PENYINGKIRAN BESI DAN NUTRIEN DARIPADA LARUT RESAP MENGGUNAKAN KARBON TERAKTIF DAN AMFOTERIK SURFAKTAN-DIUBAHSUAI ZEOLITE

oleh

ROHANA BINTI ABDULLAH

Tesis yang diserahkan untuk

memenuhi keperluan bagi

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ACSMZ	Anionic-Cationic Surfactant-Modified Zeolite
ANOVA	Analysis of Variance
BOD	Biochemical Oxygen Demand
CCD	Central Composite Design
CMC	Critical Micelle Concentra
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EC	Electrical Conductivity
ECEC	External Cation Exchange Capacity
EDX	Energy-Dispersive X-Ray Spectroscopy
F-Value	Fisher variation ratio
GAC	Granular Activated Carbon
HCl	Hydrochloric Acid
HDTMA	Hexadecyltrimethylammonium
HR	High Range
K	Potassium
KCl	Potassium Chloride
KOH	Potassium Hydroxide
MA	Medium Age
MR	Medium Range
MSW	Municipal Solid Waste

N	Nitrogen
NaOH	Sodium Hydroxide
NH_3-N	Ammoniacal Nitrogen
NH_4^+	Ammonium Ion
NO_3^-	Nitrate
NZ	Natural Zeolite
O	Old
P	Phosphorus
PO_4^{3-}	Phosphate
PtCo	Platinum Cobalt Units
QAC	Quaternary Ammonium Chlorides
Rpm	Revolution per minute
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
SLES	Sodium Laureth Sulphate or Sodium Lauryl Ether Sulphate
SMZ	Surfactant Modified Zeolite
SOP	Standard Operational Procedure
SS	Suspended Solids
TDS	Total Dissolved Solid
TKN	Total Kjeldahl Nitrogen
TLS	Taiping Landfill Site
VFA	Volatile Fatty Acids
Y	Young

LIST OF SYMBOLS

^oC	Degree Celcius
C_e	Liquid-phase concentration of the parameter at equilibrium (mg/L)
q_e	The adsorption amount at equilibrium (mg/g)
b	The Langmuir constants (L/mg)
K_F	The capacity of adsorption
1/n	The constant indicative of the adsorption intensity
Y	Response
X_i, X_j	Variables
β_o	A constant coefficient
β_j	The interaction coefficients of linear
β_{jj}	The interaction coefficients of quadratic
β_{ij}	The interaction coefficients of second order terms
k	The number of studied factors
e_i	The error
D_1	DO of diluted sample immediately after preparation, mg/L
D_2	DO of diluted sample after 5-day incubation, mg/L
P	Fraction of wastewater sample volume to total combined volume
N	Normality
M	Molarity
C_i	Initial concentration (mg/L)
C_f	Final concentration (mg/L)

x	The amount of material adsorbed (mg)
m	The weight of adsorbent (g)
c	The concentration of adsorbate in solution after adsorption is complete (mg/L)
Q	The adsorption capacity
R_L	Dimensionless constant separation factor
R^2	Coefficient of Determination

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MENGGUNAKAN KARBON TERAKTIF DAN AMFOTERIK SURFAKTAN-DIUBAHSUAI ZEOLITE

ABSTRAK

Larut resap tapak pelupusan terkenal sebagai air sisa yang kompleks di mana komposisi dan kepekatan bahan pencemar kebanyakannya dipengaruhi oleh jenis sisa dideposit dan usia tapak pelupusan. Rawatan larut resap menggunakan karbon teraktif berbutir (GAC) dalam menyingkirkan besi dan amfoterik surfaktan-diubahsuai zeolit (SMZ) bagi pengambilan NH_3-N dan nutrien lain (N, P, & K) telah dikaji. Kecekapan penjerapan telah ditentukan oleh satu siri eksperimen penjerapan kumpulan menggunakan peralatan ujian balang. GAC yang di pra-rawat dengan 1.5N NaOH digunakan kerana ia menunjukkan prestasi penjerapan besi yang lebih baik. Selain itu, zeolite yang menjalani pengubahsuaian permukaan dengan 0.03M amfoterik Miranol C2M telah dipilih untuk kajian lanjut. Keputusan kajian kumpulan menunjukkan GAC dapat menyingkirkan 90.29% besi berbanding 50.25% menggunakan KOH sebagai pemendak kimia. Sementara itu, amfoterik SMZ telah dioptimumkan menggunakan RSM dan berkesan menjerap warna, NH_3-N dan nutrien lain (N, P, & K) berbanding dengan zeolit asli. Kebolehgunaan amfoterik SMZ sebagai produk baja lambat bebas diperhatikan. Pemerhatian menunjukkan pertumbuhan bunga ati-ati yang lebih baik dicapai berbanding dengan kawalan (tanpa baja). Berdasarkan kajian isoterma penjerapan, model isoterma Freundlich sangat padan dengan data eksperimen dengan nilai R^2 yang lebih tinggi 0.638 untuk warna dan 0.716 untuk NH_3-N. Oleh itu, dapat disimpulkan bahawa GAC dan

IRON AND NUTRIENTS REMOVAL FROM LEACHATE USING ACTIVATED CARBON AND AMPHOTERIC SURFACTANT-MODIFIED ZEOLITE

ABSTRACT

Landfill leachate is well known as a complex wastewater in which the composition and concentration of pollutants are mainly influenced by the type of waste deposited and the age of landfill. The treatment of leachate using granular activated carbon (GAC) in removing iron and amphoteric surfactant-modified zeolite (SMZ) for the uptake of NH_3-N and other nutrients (N, P, & K) were investigated in this study. The adsorption efficiency was determined by a series of batch adsorption experiments using the jar test apparatus. The GAC that pre-treated with 1.5N NaOH was used because it showed better adsorption of iron performances. Besides, zeolite that underwent surface modification with 0.03M of amphoteric Miranol C2M was chosen for further study. The results of the batch studies indicated that GAC was able to remove 90.29% of iron compared to 50.25% using KOH as a chemical precipitator. Meanwhile, the amphoteric SMZ was optimized using RSM and it effectively adsorbed color, NH_3-N and other nutrients (N, P, & K) in comparison to natural zeolite. The applicability of the amphoteric SMZ as a slow releasing fertilizer product was observed. The observation showed that a better growth of *Coleus Blumei* was attained as compared to the control (without fertilizer). Based on the adsorption isotherm study, the Freundlich isotherm model fitted well with the experimental data with higher R^2 values of 0.638 for colour and 0.716 for NH_3-N. Therefore, it can be concluded that the GAC and amphoteric SMZ can be employed as an adsorbents in the leachate treatment processes.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Generally, landfill leachate consists of many different organic and inorganic compounds that may either be dissolved or suspended in the wastewater. Mostly, the leachate contains high concentrations of chemical oxygen demand (COD), biochemical oxygen demand (BOD), nitrogen, phenols, pesticides, solvents and heavy metals that can cause difficulties in the treatment of landfill leachate (Zainol et al., 2012; Halim et al., 2010b). It's difficult to treat leachate because it is a wastewater with a complex and widely variable content generated within a landfill (Gandhimathi et al., 2013).

Leachate is generated from liquids existing in the waste as it enters a landfill or from rainwater that passes through the waste (Renou et al., 2008). It should be managed through proper treatment methods because the discharge of leachate into the natural environment will cause serious problems to humans, animals and plants. This is because it may percolate through soils and subsoil, causing pollution to receiving water bodies (Aziz et al., 2010). Therefore, it is crucial to prevent contaminations of surface and ground waters by removing the contaminants from leachate (Aziz et al., 2010).

However, it is very difficult to find a successful and cost effective landfill leachate treatment. Since it's difficult to obtain a satisfactory single treatment either using physical, chemical or biological method, combination of these methods are used for landfill leachate treatment (Mojiri et al., 2013). Generally, the appropriate treatment method for leachate is decided based on the characteristic of the leachate itself (Zin et al., 2012). New leachate which contained mainly volatile fatty acids, found to be more effective if treated using biological processes compared to stabilized leachate (Turki et al., 2013; Zainol et al., 2013). While, the stabilized or old leachate is more suitable using the physical-chemical method (Zainol et al., 2012).

Many different approaches combining physical, chemical and biological methods have been developed for landfill leachate treatment (Mojiri et al., 2013). In recent years, physicochemical treatment has gained greater interest for treating landfill leachate (Aziz et al., 2010). Several technologies, for instance chemical precipitation, reverse osmosis, ion exchange, membrane filtration, oxidation, air stripping, and adsorption have been applied for landfill leachate treatment (Gandhimathi et al., 2013; Aziz et al., 2010). Among the physicochemical treatments, adsorption is the most widely used method for the removal of recalcitrant organic compounds from landfill leachate (Daud et al., 2007).

Granular or powdered activated carbon is the most frequently used adsorbent (Wiszniowski et al., 2006). Recently, the adsorption using granular or powder activated carbon has been receiving a considerable attention due to the effectiveness in removing the organic and inorganic contaminants from polluted wastewater (Mojiri et al., 2013). It has also been used in the treatment of landfill leachate for removal of dissolved organics (Halim et al., 2010b). The widely used of this adsorbent is mainly due to its inherent physical properties, large surface area, high adsorption capacity, surface reactivity and microporous structure (Mojiri et al., 2013; Daud et al., 2007).

The aim of this study is to measure the potential and the effectiveness of using GAC as an adsorbent in eliminating iron. While, amphoteric SMZ for the uptake of nutrients (N, P, & K) in the treatment of landfill leachate. Subsequently, the amphoteric SMZ that contains of nutrients from leachate will be washed with distilled water and oven dry to produce fertilizer. Its feasibility as a slow release fertilizer product would also be evaluated, so that it can be used as plant fertilizer in agricultural applications. Additionally, the effects of pH and dosage on the adsorption process will also be investigated, a part from examining the applicability of the Freundlich and Langmuir isotherm models.

1.2 Problem Statement

Leachate contamination is one of the most important issue in environmental conservation (Zin et al., 2012). In Malaysia, solid waste management has become a major environmental problem with more than 23,000 tonnes of waste are produced daily in Malaysia (Zainol et al., 2012). Moreover, the amount of waste generated continues to increase due to the rising population and development of the country. Therefore, more sanitary landfills should be introduced to cater for solid waste disposal. Unfortunately, the landfill leachate will cause environmental problems if it is not properly handled and managed.

The municipal landfill leachate has been one of the major problem in the environmental aspect due to the high organics, inorganics and heavy metal contents and toxicity characteristics (Renou et al., 2008). According to Alkassasbeh et al., (2009), there were more than 200 organic compounds that have been found in the municipal landfill leachate. Among these, about 35 compounds have been identified as potentially harmful to the environment and human health.

Removal of ammoniacal nitrogen (NH_3-N) for instance, is very crucial because it is one of the critical parameter in landfill leachate. It has been reported as the major toxicant that causes toxicity to most organisms in surface water and also contributes to eutrophication, and dissolved oxygen depletion (Aziz et al., 2004). Besides, the high concentration of heavy metals such as iron, zinc, lead, copper, cadmium and chromium can results in serious water contamination and threaten the environment (Aziz et al., 2010). While, an extreme amount of color can cause hazards to the environment as it produces large numbers of contaminants such as acids, bases, inorganic contaminants and toxic organic residues (Isa et al., 2007).

It is essential to remove these contaminants from leachate, so that the pollution of surface and groundwater can be prevented. This is because the discharge of leachate into the surface water can cause serious problems to humans, animals and plants (Aziz et al., 2010). According to Kurniawan et al., (2006), once the groundwater is contaminated with the leachate it will be difficult to control and clean up, as well as very costly to treat. Hence, the leachate should be treated before it is being discharged into the surface water in order to prevent contamination of water resources and also to avoid both acute and chronic toxicities (Aziz et al., 2011).

In recent days, an appropriate and cost-effective leachate treatment has become a priority and challenge for landfill operators (Singh et al., 2012). In this present study the GAC has been employed to remove iron from leachate. While, amphoteric SMZ has been used for adsorbing NH_3-N and other nutrients (N, P, & K) in order to produce amphoteric SMZ as a slow releasing fertilizer product. Accordingly, there are not many studies that use landfill leachate as a source of nutrients (N, P & K) in producing the amphoteric SMZ as slow release fertilizer.

1.3 Objectives

The main objectives of this study are:

1) To determine the optimum pH and sorption dosage of activated carbon and amphoteric surfactant modified zeolite.
2) To establish the adsorption capacity using the best fit isotherm model of the Freundlich and Langmuir isotherm models in the removal of color, iron and ammoniacal nitrogen in landfill leachate.
3) To evaluate the feasibility of amphoteric surfactant modified zeolite (SMZ) as a slow release fertilizer product in agricultural applications.

1.4 Scope

The landfill leachate that have been used in this study was taken in a pre-cleaned 25 L plastic bottle collected from the Taiping landfill site. The sample was placed in the laboratory and kept in a cool room at 4 °C. The characterizations of landfill leachate were performed for six months starting from November 2011 until April 2012 in order to determine the physical and chemical characteristics. For the purpose of characterizations of the landfill leachate, the parameters such as heavy metals, major cations and anions (K, NO_3, and PO_4), color, NH_3-N, BOD and COD were determined. This present study focus on treating the landfill leachate for determination of the granular activated carbon potential as an adsorbent media and followed by amphoteric SMZ that can be used as a slow release fertilizer product. Simultaneously, it should be safe to discharge to the environment. This study mainly involved the laboratory works. Series of batch studies were carried out using jar test apparatus in order to determine the percentage removal of the studied parameters.

1.5 Thesis Overview

The thesis is divided into five chapters. First and foremost, Chapter 1 consist of introduction to the landfill leachate and its associated problems. The problem statement and also the objectives of this study are also discussed in this chapter. Chapter 2 consist of literature reviews on landfill, landfill leachate as well as reviews from the previous observation done by other researchers. Chapter 3 discusses the methodology for this study and procedure for modification of zeolite and parameters measurement. The results that has been obtained from the experiments were analyzed and discussed in Chapter 4. Lastly, the overall content of this thesis briefly summarized in Chapter 5 and the appropriate suggestion were also proposed in order to provide better outcomes for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Recently, the environmental issues have become the most concern issue worldwide. There are many types of pollution related to environmental such as air pollution, water pollution, land pollution and many more. However, one of the main issue regarding the environmental problems in Malaysia is due to the improper management of solid waste (Samuding et al., 2009). The production of leachate results from the contaminated liquid effluent percolating through deposited waste due to infiltration of rain water (Sanjay et al., 2013).

Leachate that produced from municipal solid waste (MSW) landfill is mostly known as harmful and highly contaminated. Leachate emission may cause severe contamination to the environment and eutrophication of the groundwater aquifers may also occur as well as the surface water, which is contributed to the environmental issues (Wang et al., 2006). Eutrophication is defined as the growth of huge amounts of algae and other aquatic plants leading to the deterioration of the water quality (Wikipedia, 2014). Therefore, proper treatment should be introduced to minimize the bad impacts regarding the environmental issues.

In spite of this, it is very difficult to find a suitable and cost effective landfill leachate treatment method (Aziz et al., 2010). This is because leachate is categorized as complex and high strength wastewater (Gandhimathi et al., 2013). There are unable to cater the discharged standards by implementing the conventional treatment methods only, since the volume and composition of leachate itself varies (Top et al., 2011). As a result, a very suitable and effective leachate treatment method is hard to identify. Furthermore, without an adequate treatment, the leachate can contaminate soil and groundwater, as well as the surface water surrounding the landfill.

The conventional treatment methods for instance recycling, aerobic and anaerobic processes, adsorption, chemical oxidation, ion exchange, coagulation/flocculation, chemical precipitation, air stripping and sedimentation/flotation have been employed in removing the contaminants in landfill leachate (Gandhimathi et al., 2013; Sanjay et al., 2013; Halim et al., 2010b; Foul et al., 2007). Unfortunately, the uses of the conventional treatment techniques are commonly not cost effective and require additional treatment (Wiszniowski et al., 2006).

Among the treatment techniques, adsorption is the most widely employed method for the removal of recalcitrant organic compounds from landfill leachate (Kurniawan et al., 2006). The major use of adsorbents in wastewater treatments are granular or powdered activated carbon (Sanjay et al., 2013). Activated carbon is well known as a typical and effective medium that can successfully remove organic substances from landfill leachate (Othman et al., 2010). In conjunction with the adsorption using activated carbon, there are also other materials that have similar function as adsorbents such as zeolite, keolinite, illite, vermiculite, municipal waste incinerator bottom ash and activated alumina (Wiszniowski et al., 2006).

Chemical precipitation is also one of the methods used to treat the landfill leachate (Renou et al., 2008). The chemical precipitation usually involved the pH adjustment to a certain level. According to Kurniawan et al., (2006), after the pH was adjusted to pH 11 which was in an alkalic conditions using a precipitant agent for example lime, the dissolved metal ions are converted to the insoluble solid phase via a chemical reaction. The heavy metals were effectively precipitated using 8 g/L of lime. Thus, the adjustment to pH 11 was considered as an average pH that can improve the precipitation of metal.

2.2 Landfill

Landfill is the technique employed most worldwide for the disposal of municipal solid waste (MSW) in developing countries such as Malaysia (Othman et al., 2010). Basically, the wate disposed at municipal landfills consist of a mixture of commercial waste, industrial waste, household waste and treatment sludge. Mostly, these mixtures of wastes generate leachate with heavy metal concentrations in μg/L to mg/L (Baun and Christensen, 2004). There are several methods regarding the disposal of solid waste, which include the open dumping, composting, compaction, incineration, sanitary landfill, hog feeding, grinding and discharge to sewer, dumping, milling, anaerobic digestion and reduction (Aziz et al., 2010).

Among these, the frequently used method for the disposal of MSW in many countries is landfilling. Landfill is economical and uses simple disposal method (Zin et al., 2012). Solid waste will undergo some changes in terms of the biological and physico-chemical after the process of landfilling. The degradation of the organic fraction of the waste is accomplished and the phenomenon generates a highly polluted wastewater called leachate (Jamali et al., 2009). This leachate has become a main issue related to the negative environmental impacts.

Currently, more than 230 landfills are practiced in Malaysia and there are commonly old dumpsites. The wastes are disposed without any protection towards the environment (Aziz et al., 2010). A major concern associated to this disposal method is the leachate produced from the landfills (Zainol et al., 2012). Thus, the current practices of sanitary landfill have been introduced to upgrade the old system which simply disposing the waste. The designs of the sanitary landfills are typically to manage the gases and the production of leachate via more systematic approach (Speer et al., 2010).

2.2.1 Types of Landfill

a) Aerobic Landfills

The aerobic landfill system usually employs air addition and leachate recirculation, in order to maintain the humidity of the air and also to cater nutrients for microorganisms (Gorden et al., 2008). The aerobic landfill process involves the growth and control of aerobic and facultative bacteria within the waste instead of anaerobic micro-organisms (Hudgins et al., 2010). Some of the benefits of using this method are the reduction in methane generation and also the increase in the stabilization of solid waste. Nevertheless, the aerobic landfills commonly require high maintenance costs, especially for the piping system that provides oxygen to the waste (Foul, 2007). Figure 2.1 shows a schematic design of aerobic landfill (Foul, 2007).

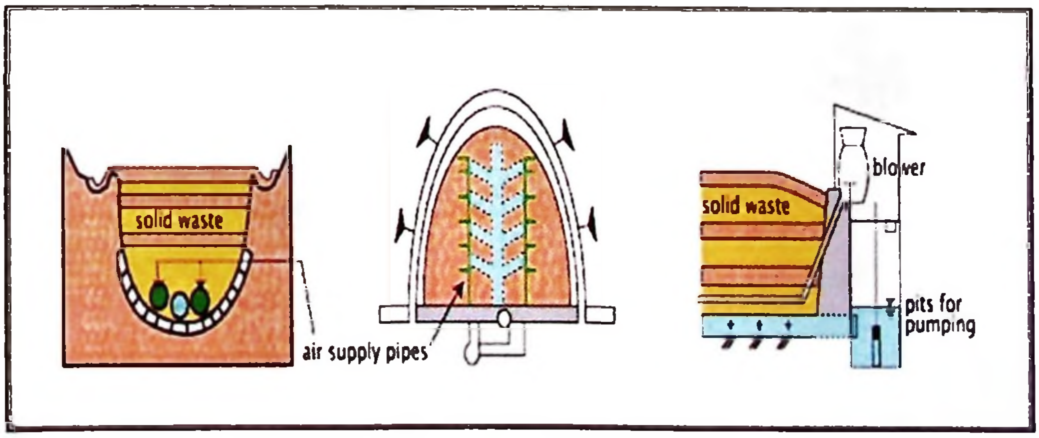

Figure 2.1 The schematic design of aerobic landfill (Foul, 2007)

b) Anaerobic Landfills

According to Foul, (2007), anaerobic landfill can be categorized into normal anaerobic landfill and also anaerobic sanitary landfill. The normal anaerobic landfill is quite similar to an open dumping. In contrast with the anaerobic sanitary landfill, the landfill usually has a cover layer over the wastes. An improved anaerobic sanitary landfill has additional cover layer collection system for leachate, as has been practiced at Taiping landfill (Zin et al., 2012; Zainol et al., 2012).

The solid wastes are typically disposed in a dug space, where an anaerobic condition of water is filled as practiced in anaerobic landfill. Generally, the sandwich-shaped cover demonstrates the anaerobic sanitary landfills (Aziz et al., 2010). Figure 2.2 shows a schematic design of the anaerobic landfill.

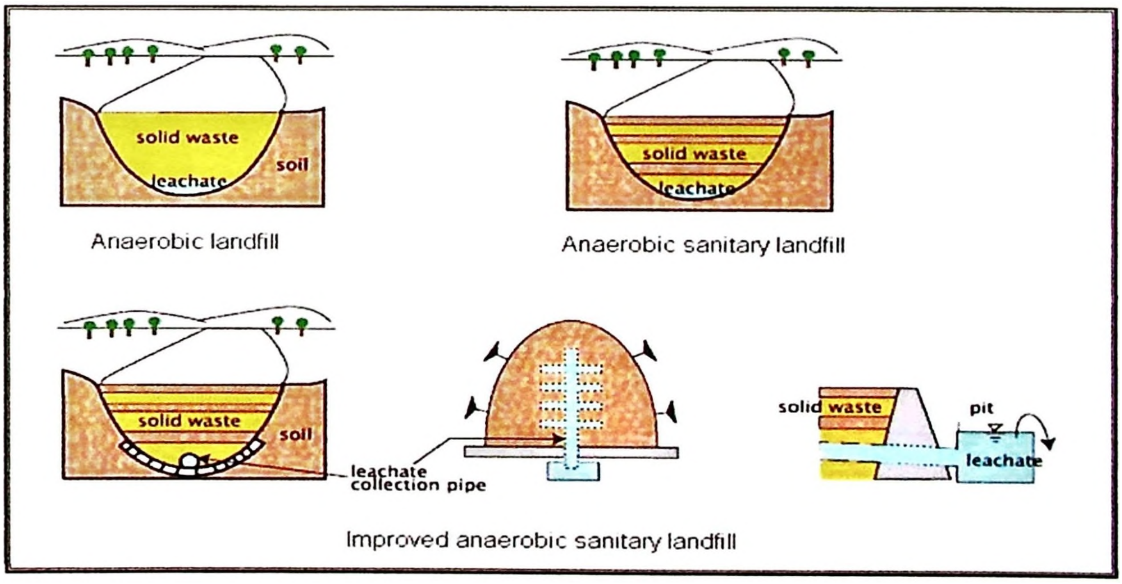

Figure 2.2 The schematic design of the anaerobic landfill (Foul, 2007)

c) **Semi-aerobic Landfills**

According to Matsufuji and Kouji, (2007), the semi-aerobic landfill structure is preparing a collection and discharge pipe with a large cross section in the bottom of the landfill that rapidly collects and discharges leachate away from the landfill site. The leachate collection pipes are significant to permit the flow of air inside and outside of the solid waste. This is essential, so that the aerobic zone inside the landfill can be enlarged in order to maintain active aerobic consortia, and also to increase the rate of waste decomposition (Foul, 2007).

Semi-aerobic landfill system is also a viable method for reducing pollution from landfills and its application was also highly feasible based on the cost-benefit evaluation of the entire implementation process, from the development stage to final closure (Sutthasil et al., 2013). There are only three sites in Malaysia that can be considered as semi-aerobic landfill, and one of them is the Pulau Burung Landfill as reported by Aziz, et al., (2004). Figure 2.3 shows a schematic design of semi-aerobic landfill.

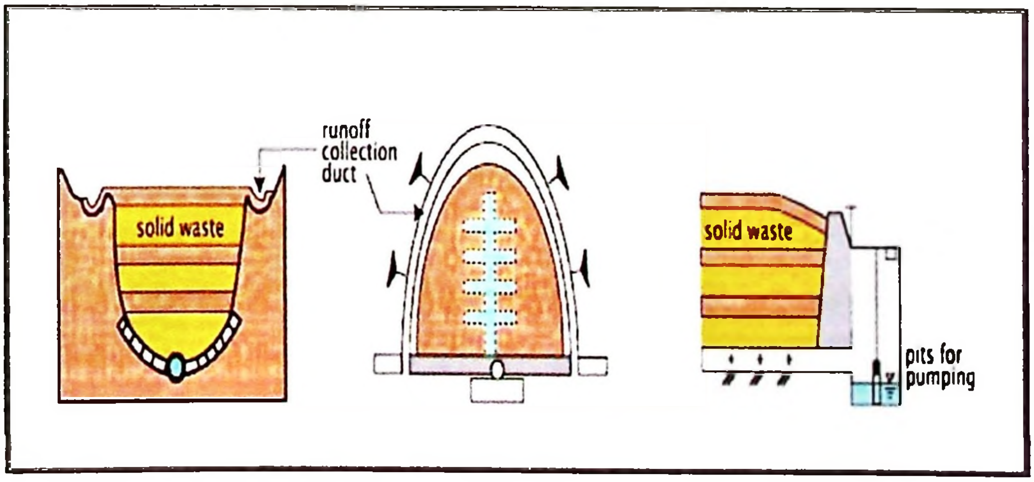

Figure 2.3 The schematic design of semi-aerobic landfill (Foul, 2007)

2.3 Leachate

The generation of leachate is one of the main concerns associated with landfills (Zainol et al., 2012). Landfill leachate is produced as a consequence of precipitation, surface run-off and infiltration or intrusion of groundwater percolating through a landfill (Bhalla et al., 2012). At the same time, the leachate is transporting a various kinds of pollutants such as ammonia, heavy metals, COD and suspended solids (Wiszniowski et al., 2006; Ziyang at al., 2009). The high levels of organic and inorganic matters, heavy metals, ammoniacal nitrogen, inorganic salts and chlorinated organics made the leachate to be considered as a high-strength wastewater (Li et al., 2009). Therefore, a proper leachate collection and treatment are required and needed in order to minimize the negative environmental impact.

According to Sanjay et al., (2013), the quality of leachate is determined primarily by the composition and solubility of the waste constituents. It is also well established that the variation of leachate composition depends on many factors such as waste composition, site hydrology, the availability of moisture and oxygen, design and operation of landfill and its age (Ziyang and Youcai, 2007; Aziz et al., 2004).) In fact, a landfill will continue to produce contaminated leachate even after a landfill site is closed and this process could last for 30-50 years (Bhalla et al., 2012).

The landfills can be categorized as young for <5 years, middle aged for 5-10 years and old for >10 years (Renou et al., 2008). Apart from that, the ratio of BOD/COD values give an indication that the leachate is stabilized (if <0.1), intermediate (0.1–0.5), or fresh (if >0.5) (Comstock et al., 2010). Generally, leachate that generated from mature sanitary landfill contains a combination of high-strength nonbiodegradable organic pollutants (Halim et al., 2012). Table 2.1 shows the landfill leachate classification against age.

Table 2.1 Landfill leachate classification vs. age (Foo et al., 2009; Renou et al., 2008; Mojiri, 2011).

	Recent	Intermediate	Old
Age (Years)	< 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	0.5-1.0	0.1-0.5	< 0.1
Organic compounds	80% volatile fat acids (VFA)	5-30% VFA + humic and fulvic acids	Humic and fulvic acids
Ammonia nitrogen (mg/L)	< 400	N.A	> 400
TOC/COD	< 0.3	0.3-0.5	> 0.5
Kjeldahl nitrogen (g/L)	0.1-0.2	N.A	N.A
Heavy metals	Low-medium	Low	Low
Biodegradability	Important	Medium	Low

In general, leachate that is produced from young landfill is also known as acidogenic (aerobic) landfills. This acidogenic landfills are usually contains large amounts of readily biodegradable organic matter (Bhalla et al., 2012). The presence of high levels of BOD_5 in young leachate makes it suitable for biological treatment (Othman et al., 2010). According to Jamali et al., (2009), the high concentrations of COD and BOD, and also BOD/COD ratio in young leachates make it suitable for anaerobic treatment prior to aerobic process. Unfortunately, it is unsuitable to be practiced for the older or stabilized leachates.

In contrast with the young landfills leachate, leachate that was generated from a stabilized landfill which is over 10 years generally contains high concentration of

NH_3-N, moderately high strength of COD and BOD/COD ratio lower than 0.1 (Zainol et al., 2012). As the landfill matures, the methanogenic phase occurs. In this stage, the methanogenic microorganisms generate in the waste and the VFA are changed to biogas (Renou et al., 2008). Accordingly, physical–chemical processes are found to be more suitable and effective processes for the treatment of stabilized leachate due to the high fraction of non-biodegradable organic material (Comstock et al., 2010).

2.4 Characteristic of Landfill Leachate

An understanding of physical, chemical and biological characteristics of wastewater is very essential in design, operation, and management of collection, treatment and disposal (Walsh, 2007). Generally, the characteristics of landfill leachate depend mainly on the type of MSW being dumped, the degree of solid waste stabilization, site hydrology, moisture content, seasonal weather variations, age of the landfill and stage of the decomposition in the landfill (Bhalla et al., 2012).

According to Kurniawan et al., (2006), the landfill site may still generate leachate highly contaminated with NH_3–N over 50 years after filling operations have been stopped. The characteristics of the landfill leachate are defined based on the basic parameters such as pH, BOD_5, COD, BOD/COD ratio, NH_3-N, heavy metals, total Kjeldahl nitrogen (TKN) and suspended solids (SS) (Abbas et al., 2009). The age and the degree of solid waste stabilization of the landfill have also significantly effect the landfill leachate characteristics (Renou et al., 2008). Table 2.2 shows the leachate composition from several countries around the world as reported by Renou et al., (2008).

Table 2.2 The compositions of leachate (Renou et al., 2008)

Landfill site	Age	pH	NH_3-N	BOD	COD	BOD/COD
Canada	Y	5.8	42	9660	13800	0.7
Canada	Y	6.58	10	90	1870	0.05
China, Hong Kong	Y	7.7	2,260	4200	15700	0.27
China, Hong Kong	Y	7.0–8.3	3,000	7300	17000	0.43
	Y	6.8–9.1	11000	5000	13000	0.38
	Y	7.8–9.0	13000	22000	50000	0.44
China, Mainland	Y	7.4–8.5	630–1,800	3700–8890	1900–3180	0.36–0.51
Greece	Y	6.2	3,100	26,800	70,900	0.38
Italy	Y	8	3,917	4000	19,900	0.2
Italy	Y	8.2	5,210	2300	10,540	0.22
South Korea	Y	7.3	1,682	10,800	24,400	0.44
Turkey	Y	7.3–7.8	1,120–2,500	10,800–11,000	16,200–20,000	0.55–0.67
		5.6–7.0	2,020	21,000–25,000	35,000–50,000	0.5–0.6
Turkey	Y	5.6–7.0	2,020	21,000–25,000	35,000–50,000	0.5–0.6
Turkey	Y	7.7–8.2	1,946–2,002	6380–9660	10,750–18,420	0.52–0.59
Canada	MA	6.9–9.0	–	–	3210–9190	–
China	MA	7.6	–	430	5800	0.07
China, Hong Kong	MA	8.22	–	1436	7439	0.19
Germany	MA	–	884	1060	3180	0.33
Germany	MA	–	800	800	4000	0.2
Greece	MA	7.9	940	1050	5350	0.2
Italy	MA	8.38	1,330	1270	5050	0.25
Italy	MA	8	–	1200	3840	0.31
Poland	MA	8	743	331	1180	0.28
Taiwan	MA	8.1	5,500	500	6500	0.08
Turkey	MA	8.15	1,270	–	9500	–
Brazil	O	8.2	800	150	3460	0.04
Estonia	O	11.5	–	800	2170	0.37
Finland	O	–	159	62	556	0.11
Finland	O	7.1–7.6	330–560	84	340–920	0.09–0.25
France	O	7.5	430	7.1	500	0.01
France	O	7.7	0.2	3	100	0.03
France	O	7	295	–	1930	–
Malaysia	O	7.5–9.4	–	48–105	1533–2580	0.03–0.04
South Korea	O	8.57	1,522	62	1409	0.04
Turkey	O	8.6	1,590	–	10,000	–

*Y: young; MA: medium age; O: old; NH_3-N, BOD and COD are in mg/L

2.4.1 Temperature

Temperature of raw leachate was depending on the climatic condition of the landfill site (Zin et al., 2012). This is due to fluctuation of ambient temperature as temperature poses impact to bacterial growth and chemical reaction (Lee et al., 2012). According to Lee et al., (2012), temperature also poses impact to solubility of many compounds to increase or decrease that affect the quality of leachate.

2.4.2 Color

According to Bhalla et al., (2012), the color of leachate samples were orange brown or dark brown. The presence of high concentration of color in landfill leachate is due to the presence of high organic substances (Zainol et al., 2012; Aziz et al., 2010). In general, the high levels of organic substances such as humic and fluvic compounds found in the stabilized leachate (Aziz et al, 2011).

2.4.3 pH

Leachate is generally found to have pH between 4.5 and 9 (Bhalla et al., 2012). The pH of landfill leachate is varied according to the age of landfills (Aziz et al., 2010). Generally, the pH of a stabilized leachate is higher than that of a young leachate (Zainol et al., 2012). For new landfills, pH values are range between 4.5-7.5 (Aziz et al., 2010) and for mature landfills, pH varies from 6.6-7.5 (Zin et al., 2012; Aziz et al., 2010). The difference could be due to the stabilized leachate that is produced after or during the fermentation of methane; hence the pH is higher than 7.5 (Zainol et al., 2012). According to Bhalla et al., (2012), the pH of leachate increased with time due to the decrease of the concentration of the partially ionized free volatile fatty acids.

2.4.4 Chemical Oxygen Demand

Chemical oxygen demand (COD) represents the amount of oxygen required to completely oxidize the organic waste constituents chemically to inorganic end products (Bhalla et al., 2012). COD is usually indicated by the presents of aggregate organic constituents (Halim et al., 2010a). Based on the Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, Malaysian Environmental Quality Act 1974, the value for COD of leachate should be less then 400 mg/L before safely discharge into environment (Zin et al., 2012). Halim et al., (2010a) has reported that the used of activated carbon was the most effective for COD removal in landfill leachate compared to composite media and zeolite.

2.4.5 Biochemical Oxygen Demand

Biochemical oxygen demand (BOD) is a measurement of the amount of oxygen uptake by microorganism during biological degradation of organic compound (Zin et al., 2012). According to Bhalla et al., (2012), BOD_5 is the measure of biodegradable organic mass of leachate and that indicates the maturity of the landfill which typically decreases with time. The standard five-day BOD_5 value is commonly used to determine the amount of organic pollution in water and wastewater (Aziz et al., 2010). Generally, BOD_5 varies with the age of the landfill (Zainol et al., 2012). The high concentration of BOD (4000–13,000 mg/L) is illustrated by young acidogenic landfill leachate (Foo and Hameed, 2009). Young leachates are more polluted than the mature ones where BOD_5 may reach up to 81,000 mg/l for young and 4200 mg/l for mature samples (El-Salam and Abu-Zuid, 2014).

2.4.6 Ammoniacal Nitrogen

Ammoniacal nitrogen (NH_3–N) has been identified as the main source of acute toxicity (Othman et al., 2010). The concentration NH_3–N increases with the increase in age of the landfill due to hydrolysis and fermentation of nitrogenous fractions of biodegradable refuse substrate (Kamaruddin et al., 2013). The NH_3–N present in mature landfill leachate in high concentrations causes difficulties in their biological treatment because of the inhibition of ammonia oxidizing and nitrite oxidizing bacteria by free ammonia (FA) and nitrous acid (FNA) (Ibrahimpašić et al., 2010).

Mojiri, (2011), has reported that the concentration of NH_3–N was between 2000-3000 mg/L in mature landfill leachate. While, Sabahi et al., (2009) has reported that the amount of ammonia (NH_3) in leachate is 1379.16 mg/L and 1020 mg/L in their study. The high concentration of untreated NH_3–N leads to motivated algal growth, decreased performance of biological treatment systems, accelerated eutrophication, promoted dissolved oxygen depletion, and increased toxicity of living organisms in water bodies (Aziz et al., 2010; Kurniawan et al., 2006).

According to Halim et al., (2010a), the biological degradation by the microorganism is occurs due to the high level of NH_3–N in leachate. The ammonium ion (NH_4) is converted into ammonia (NH_3) based on pH via the following reaction (Atxotegi, 2003):

$$NH_4^+ \longrightarrow NH_3 + H^+ \qquad \text{Equ. 2.1}$$

or

$$NH_4OH \longrightarrow NH_3 + H_2O \qquad \text{Equ. 2.2}$$

2.4.7 Nitrate

Nitrates (NO_3^-) are the primary contaminant that leaches into groundwater (Bhalla et al., 2012). An excessive nutrient enrichment can results in eutrophication which causes water contamination due to the algal blooms, oxygen depletion of surface waters and subsequently, leading to harmful of aquatic life, particularly fish (Zhan et al., 2011). Typical nitrate values of 25 mg/L for new (less than two years) and 5-10 mg/L for mature landfills (greater than 10 years) were recorded (Aziz et al., 2010). According to García and Cardona-Gallo, (2013), ammonium and nitrates removal from landfill leachates has been tested, namely air stripping, biological processes, precipitation and adsorption.

2.4.8 Phosphate

Phosphate (PO_4^{3-}) in leachate is also changed over time. Low phosphorus contents are usually found in leachate with the concentration of total phosphorus of 30.3 mg/L (Cheng et al., 2011). For mature leachate, value of total phosphorus should be within 5-10 mg/L and range for new landfill (<2 years) is within 5-100 mg/L (Zin et al., 2012). Bhalla et al., (2012) reported that the total phosphorus values for leachate at landfilling sites were 52.8 mg/l, 83.5 mg/l and 64.3 mg/l, respectively.

2.4.9 Heavy Metals

According to Varank et al., (2011), several researchers have reported that heavy metals in landfill leachate at present are not at major concern. Generally, the concentration of heavy metals in landfill leachate is fairly low (Bhalla et al., 2012). The concentrations of heavy metals (such as iron) in methanogenic phase are normally lower than the concentrations in acidogenic phase (Aziz et al., 2010). This is because as leachate stabilized, the concentration of heavy metals will be reduced due to adsorption and precipitation reaction (Zin et al., 2012). Conversely, the concentration of heavy metals in landfill is generally higher at earlier stages because of higher metal solubility as a result of low pH caused by production of organic acids (Bhalla et al., 2012).

Besides that, Słomczyńska and Słomczyński, (2004) have reported that the high concentrations of heavy metals found in the leachates were iron and followed by zinc. Table 2.3 shows the composition of heavy metals in landfill leachate as reported by Renou et al., (2008) in their previous study.

Table 2.3 The composition of heavy metals in landfill leachate (Renou et al., 2008)

Landfill site	Age	Fe	Cu	Mn	Si	Al
Italy	Y	2.7	-	0.04	-	-
Canada	MA	1.28-4.90	-	0.028-1.541	3.72-10.48	<0.02-0.92
Hong Kong	MA	3.811	0.12	0.182	-	-
South Korea	MA	76	0.78	16.4	-	-
Spain	MA	7.45	0.26	0.17	-	-
Brazil	O	5.5	0.08	0.2	-	<1
France	O	26	0.005-0.04	0.13	<5	2
Malaysia	O	4.1-19.5	-	15.5	-	-
South Korea	O	-	0.031	0.298	-	-

*Y: young; MA: medium age; O: old; all values are in mg L−1.

2.4.10 Major and Minor Ions

A significant portion of the landfill leachate is contributed by the inorganic constituents, which comprising of the ions calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonium (NH_4^{+}), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^{-}), sulphates (SO_4^{2-}) and bicarbonates (HCO^{3-}) in the microgram per liter to low milligram per liter level (Foo and Hameed, 2009).

Chloride is a non-degradable conservative parameter and the change of its concentration is commonly used to assess the variation of leachate dilution (Varank et al., 2011). According to Bhalla et al., (2012), the concentration of chlorides may range between 200-3000 mg/l for a 1-2 year old landfill and the concentration decreases to 100-400 for a landfill greater than 5-10 years old. Zainol et al., (2012) reported that the concentration of chloride for leachate from Kuala Sepetang and Kulim landfill site varied from 83.18-1484.33 and 194-292.35 mg/L, respectively.

On the other hand, the sulphate content of leachate mainly depends on the decomposition of organic matter present in the solid wastes (Bhalla et al., 2012). Typical sulphate values of 300 and 20-50 mg/L were recorded for new (less than two years) and mature (more than 10 years) landfills, respectively (Zainol et al., 2012).

2.5 Surfactant

The term surfactant is known as a combination of ''Surface Active Agent'' (Kume et al., 2008). The surfactants can be described as a substance that can modify the surface characteristics of solids surface and therefore, create sorbents that immobilize other compounds (Karapanagioti et al., 2005). Typically, the surfactant molecule has a hydrophilic (water-loving) head and a long hydrophobic (water-hating) tail (Morsy, 2014).

Surfactant can be categorized according to the nature of the chain-carrying part of their molecular structure named as anionic which possess a negatively charged, cationic that possess a positively charged, nonionic which is uncharged and amphoteric surfactant that presents both positively and negatively charged at an intermediate pH (Widiastuti et al., 2008; Kume et al., 2008). According to Wang and Peng, (2010), an acid/base treatment and surfactant impregnation are usually practiced by ion exchange, particularly zeolite in order to change the hydrophilic or hydrophobic properties for the adsorption of miscellaneous ions or organics.

The surfactant concentration at or below its critical micelle concentration (CMC), a monolayer or 'hemimicelle' molecules are formed at the solid–aqueous interface through the strong Coulombic interaction (Wang and Peng, 2010). However, when the surfactant concentration is above the CMC, the surfactant molecules in solution will form a bilayer or 'admicelle'. As a result, the surfactant will be exposed to a negatively charged solid surface for example zeolite thus, reversed the charge on the solid surface from negatively charge to positively charge (Chutia et al., 2009). Based on the reversal of charge, the total surfactant sorption capacity (SSC) of a zeolite becomes roughly double of the external cation exchange capacity (ECEC) (Colella, 2007).

2.5.1 Anionic Surfactant

Anionic surfactant include alkylbenzene sulfonates (detergents), (fatty acid) soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent) and lignosulfonates (dispersants) (Salager, 2002). As for the household industry, the most common anionic surfactant is the one that contains with the sulphonate, sulphate or carboxylate (soap) group attached to them (Kume et al., 2008).

According to Widiastuti et al., (2008), linear alkylate sulfonate or linear alkylbenzenesulfonate (LAS) is the most common anionic surfactant found in laundry detergents due to their very interesting foaming characteristics that can be controlled easily by foam inhibitors, low prices, well formulated in all-purpose surfactant formulas, biodegraded and easily analysed.

2.5.2 Cationic Surfactant

Cationic surfactant is typically soaps or detergents, in which the hydrophilic or water-loving, end contains a positively charged ion or cation. Some of the examples of the cationic surfactants are as shown in Table 2.4.

Table 2.4 Examples of cationic surfactants (Wang and Peng, 2010; Colella, 2007)

No.	Cationic Surfactants
1	Hexadecyltrimethylammonium (HDTMA)
2	Tetramethylammonium
3	Cetyltrimethylammonium (CTMA)
4	Octadecyldimethylbenzyl ammonium (ODMBA)
5	Benzyltetradecyl ammonium (BDTDA)
6	N-cetylpyridinium (CPD)
7	Stearyldimethylbenzylammonium (SDBAC)
8	Dodecyltrimethylammonium (DDTMA+)
9	Akylbenzyldimethylammonium (ABDMA+)
10	Stearylbenzyldimethylammonium (SBDMA+)
11	Hexadecylpyridinium (HDP+)
12	Dioctadecyldimethylammonium (DODDA+)