell and Vesilind, 2012; Aziz et al., 2004; Schrab et al., 1993). Leachate is a potential source of ground and surface water contamination (Schrab et al., 1993; Christensen et al., 2001; Scottish Environment Protection Agency (SEPA), 2003).

2.2.2 Seriousness of COD, colour and NH_3-N in PBLS

Organic loading in leachate is usually determined by measuring COD, BOD_5, and total organic carbon (TOC). Colour is also an important indicator of organic loading; high colour intensity indicates high organic content in leachate (Aziz et al., 2007).

Ammonia removal has become an important concern in leachate treatment, the latest development regarding the pollution control from solid waste transfer station and landfill in Malaysia reported NH_3–N as one of the parameters included in the standard discharge limits for pollutants in landfill leachate. High levels of NH_3–N in landfill leachate over a long period of time represent one of the most important problems routinely faced by landfill operators. NH_3–N is extremely toxic to aquatic organisms (Bashir et al., 2010b). This research focuses on leachate generated by PBLS. Table 2.2 illustrates the general characteristics and composition of landfill leachate from PBLS. COD, ammonia, and colour are the most problematic chemical parameters in this leachate (Aziz et al., 2004, 2007, 2009; Mohajeri et al., 2010a,b; Bashir et al., 2010a,b, 2011; Ghafari et al., 2009).

Table 2.2: General characteristics of landfill leachate from semi-aerobic Pulau Burung Site, Nibong Tebal, Pulau Pinang, Malaysia

No.	**Parameter**	**Semi-aerobic Pulau Burung site**				**Standard**
		Un-aerated		**Intermittently aerated**		**Discharge**
		Range	**Average**	**Range**	**Average**	
1	Phenols (mg/L)	0.35-2.07	1.2	2.85-10.5	6.7	-
2	Total nitrogen (mg/L N-TN)	200-700	483	700-1800	1200	-
3	Ammonia-N (mg/L NH_3-N)	360-730	542	1145-2150	1568	-
4	Nitrate-N (mg/L NO_3 _$^-$ N)	900-3200	2200	2900-7900	5233	-
5	Nitrite-N (mg/L NO_2 _-N)	44-270	91	20-120	49	-
6	Total phosphorus (mg/L $PO_4{}^{3--}$TNT)	10 - 43.0	21	10 -25	17	-
7	Ortho-Phosphorus (mg/L $PO_4{}^{3-}$mv)	84 - 274	141	94-210	159	-
8	BOD_5 (mg/L)	67 - 93	83	146 - 336	243	50
9	COD (mg/L)	600 - 1300	935	1680 - 4020	2345	400
10	BOD_5/COD	0.051-0.12	0.096	0.036-0.186	0.124	> 0.3
11	pH	8.05 - 8.35	8.20	8.14-8.37	8.28	5.5 - 9
12	Electrical conductivity (ms/cm)	10.14 - 13.63	12.17	21.5 - 22.5	22.10	-
13	Turbidity (FAU)	600 - 3404	1546	149-211	180	-
14	Colour (Pt Co)	1944 - 4050	3334	2310 - 4390	3347	-
15	Total solids (mg/L)	5138 - 7404	6271	8860 - 11084	9925	-
16	Suspended solids (mg/L)	906-2220	1437	374-1372	837	100
17	Total iron (mg/L Fe)	2 - 29.5	7.9	0.9-8.8	3.4	5
18	Zinc (mg/L Zn)	0-3	0.6	0.01-2	0.5	1
19	Total coliform	-	-	-	<50	-

Source: Aziz et al., (2010)