Musa acuminata BASED ACTIVATED CARBON INCORPORATED WITH IRON OXIDE NANOPARTICLES AS ADSORBENTS IN LANDFILL LEACHATE TREATMENT

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By

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ANOVA	Analysis of Variance
AOP	Advance Oxidation Process
ANOVA	Analysis of Variance
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
BBD	Box-Behnken Design
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BOD	Biochemical Oxygen Demand
BPS	Banana Pseudo-Stem
BTC	Breakthrough Curve
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
COD	Chemical Oxygen Demand
CCRD	Central Composite Rotatable Design
DO	Dissolved Oxygen
DOM	Dissolved Organic Matter
DOC	Dissolved Organic Content
EBCT	Empty Bed Contact Time
EC	Electro-coagulation
EF	Electro-floatation
EO	Electro-oxidation
EDX	Energy Dispersive X-ray

FAs	Fatty Acids
FC	Fixed Carbon
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
GAC	Granular Activated Carbon
HA	Humic Acid
HS	Humic Substances
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IN	Iodine Number
IOAC	Iron Oxide-Activated Carbon
IONPs	Iron Oxide Nanoparticles
IPD	Intra Particle Diffusion
IR	Impregnation Ratio
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene Blue
MF	Microfiltration
MO	Methyl Orange
MLS	Matang Landfill Site
MSW	Municipal Solid Waste
MTZ	Mass Transfer Zone
NF	Nanofiltration
NMs	Nanomaterials
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Unit
PAC	Powdered Activated Carbon

PAHs	Polycyclic Aromatic Hydrocarbons
PFO	Pseudo First Order
PSO	Pseudo Second Order
PZC	Point of Zero Charge
RBC	Rotating Biological Contactor
RMSE	Root Mean Square Error
RO	Reverse Osmosis
RSM	Response Surface Methodology
SB	Sugarcane Bagasse
SDS	Sodium Dodecyl Sulphate
SEM	Scanning Electron Microscope
SBR	Sequencing Batch Reactors
SS	Suspended Solid
SUVA	Specific UV Absorbance
UF	Ultra Filtration
UV_{254}	UV Absorbance at Wavelength of 254 nm
XRD	X-ray Diffraction
TEM	Transmission Electron Microscopy
TOC	Total Organic Carbon
TSS	Total Suspended Solid
VFAs	Volatile Fatty Acids
VM	Volatile Matter
XOCs	Xenobiotic Organic Compounds

LIST OF SYMBOLS

q_e	Amount adsorbate at equilibrium (mg/g)
q_t	amount adsorbate at time(mg/g)
q_m	Monolayer capacity of the adsorbent (mg/g)
q_s	Theoretical saturation capacity (mg/g)
t	Time (min)
b	Langmuir adsorption equilibrium constant (L/mg)
k_1	PFO rate constant (1/min)
k_2	PSO rate constant (g/mg.min)
k_{ID}	IPD rate constant (mg/g/min$^{0.5}$)
C_i	Thickness of boundary layer (mg/g)
C_e	Equilibrium concentration (mg/L)
C_o	Initial concentration (mg/L)
C_t	Concentration at time (mg/L)
R_L	Separation factor
n	Adsorption intensity
K_F	Constant relating the adsorption capacity (L/g)
K_T	Temkin equilibrium binding constant (L/g)
b_T	Temkin isotherm constant (mg/L)
R	Gas constant (8.314 J/mol.k)
T	Absolute temperature (K)
B	Constant related to adsorption energy (mol^{2}k/J^2)
k_{ad}	Adsorption equilibrium constant
k_D	Adsorption equilibrium constant (l/g)

E	Free energy (kJ/mol)
ε	Polanyi potential
$\Delta G°$	Free energy (kJ/mol)
$\Delta S°$	Change in entropy (kJ/mol)
$\Delta H°$	Change in enthalpy (J/mol.K)
A	The area below the BTC
T_{total}	The total flow time (min)
Q	The flow rate (mL/min)
N_o	Saturation concentration (mg/L)
Z	Bed depth (cm)
F	Ratio of the Q to the column sectional area
k_{AB}	Adam-Bohart rate constant (L/mg min)
k_{Th}	Thomas rate constant (L/mg min)
Q_o	Maximum solid-phase concentration of solute (mg/g)
M	The amount of sorbent (g)
F	The flow rate (mL/min)
k_{YN}	Yoon and Nelson rate constant (1/min)
τ	Time required 50% adsorbate breakthrough (min)
%R	Percentage removal

KARBON TERAKTIF BERASASKAN *Musa acuminata* DIGABUNGKAN DENGAN PARTIKEL-NANO BESI OKSIDA SEBAGAI PENJERAP DALAM RAWATAN LARUT RESAP TAPAK PELUPUSAN

ABSTRAK

Kajian ini dijalankan untuk mengkaji keberkesanan karbon teraktif (AC) yang dihasilkan daripada batang-pseudo pisang, besi oksida (IONPs) bersama dengan nanokompositnya iaitu besi oksida-carbon teraktif (IOAC) untuk merawat larut resap tapak perlupusan. Penyediaan AC dijalankan melalui pengaktifan menggunakan zink klorida ($ZnCl_2$) manakala IONPs dan IOAC disediakan terus melalui process penurunan oleh sodium borohidrat ($NaBH_4$). Keadaan optimum penyediaan AC yang diperolehi melalui kaedah gerak balas permukaan (RSM) adalah pada suhu pengaktifan 760 °C 5±, masa pengaktifan 90 minit dan nisbah pemadatan 1:4.5 g/g. Luas permukaan BET bagi AC, IOAC dan IONPs masing-masing adalah 1329 m^2/g, 1173 m^2/g and 140 m^2/g. Imej SEM yang diperolehi menunjukkan bahawa AC mempunyai ciri-ciri permukaan yang baik dan struktur liang-meso yang berkembang baik. Hasil kajian juga menunjukkan IONPs telah berjaya digabungkan pada permukaan dan liang AC dan memperkenalkan partikel bersaiz nanometer dalam penghasilan nanokomposit IOAC. Kajian kinetik, isoterma dan termodinamik penjerapan telah dibangunkan untuk merekabentuk model untuk rawatan larut resap. Keputusan kajian termodinamik menunjukkan bahawa kesemua proses penjerapan semasa rawatan larut resap tapak perlupusan adalah endotermik dan secara spontan. Sistem penjerapan menepati pseudo-tertib kedua (PSO) berbanding dengan pseudo-tertib pertama (PFO). Data keseimbangan mematuhi dengan baik isoterma Langmuir,

Freundlich, Temkin dan Dubinin–Radushkevich. Berdasarkan pada penjerapan maksima monolapisan daripada isoterma Langmuir, susunan keberkesanan telah dikenal pasti sebagai IOAC > IOAC > IONPs. Hasil kajian daripada proses penjerapan berterusan melalui kolum lapisan tetap menunjukkan bahawa ketinggi dasar yang lebih besar memberikan peratusan penyingkiran COD, DOC, color and UV_{254} yang tinggi. Peratus penyingkiran juga meningkat apabila kadar aliran dan juga kepekatan influen dikurangkan. Keadaan penjerapan yang terbaik telah ditentukan pada ketinggian dasar 12.5 cm, kadar aliran 7.5 mL/min dan kepekatan larut resap yang dicairkan sebanyak dua kali. Model penjerapan dinamik menunjukkan bahawa model Thomas dan Yoon–Nelson disahkan untuk keseluruhan julat operasi manakala Adam-Bohart hanya terpakai pada permulaan operasi (C_t/C_0 < 0.5). Keputusan dari kajian ini mencadangkan bahawa IOAC boleh menjadi penjerap yang berdaya maju dalam mengurus masalah bahan organik yang tinggi yang berkaitan dengan larutan resap tapak perlupusan.

***Musa acuminata* BASED ACTIVATED CARBON INCORPORATED WITH IRON OXIDE NANOPARTICLES AS ADSORBENT IN LANDFILL LEACHATE TREATMENT**

ABSTRACT

The study was conducted to investigate the effectiveness of activated carbon (AC) derived from banana pseudo-stem (BPS), iron oxide nanoparticle (IONPs) together with their nanocomposite iron oxide-activated carbon (IOAC) adsorbent for treatment of landfill leachate. The preparation of AC was performed with $ZnCl_2$ activation while IONPs and IOAC were directly prepared via sodium borohydride ($NaBH_4$) reduction method. The optimum conditions for the preparation of AC obtained by the Design of Experiments (DOE) were at 760 °C ±5 °C activation temperature, 90 min activation time and 1:4.5 g/g impregnation ratio. The BET surface area of the prepared AC, IOAC and IONPs were 1329 m^2/g, 1173 m^2/g and 140 m^2/g respectively. The obtained SEM image of AC shown an excellent surface characteristic and well developed mesoporous structure. The results also proved that the IONPs were successfully deposited onto the surface and pores of the AC and induce a nanometer particle size of IONPs in order to produce IOAC nanocomposite. Adsorption kinetics, isotherm, and thermodynamic studies were developed to design the model for leachate treatment. The thermodynamic results showed that the overall adsorption process during treatment of landfill leachate was endothermic and spontaneous. The adsorption system agreed well with the pseudo-second-order kinetic model (PSO) as compared with the pseudo-first-order (PFO) model. The equilibrium data were fitted well with Langmuir, Freundlich, Temkin and Dubinin-Raduskevich isotherms. Based on the maximum monolayer adsorption from Langmuir isotherm, the order of effectiveness

was identified as IOAC > AC > IONPs. Results from continuous fixed-bed column adsorption study showed that the greater the adsorbent bed height resulted in higher percentage removal of COD DOC, color and UV_{254} . The percentage removal also improved visibly as the decreased in inlet flow rate and influent concentration. The best adsorption conditions determined in bed height of 12.5 cm, inlet flow rate of 7.5 mL/min and concentration of landfill leachate with two times dilution. The dynamic adsorption models showed that Thomas and Yoon–Nelson models were valid for the entire range of operation while Adam-Bohart model was applicable only during the initial period of operation ($C_t/C_0 < 0.5$). The results from this study suggested that IOAC could be a viable adsorbent in managing higher organic matter problems associated with landfill leachate.

CHAPTER ONE

INTRODUCTION

1.1 Background Study

Malaysia is a tropical country and also known as a middle-income economy and located in the middle of South-east Asia. Malaysia is expected to become a developed country as early as the year 2020. It was identified that tremendous increasing population and urbanization growth and several other factors influence the municipal solid waste (MSW) generation directly in Malaysia (Tarmudi et al., 2009). According to Vithanage et al. (2014), solid waste is generated by three primary sources: (i) domestic solid waste, (ii) commercial solid waste and (iii) industrial solid waste.

Johari et al. (2012) claimed that the management of solid waste continues to be a significant challenge in urban areas throughout the world, particularly in the rapidly growing cities and towns of the developing countries. In 2003, the average amount of MSW generated in Malaysia was 0.5–0.8 kg/person/day; it has increased to 1.7 kg/person/day in main major cities (Kathirvale et al., 2004). In 2007, with a population of over 25 million, Malaysian households produced nearly 18,000 tons of household waste daily (Moh et al., 2017). By the year 2020, the quantity of MSW produced was estimated to increase up to 31,000 tons (Manaf et al., 2009). Unfortunately, by the year 2012, there are 33,000 tons of MSW was produced by Malaysians per day, as stated by Moh et al. (2017).

Presently landfilling is the most extensively employed method for MSW disposal system in Malaysia. Fazeli et al. (2016) claimed that the most dominant waste disposal method in Malaysia is unsanitary landfilling. Around 80% of the collected

MSW in Malaysia is landfilled, whereas most of the dumpsites are open, unsanitary, and over-loaded incapacity. Nowadays, there are more than one hundred of landfills that are still operating. In the year 2001, there are 155 operational landfills identified in west Malaysia (Manaf et al., 2009), but the number had increased to 161 in 2002, and continuously increased to 176 in 2007 (Fazeli et al., 2016). However, in 2012, the Ministry of Urban Wellbeing, Housing and Local Government, reported on 165 operational landfills that service 95% of Malaysia's total waste disposal with only 8 of them sanitary and 11 under different extends of construction (Johari et al., 2012).

Although landfilling offered solution for MSW, the problem associated with landfilling cannot be denied. Butt et al. (2014) clearly highlighted the problems associated with MSW, production of greenhouse gases (carbon dioxide, CO_2 and methane, CH_4) and generation of wastewater known as leachate. Unlike landfill gas and (more or less) degraded landfill waste, by its nature, landfill leachate specifically can pollute all of the three aforesaid principal factors. Landfill leachate contains organic and inorganic pollutants, including ammonia, heavy metals, humic substance (HS), persistent synthetic organic pollutants and inorganic salts of high concentration as described in Section 2.4.

Referring to Butt et al. (2014), they did mention several problems exist in term of collected, treated and discharged of the leachate safely. Believed that landfill leachate has a great potential to (either directly or indirectly) pollute lithosphere (land/ soils), atmosphere (air), hydrosphere (water), and even any combination of these must appropriately be encountered. These three fundamental constituents of the environment are also the main media of contaminants transport. Therefore, the more intensive and comprehensive study must be done to solve this kind of problems.

The term “nano” is derived from the Greek word for “dwarf”. A nanometer (nm), from Greek “nanos” for “dwarf” is equal to one billionth of a meter or 10^{-9} of a meter (Vunain et al., 2016). According to Ali (2012) and Vunain et al. (2016), the particles having at least one dimension and a size ranging from 1 to 100 nm are called nanoparticles (NPs). While Vunain et al. (2016) stated that the nanotechnology could be defined as the art of science that involve manipulating of nanoparticles. One of the promising and well-developed environmental applications of nanotechnology has been in the water and wastewater treatment. Variety of nanomaterials being utilized to help purify water through various mechanisms such as adsorption and sequestration of heavy-metal ions and other pollutants, removal and inactivation of pathogens, and finally the transformation of toxic materials into less toxic compounds.

1.2 Problem Statement

Leachate is a liquid generated from landfilling activity and can be an enormously powerful pollutant for surface and groundwater. According to Rivas et al. (2006), leachate from landfills can be a major hazard to health and environment if the landfill is not operated correctly and taken care. This leachate potentially migrates into the ground and significantly contaminate the groundwater system (Kanmani and Gandhimathi, 2013). In addition, Sivula et al. (2012) claimed that moving of leachate into the nearby underground water supplies with all the negative consequences will give bad implication in the treatment process which produces water that would be incompatible with the standards for drinking water quality set by the governments or by international standards. Previously, Kjeldsen et al. (2002) and Zolfaghari et al. (2016a) have identified four groups of pollutants contained in leachate: (i) inorganic macro components (ii) heavy metals, (iii) dissolved organic matter, (iii) xenobiotic organic compounds.

Furthermore, Foo and Hameed (2009) claimed that around 100 over toxic and hazardous compounds had been identified in landfill leachate. In addition, landfill leachate also contains a high composition of recalcitrant organic matter such as humic acid (HA) and fulvic acid (FA) (Chys et al., 2015). Ibrahim et al. (2017) mentioned that the dark brown, grey or black are the colors produced by the presence HAs while light yellow, yellow and brown are the colors attributed by FAs. Releasing of the mentioned compounds into the environment will directly give impact to the survival of aquatic life form, ecology and food chains.

Various methods have been used for the treatment of landfill leachate such as biological (e.g., aerated lagoon, activated sludge, aerobic and anaerobic treatment) and physicochemical treatment (e.g., coagulation/flocculation, chemical oxidation, membrane filtration, air floatation and adsorption. Among these various methods, adsorption is also a well-recognized means of leachate treatment. Iron oxide is one of the famous examples of metal oxide used as an adsorbent. Tang and Lo (2013) claimed that the adsorption ability of the iron oxides arises from the surface hydroxyl groups' intervention during dissociative chemisorption of the adsorbate (pollutants). Recently, iron oxide in the range of nanoparticles (size less than 100 nm) have been widely used in environmental applications and have shown promising performance in pollutants removal or toxicity mitigation. However, these applications require nanomaterials of a specific size, shape, surface characteristics and, in some cases utilize the magnetic properties of iron oxide (Xu et al., 2012; Tang and Lo, 2013).

Generally, iron oxides exist in the environment with diverse forms. Goethite has been the iron oxide most studied by its highest thermodynamic stability.

Substituted goethite is interesting due to its adsorption properties, able to be modified by the presence of a foreign ion. Interestingly, the magnetic properties of magnetite particles allow the fast-magnetic separation of metal ions from industrial effluent and nuclear waste stream. Hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) are the most common species of iron oxide as reported by Xu et al. (2012).

Over the past few years, the synthesis and utilization of iron oxide nanomaterials with novel properties and functions have been widely studied, due to their nanoscale size, high surface area to volume ratios and super-paramagnetism (Xu et al., 2012). However, because of these properties, the naked iron oxides nanoparticles tend to agglomerate due to inter-particle magnetic and Van der Waals interactions. Agglomeration increases the effective particle size; reduce surface area resulting in precipitation. Therefore, supported NPs on AC has been regarded as an effective approach to overcome the related problem (Gonçalves et al., 2013; Castelló et al., 2015). Furthermore, previous literature reported by Raizada et al. (2014), He et al. (2016) and Mohammed et al. (2016) also stated that finely sized nanoparticles are difficult to separate from treated water. They suggested that hybrid materials composed of iron oxide NPs onto the AC potentially could overcome this limitation.

Previous research studies recognized that AC demonstrated to be the most cost-effective for the sorption of pollutants from landfill leachate (Foo and Hameed, 2009; Aziz et al., 2012; Foo et al., 2013b; Azmi et al., 2015). Recently, the preparations of ACs by using low-cost precursor from agriculture waste have been employed extensively as a new precursor in the production of ACs. The abundance and continuous availability of the biomasses are the main reason. However, to the best of our knowledge, very limited investigations have utilized banana pseudo-stem (BPS) as a precursor to prepare AC.

In tropical countries such as Malaysia, the harvesting activity of banana left behind a large amount of residue because each plant produces only one bunch of bananas in a lifetime. It has been estimated that 220 tons per hectare of BPS have produced annually (Ahmad and Danish, 2018). This undoubtedly causes disposal issues, which can lead to severe environmental pollution. BPS is known as biodegradable material and composed of concentric layers of leaf sheaths. BPS considered as the main residual wastes of the banana crop. Traditionally, crop residue such as BPS is left lying around on the ground, and it will undergo biodegradation process over a long period. In addition, the huge biodegradation number of crop residue is becoming more challenging due to its of time-consuming and most probably incomplete conversion of biomass. Thus, the open burning of agricultural residues is still a very common practice for the farmers. It is well known that the impact of open burning on heavy haze formation gives a significant impact on atmospheric chemistry, global climate change and also to human health (Othman et al., 2014; Sahani et al., 2014; Ahmed et al., 2016). Hence, in this study, BPS has been selected as a precursor to produce AC due to its abundance, low-cost, excellent properties and special structure.

Normally, AC can be prepared either by physical or chemical activation. According to Vargas et al. (2011), the most studied chemical activation parameters are types of activating agent, time, temperature, and impregnation ratio (IR) (activating agent/precursor). Thus, it is important to study the production of AC and focus on the effects of the mentioned parameters. Conventionally, optimization was carried out by varying a single factor at a time while keeping the others constant. This approach is not only time and energy-consuming, but also usually incapable of achieving the accurate optimum because of the ignoring interactions among preparation parameters.

However, the main advantage of using response surface methodology (RSM) as an optimization tool is to reduce the number of experimental runs needed and provide sufficient information for statistically acceptable results. Therefore, it is less laborious and time-consuming in comparison with full factorial experimentation studies

There are numerous studies performed on adsorptive removal of pollutants by a variety of adsorbent. The performance evaluation mostly based on the removal of artificial pollutants. However, the study on the possible synergistic effect of the adsorbent toward real sample such as landfill leachate treatment was very limited. Although many aspects of adsorption conditions have been discussed previously, the application on landfill leachate treatment performance has not been given significant consideration. Based on the above scenario explained, it is believed that the preparation of new adsorbent that directly applies to treat leachate requires a more in-depth understanding. Extensive investigations should be done for their possible application on landfill leachate treatment in existing sites. Therefore, this study serves to explore the treatment of landfill leachate by adsorption and comparing the effectiveness of three new adsorbents which are AC, IOAC and IONPs in the removal of COD, color, DOC and UV_{254} in landfill leachate.

1.3 Objectives of Study

This research aims to investigate the effectiveness of activated carbon (AC), iron oxide nanoparticles (IONPs) and iron oxide-activated carbon (IOAC) nanocomposite adsorbents for landfill leachate treatment. The main objectives of this study were:

1. To synthesis AC from banana pseudo-stem via zinc chloride ($ZnCl_2$) activation method and optimization with response surface methodology (RSM).

2. To establish the physicochemical characterizations of the prepared adsorbent (AC, IONPs and IOAC nanocomposite) in terms of surface area, surface morphology and surface chemistry.
3. To determine the effectiveness of the prepared adsorbents based on isotherms, kinetics and thermodynamic study in term of adsorptive removal of COD, DOC, color and UV_{254} in landfill leachate.
4. To evaluate the adsorption performance of IOAC nanocomposite in continuous flow adsorption study under different operating conditions (adsorbent bed height, feed flow rate and initial inlet concentration).
5. To analyze the continuous flow adsorption study experimental data with several dynamic adsorption models such as Adam–Bohart, Thomas as well as Yoon and Nelson model.

1.4 Scope of Work

In this research, three new adsorbents, namely AC derived from BPS, IONPs and IOAC nanocomposite were employed in landfill leachate treatment. The effectiveness of the prepared adsorbents was verified with several necessary comparisons. This study was focused on several aspects, as follows:

1. The AC was prepared from BPS and optimized by a response surface methodology (RSM) design known as Box-Behnken design (BBD). Three different independent factors selected were activation temperature (400 to 800 °C, activation time (30 to 90 min) and impregnation ratios (1:1 to 1:5).
2. The characterizations of the prepared adsorbents (AC, IONPs and IOAC nanocomposite) were established by using several instrumentals analyses such as nitrogen gas adsorption analyzer for surface area, scanning electron

microscope (SEM) for surface morphology and the surface chemistry by using FTIR spectroscopy analysis.

3. The effectiveness of the prepared adsorbents was determined based on batch adsorption study in term of adsorptive removal of COD, DOC, color and UV_{254} in landfill leachate. The experimental data were further analyzed with four adsorption isotherms, namely Langmuir, Freundlich, Temkin and Dubinin Raduskkevich. While the adsorption kinetics were fitted with pseudo-first-order (PFO), pseudo-second-order (PSO) and intraparticle diffusion (IPD) model. The thermodynamic analyses were performed at the temperature from 25-40 °C.
4. The performance of IOAC nanocomposite was further evaluated by continuous flow adsorption study under different operating conditions such as adsorbent bed height (7.5-12.5 cm), inlet flow rate (7.5-12.5 mL/min) and different initial inlet concentration (dilution). Finally, the data obtained from continuous flow adsorption were fitted with three dynamic adsorption models (Adam–Bohart, Thomas as well as Yoon and Nelson model).

1.5 Organization of Thesis

The thesis consists of five main chapters. Chapter One gives the introductory of this research project. It presents an overview of the leachate pollution in Malaysia. The need for leachate treatment and management. This chapter also consists of the problem statement, objectives of the study and the organization of the thesis are summarized in the last section of this chapter.

Chapter Two presents the literature review which covered the general information of landfill leachate, including the generation of leachate, composition and followed by landfill leachate treatment methods. In addition, this chapter also provides information on adsorbent preparation parameters and the adsorption operating condition. Furthermore, batch adsorption study, including adsorption isotherm, adsorption kinetic and thermodynamic, were also reviewed. At the end of the chapter, describe the fixed bed adsorption in term of adsorption parameters, dynamic adsorption model, error of analysis and followed by a summary of the literature review.

Chapter Three describes a detailed methodology of the present study to achieve the objectives of the study. The experimental work consists of sample collection and preparation, adsorbents preparation and characterization, batch adsorption study and continuous flow adsorption study. This chapter ended with the schematic flow diagram showing the overall carried out throughout the research.

Chapter Four consist of results and discussions. This chapter reported the findings obtained from the experimental studies. This chapter is divided into several sections including preparation and characterization of landfill leachate and adsorbent used, batch adsorption performance of prepared adsorbent including adsorption isotherm, kinetic and thermodynamic studies. This chapter also discussed the performance of fixed-bed column study and modelling the breakthrough curve (BTCs) into several models. Chapter Five is the last chapter in the thesis, which consists of conclusions and recommendations. This chapter presents the conclusion for the obtained findings. Several recommendations for the future study also included in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview of Solid Waste Management in Malaysia

Most of the existing solid waste landfill sites in developing countries are practising, either open dumping or controlled dumping (Chong et al., 2005). Sanitary landfill is the most common disposal method for municipal solid wastes (MSW). Solid waste management is the biggest environmental issue in Malaysia, highly dependent on landfilling as the main disposal method in managing this continuous increase of solid waste generation annually (Moh et al., 2017). A typical solid waste management system in developing countries such as Malaysia deals with improper collection services such as irregular collection services and low collection coverage. Moh et al. (2017) also noted that several countries are facing the unsustainable disposal of solid waste without air and water pollution control, including open burning and open dumping. Besides that, scavenging activities and consequences of illegal dumping may contribute to the breeding of flies and vermin also part of the main problem with solid waste management.

Figure 2.1 illustrates the MSW generation by states in Peninsular Malaysia based on year. It was observed that Malaysian solid waste contains a higher concentration of organic waste and consequently has high moisture content and a bulk density above 200 kg/m^3. A waste characterization reported by Fazeli et al. (2016) found that the main components of Malaysian waste were organic, paper, and plastic, which comprise 80% of overall weight. Whereas Figure 2.2 illustrates the waste composition in Malaysia from 1980 to 2005. These characteristics reflect the nature and lifestyle of the Malaysian population (Manaf et al., 2009).

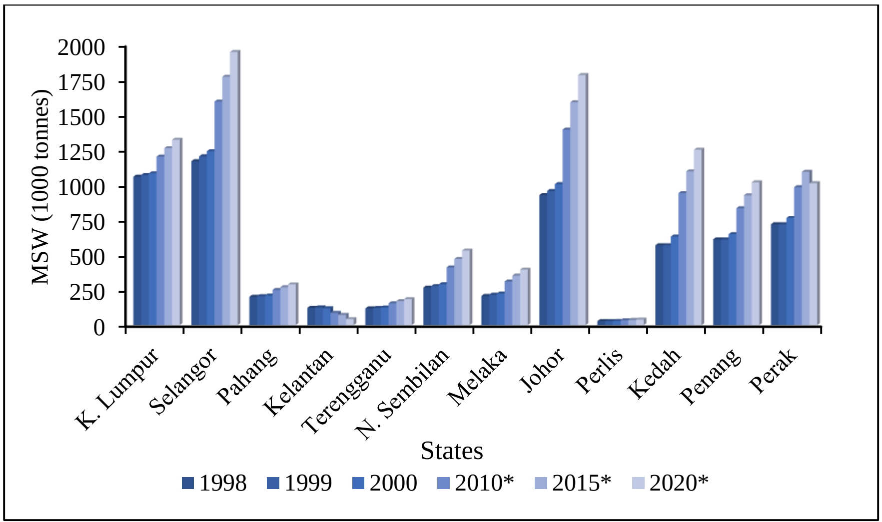

Figure 2.1 MSW generation by states in Peninsular Malaysia in thousand tonnes. Source: Johari et al. (2012). (Note: *based on prediction)

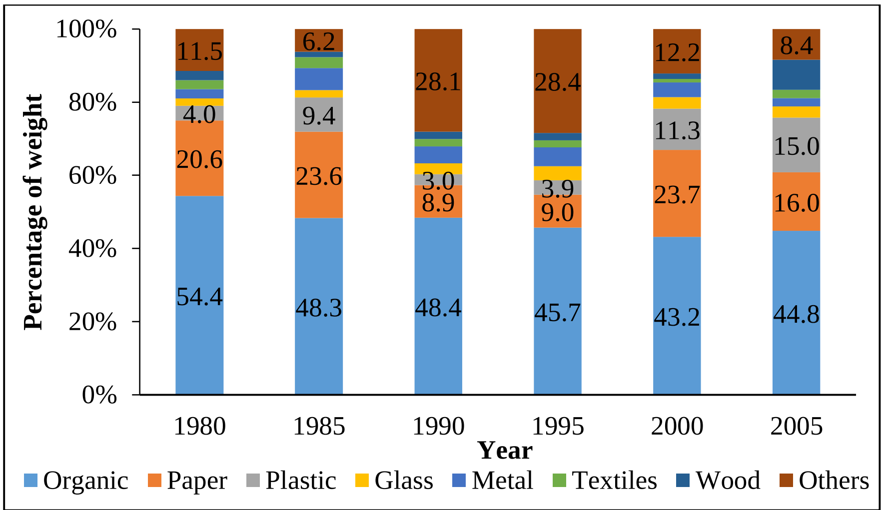

Figure 2.2 Waste composition in Malaysia from 1980 to 2005. Source: Fazeli et al. (2016)

2.2 Types of Landfill

Referring to Vithanage et al. (2014), landfill considered as one of the most environmentally friendly and cheapest means of waste disposal; it is also the main MSW disposal means in Malaysia. Therefore, Malaysia government should encourage and indulge in sustainable landfill management. Table 2:1 shows level classifications of landfill sites in Malaysia. Basically, the classification of a landfills based on the decomposition processes: (1) anaerobic landfill, (2) anaerobic sanitary landfill with daily cover, (3) improved aerobic sanitary landfill with buried leachate collection pipes, (4) semi-aerobic landfill with natural ventilation and leachate collection facilities and (5) aerobic landfill with forced aeration.

Table 2:1 Classification of landfill sites in Malaysia.

Levels		Available facilities
I	Controlled dumping	Minimum infrastructure (fencing and perimeter drains)
II	Sanitary landfill with daily cover	Class I facilities (with gas removal system, separate unloading and working area, daily cover and enclosing bund (divider constructed as the embankment of different waste cells) Elimination of informal scavenging and provision of environmental protection facilities.
III	Sanitary landfill with leachate circulation	Class II facilities (with leachate recirculation system allowing the collection, recirculation and monitoring of landfill leachate)
IV	Sanitary landfill with leachate treatment	Class III facilities (with leachate treatment system)

Source: Moh et al. (2017)

2.3 Formation of Landfill Leachate

It is important to understand the definition of landfill leachate before we go deeper into the generation process of leachate. According to Renou et al. (2008), landfill leachate is generated as a compound produced in the biodegradation of waste and is a product of both the rainwater as it percolates through waste and the inherent water of the waste itself. In addition, Aziz et al. (2010) defined the landfill leachate as a liquid formed primarily by the percolation of precipitation water through an open landfill or the cap of a completed site. Landfill leachate contains large amounts of organic contaminants measured as COD, BOD_5, NH_3-N, halogenated hydrocarbons, suspended solid, significant concentration of inorganic salts together with heavy metals (Uygur and Kargı, 2004; Renou et al., 2008).

Moreover, the leachate also rich in phenol, nitrogen and phosphorus-based compounds. Previous researchers clearly noticed that landfill leachate is one of the main sources of groundwater and surface water pollution if it is not properly collected, treated and safely disposed of as it may percolate through the soil and reaching water aquifers (Tatsi et al., 2003; Abd El-Salam and I. Abu-Zuid, 2015). In Malaysia, the risks of the landfill leachate on the natural environment are determined by comparing leachate quality with Malaysian standards (Quality, 2009) as suggested by Aziz et al. (2010).

In general, the principal of waste decomposition process is likely to occur in five different phases which are hydrolysis, acidogenesis, acetogenesis, methanogenesis and stabilization as illustrated in Figure 2.3. Based on the figure, the decomposition process of the phases depends on the availability of organic components, nutrients, waste moisture content and the degree of initial compaction in the landfill (Sang et al., 2012). In fact, the waste decomposition processes occurred as soon as the waste had been filled in the landfill.

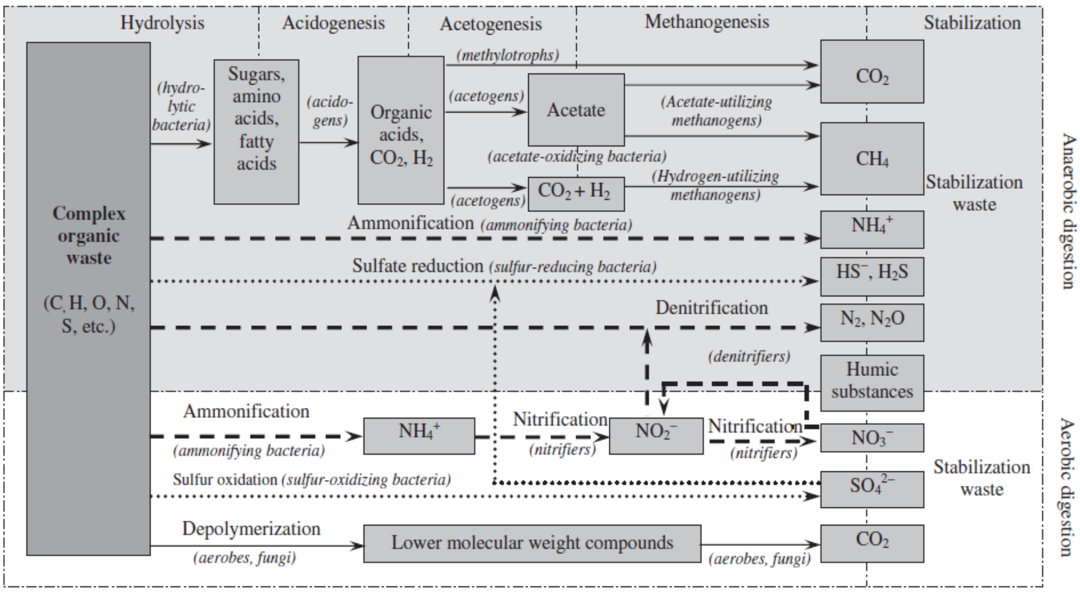

Figure 2.3 Schematic diagram of MSW decomposition in a landfill.
Source: Sang et al. (2012)

2.4 Physicochemical Properties of Landfill Leachate

Landfill leachate composition and characteristic varies significantly among landfills depending on waste age, waste composition, as well as landfilling technology (Kjeldsen et al., 2002; Naveen et al., 2017). The characteristics of the generated liquid from a landfill depends on a host of diverse factors. Primarily the physicochemical changes of landfill leachate depend on the phase degradation of the waste in a landfill, which follow an order of time. These characteristics also depend upon the landfill methods, composition, characteristics and age of the disposed waste, regional and seasonal variations and filling techniques (filling height, density, stabilization and pre-treatment, leachate collection system and the linings used for the landfill). According to the previous study reported by Liu et al. (2015), Zolfaghari et al. (2016b) and Ghosh et al. (2017), the dissolved compounds in landfill leachate comprised of: (i) dissolved organic matter, (ii) inorganic macro components, (iii) heavy metals and (iv) xenobiotic organic compounds. Moreover, Garaj-Vrhovac et al. (2013) noted that various interactions between the mentioned compounds could have additive and synergistic effects on the toxicity of the leachate.

2.4.1 Dissolved Organic Matter (DOM)

Several kinds of literature published by Kang et al. (2002), Bilgili et al. (2008), Huo et al. (2008) and Liu et al. (2015) claimed that DOM plays a significant geochemical as well as biochemical role in the landfill system and interacts with several inorganic and organic pollutants. In addition, He et al. (2006) stated that DOM is the main category of polluting compounds in landfill leachate components. Total organic carbon (TOC) and refractory compounds of HS are among the main parameters of DOM in leachate. COD, BOD and HS are fundamentals quality parameters in leachate quality assessment. COD and BOD in leachate are measured through the oxygen demand measurement. The measurement of both COD and BOD amount is important in classifying the leachate condition. Comstock et al. (2010) stated that landfill leachate normally classified as fresh, intermediate and stabilized based on the value of BOD_5/COD ratio which is more than 0.5, within 0.1 to 0.5 and less than 0.1 respectively. In fact, this classification is important to be used as a reference for leachate treatment facility design, as claimed by Mojiri et al. (2014).

Other than that, humic substances are another important element of DOM concentration. Humic substances can be defined as complex dissolved organic products that consist of HAs and FAs. Humic substances are the non-biodegradable compound that remains abundant in leachate, and the HAs molecule proposed by Bhatnagar and Sillanpää (2017) as illustrated in Figure 2.4.

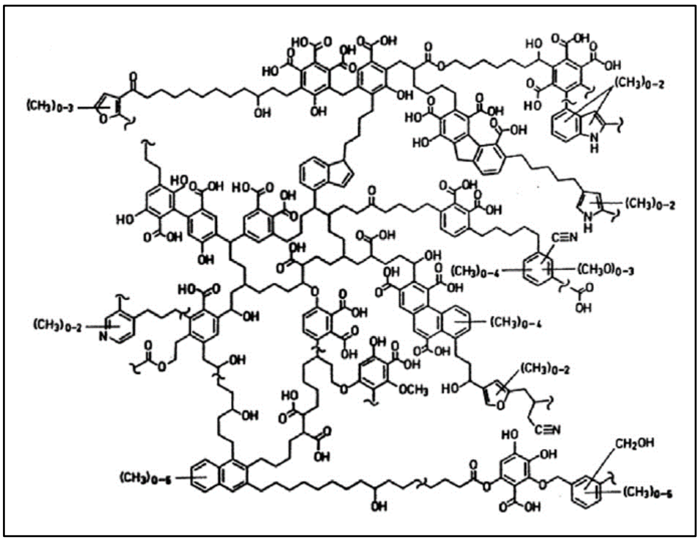

Figure 2.4 A proposed structure of the humic acid molecule.
Source: Bhatnagar and Sillanpää (2017).

HAs are insoluble under acidic conditions but soluble at higher pH, whereas FAs are soluble under both acid and alkaline conditions (Schellekens et al., 2017). Moreover, Zouboulis et al. (2003) claimed that a higher concentration of humic substances renders leachate to appear brown or even black in color. This color appearance reflects the concentration of the humic substances and the level of pollution in the landfill leachate. Basically, there are several analytical methods that are commonly used to characterize both whole water samples of DOM and DOM isolates including DOM, TOC, DOC, ultraviolet absorbance at 254 nm (UV_{254}), and specific UV absorbance (SUVA).

2.4.2 Heavy Metals

The primary sources of heavy metals in landfills are due to the co-disposed of mine wastes, industrial wastes, incinerator ashes and household hazardous substances such as batteries, paints, dyes and inks (Kanmani and Gandhimathi, 2013). Several researchers had identified variety of heavy metal components that are commonly found in landfill leachate such as cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), Iron (Fe), manganese, (Mn) and zinc (Zn) (Aziz et al., 2010; Modin et al., 2011; Abd El-Salam and I. Abu-Zuid, 2015; Shehzad et al., 2015; Moody and Townsend, 2017; Naveen et al., 2017). In fact, the presence of heavy metals in landfill leachate is attributed to acetogenic (acidic condition) decomposition phase.

In consequence, the concentration of heavy metals elements is relatively low for matured landfill leachate (basic condition). Basically, during the methanogenic phase, heavy metals are insoluble and remain at low concentrations (less than 2 mg/L). The positive effect of pH on the distribution of heavy metals in landfill leachate was further demonstrated by Xie et al. (2015). The authors claimed that the pH is one of the most significant contributing factors to metal speciation and distribution in landfill leachate. Xie et al. (2015) also recommended the mechanism of heavy metal distribution in landfill as illustrated in Figure 2.5.

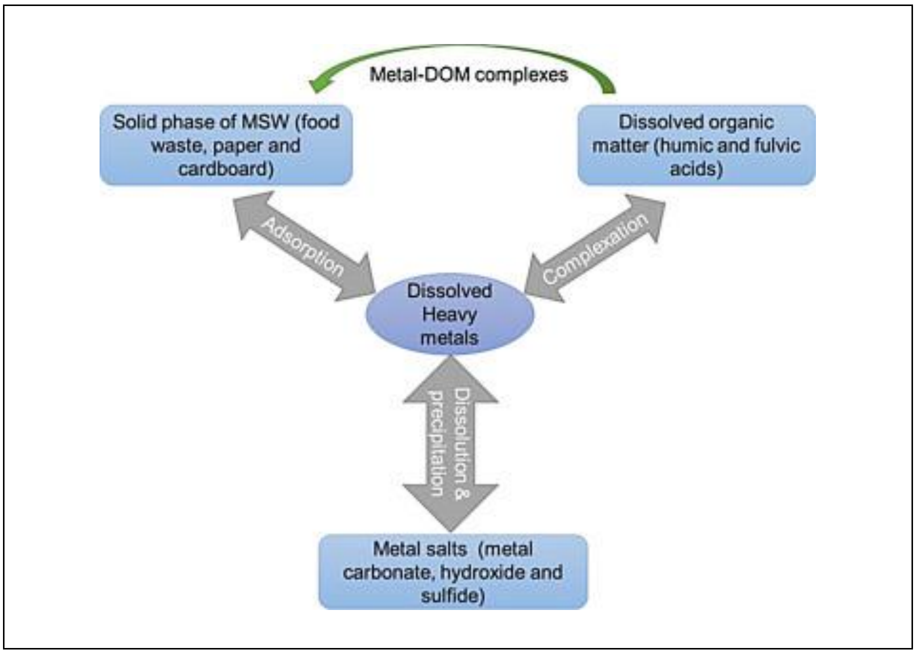

Figure 2.5 Proposed mechanism of heavy metal distribution in a landfill.
Source: Xie et al. (2015).

2.4.3 Inorganic Macrocomponents

According to Kjeldsen et al. (2002), inorganic macro components mainly found in landfill leachate consist of cationic such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonium (NH^{4+}) and anionic for example chloride (Cl^{-}), sulphate (SO_4^{2-}), nitrite (NO_2^{-}), nitrate (NO_3^{-}) and hydrogen carbonate (HCO_3^{-}) elements. The concentrations of these mentioned constituents depend on the landfill stabilization. As explained previously, during the decomposition process of the methanogenic phase, the concentrations of the ionic constituents are low due to the enhancement of the precipitation process. The process had increased the pH value and led to the forming of complexes and lowering the concentration of the cations. Besides, during this methanogenic phase, the concentrations of anions also decrease due to their microbial reduction activities. The concentrations of the ions decrease with time during the leaching process.

The presence of nitrogen in leachate derived from protein and other nitrogen-containing organic compounds and will promote the formation of nitrogen degradation product such as NH_3-N, NO_3^- and nitrite NO_2^-. NH_3-N identified as the most important pollutants in water resource and soil (Erses et al., 2008). NH_3-N is an inorganic ion form of nitrogen impurity. High concentrations of NH_3-N lead to the eutrophication and resulting in a reduction of dissolved oxygen in aqueous media (Huang et al., 2014).

2.4.4 Xenobiotic Organic Compounds (XOCs)

XOCs in landfill leachate are generally originating from household or industrial chemicals such as plastics, paints, pesticides and solvents (Kjeldsen et al., 2002). Normally, the XOCs present in relatively low concentrations (less than 1 mg/L of individual compounds). An intensive study by Baun et al. (2004) revealed that there were 55 different XOCs compounds and ten degradation products of XOCs were determined during monitoring and toxicity testing of leachate samples from 10 Danish landfills. They grouped the compounds into BTEX (benzene, toluene, ethylbenzene and xylene), C3-benzenes (organic aromatic compounds which contain a benzene ring and three other carbon atoms), bicyclo compounds (saturated compounds consisting of two fused rings, having two or more atoms in common, containing at least one heteroatom, and that takes the name of an open chain hydrocarbon containing the same total number of atoms), naphthalenes, chlorinated aliphatics, phenols, pesticides, and phthalates.

Another literature reported by Kalmykova et al. (2013) found that naphthalene was the highest concentrations among the polycyclic aromatic hydrocarbons (PAHs), followed by fluorene, phenanthrene, fluoranthene and acenaphthene. The present of alkylphenols, bisphenol A and phthalates were also noticed in landfill leachate

(Kalmykova et al., 2013; Kalmykova et al., 2014). Besides that, the presence of aromatic hydrocarbons and halogenated hydrocarbons also reported by Kulikowska and Klimiuk (2008) and Hu et al. (2016a) respectively.

2.5 Classification of Landfill Leachate

The characteristics of landfill leachate are influenced by many parameters, but the age of the landfill appears to be the most important (Kjeldsen et al., 2002). There are three types of leachate have been defined according to landfill age. According to the age of the landfill, leachates can be divided into three groups such as a young, intermediary, and mature, (Zhang et al., 2016). The characteristics of the landfill leachate usually are represented by the basic parameters COD, BOD, the ratio BOD_5/COD, pH, and suspended solids (SS). Table 2:2 are used to summarize the classification of landfill leachate according to the composition changes. Young leachates are generally characterized by high concentrations of COD more than 10,000 mg/L, with a large proportion of biodegradable compounds (BOD_5/COD > 0.5). By comparison, mature leachate is characterized by moderate COD values less than 5000 mg/L, with a predominance of refractory organic compounds (BOD_5/COD < 0.5). Due to their high proportion of biodegradable compounds, young leachates are usually treated using biological systems. However, biological technologies are ineffective for the treatment of mature leachate (Foo and Hameed, 2009; Foo et al., 2013a; Zamri et al., 2015).

According to Kurniawan et al. (2006), during the methanogenic phase, methanogenic bacteria degrade the VFAs and reduce the organic strength of leachate, leading to a pH higher than 7.0. Only humic-like compounds that have high molecular weight remain in the leachate after degradation. Along with the increasing age and domination of anaerobic decomposition over a period of 20–50 years, the stabilized leachate is featured by a high molecular weight (refractory compounds such as HAs and FAs-like fractions, which are not easily degradable), high strength of NH_3-N (>400 mg/L), moderately strength of COD (<4000 mg/L), and a low BOD/COD ratio of less than 0.1.

Table 2:2 Classification of landfill leachate according to the composition changes.

Type of leachate	Young	Intermediate	Stabilize
Age (years)	<5	5–10	>10
pH	<6.5	6.5–7.5	>7.5
COD (mg/L)	>10,000	4,000–10,000	<4,000
BOD_5/COD	0.5–1.0	0.1–0.5	<0.1
Organic compounds	80% volatile fatty acids (VFAs)	5–30% VFAs+ HA+ FA	HA and FA
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 (mg/L)	Low to medium	Low	Low
Biodegradability	Important	Medium	Low

Source: Foo and Hameed (2009)

2.6 Landfill Leachate Treatment

Presently, management of landfill leachate and the effectiveness of treatment are the major issues in the context of landfill site management. Because of their toxicity and in order to meet regulatory safe discharge standards, it is essential to remove pollutants from landfill leachate before it is released into the environment. There are various techniques available for the treatment of landfill leachate. Excellent review and evolution of landfill leachate treatments have been reported by Wiszniowski et al. (2006), Renou et al. (2008) and Abbas et al. (2009). They had classified leachate treatments into three major groups: (i) conventional leachate treatment (recycling and combined treatment with domestic sewage), (ii) biological treatment (aerobic and anaerobic processes) and (iii) physical/chemical treatment (chemical oxidation, adsorption, chemical precipitation, coagulation/flocculation, sedimentation/flotation and air stripping.

2.6.1 Conventional Leachate Treatment

Previously, leachate treatments are combined with the domestic sewerage treatment plant. The landfill leachate was transported into the sewer system and combined treatment with domestic sewage at conventional sewage plant before discharge. It was preferred for its easy maintenance and low operating costs (Yu et al., 2010). There were mainly two methods for the combined treatment of landfill leachate. One was the physical-chemical and biological treatments of landfill leachate (Adegoke and Bello, 2015). The treatment of landfill leachate in municipal wastewater treatment plants was investigated by several researchers, including Yu et al. (2010), Kalka (2012) and Brennan et al. (2017).

In the case of young leachate, a significant result decrease in the nitrification was reported. Moreover, the co-treatment of old leachate in a municipal wastewater treatment plant represents the most sustainable solution for ongoing leachate treatment in the cases examined by Schuk and James (1986). However, this alternative has been increasingly questioned because of low biodegradability and the present of heavy metals and organic inhibitory compounds in the leachate that possible to reduce treatment efficiency. The study done by Kalka (2012) proved that landfill leachate significantly disrupted the biological treatment of wastewater. They also claimed that, after biological treatment, wastewater enriched with 10% landfill leachate did not achieve the water quality standards and harmful to the aquatic organisms.

The recycling of the leachate is an onsite treatment process and one of the least expensive options available where the leachate is collected and then returned directly back to the landfill. This is an attractive technology that can reduce the volume of leachate and reduce pollutants in the leachate by degradation in the landfill body. In addition, this technique enhances the biodegradation of organics in waste as well in the leachate, especially in dry regions, since it contributes moisture and extends the retention time (Ogata et al., 2016). Report published by Huang et al. (2016) mentioned that leachate recirculation could help improve the attributes of a landfill in the following ways: (i) increased moisture content, (ii) improved leachate quality, (iii) increased, methane production, (iv) increased waste subsidence and (vi) lowered heavy metals concentration. Further, leachate recirculation also assists in term of nutrient and enzymes distribution, pH buffering, dilution of inhibitory compounds, liquid storage and evaporation opportunities.

2.6.2 Biological Treatment

Generally, biological treatments used for the removal of high strength BOD landfill leachate. This treatment process was done via microorganism biodegradation, which can degrade organics compound to CO_2 and sludge under aerobic condition while CO_2 and CH_4 for anaerobic conditions. The details describe fundamentals, advantages and limitations of biological processes on landfill leachate treatment clearly discussed by Renou et al. (2008), Abbas et al. (2009) and followed by Bove et al. (2015).

Biological treatment has been shown very effective in removing organic and nitrogenous matter (Abbas et al., 2009), including immature leachate when the BOD_5 concentration is high, and the BOD_5/COD ratio is more than 0.5 (Renou et al., 2008). However, as the biodegradation of solid waste progress, the efficiency of the biological process reduces due to the increasing quantity of refractory compounds, namely FAs and HAs constituents in the leachate. Most of the researcher noted that biological processes are useful to treat relatively younger landfill leachate while less efficient for the treatment of older ones (Renou et al., 2008; Abbas et al., 2009 ; Zhang et al., 2016). Bio-refractory contaminants contained mainly in older leachates are not amenable to conventional biological processes, whereas the high ammonia content might also be inhibitory to activated sludge microorganisms. Furthermore, a supplementary addition of phosphorus is often necessary as landfill leachates are generally phosphorus-deficient.

However, there are some queries that have yet to be considered in-depth for the application of biological treatment of landfill leachate prospect. As identified by previous researchers, they claimed that the landfill leachate quality is quite different and unstable (Tatsi et al., 2003; Guo et al., 2010; Peng, 2017). Therefore, purely biological treatment technology is difficult to meet compliance requirements; it should strengthen the pre-or post-processing technology. Peng (2017) also mentioned that a combination of biological treatment with the other treatment process would be a trend to overcome the mentioned problems.

2.6.3 Physical/Chemical Treatment

Physical and chemical process treatments commonly applied in the combine process. This process includes reduction of suspended solids, colloidal particles,