# TREATMENT OF LEACHATE LANDFILL BY ADSORPTION USING CHARCOAL WASTE FROM ACETYLENE GAS PRODUCTION

KHAIRUN NEESA BINTI ROHAIZAD

SCHOOL OF CIVIL ENGINEERING
UNIVERSITI SAINS MALAYSIA
2021

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by

KHAIRUN NEESA BINTI ROHAIZAD

This dissertation is submitted to

**UNIVERSITI SAINS MALAYSIA**

As partial fulfilment of requirement for the degree of

**BACHELOR OF ENGINEERING (HONS.)
(CIVIL ENGINEERING)**

School of Civil Engineering
Universiti Sains Malaysia

August 2021

**Appendix A8**

UNIVERSITI SAINS MALAYSIA

**SCHOOL OF CIVIL ENGINEERING**
**ACADEMIC SESSION 2020/2021**

**FINAL YEAR PROJECT EAA492/6**
**DISSERTATION ENDORSEMENT FORM**

Title: Treatment of Leachate Landill by Adsorption Using Charcoal Waste From Acetylene Gas Production

Name of Student: Khairun Neesa binti Rohaizad

I hereby declare that all corrections and comments made by the supervisor(s)and examiner have been taken into consideration and rectified accordingly.

Signature:

Khairun Neesa

Date : 29/7/2021

Endorsed by:

(Signature of Supervisor)

Name of Supervisor:
Dr. Mohamad Fared Murshed
Date: 4.8.2021

Approved by:

(Signature of Examiner)

Name of Examiner:
Dr. Nurul Hana Mokhtar Kamal
Date: 5/8/2021

## ACKNOWLEDGMENT

First and foremost, praises and thanks to Allah for his showers of blessing throughout my research work to complete the research successfully. I would like to express my uttermost gratitude to my supervisor, Dr. Mohamad Fared Murshed, for his endless guidance, motivation and supports throughout my study. Thank you for always providing me with lots of knowledge and ideas on how to carry out and complete my research work.

I would like to thank the postgraduate students in the laboratory, especially Mohd Sharizal Mohd Sapingi and Nur Hayati Mohd Yusoff for their willingness to assist me in my lab work and thesis writing. Both have been giving me extra knowledge and experience while conducting this project. A sincere thanks to the technicians of Environment Laboratory, Universiti Sains Malaysia, especially Mr Mohammed Nizam Mohd Kamal for the guidance, opinion and suggestion for my study. Without their advice and guidance, this will be a difficult journey for me to complete this study. Futhermore, a special thanks to Pulau Burung Sanitary Landfill for the permission to collect the leachate sample generated from the landfill in order to complete my study.

I would like to thanks my parents Mr. Rohaizad Abd Samad and Mrs. Jalita Din and my sister Ms Julia Wathiqah for their constant blessing, support, love and financial aid during my studies. Not forgetting all my lab mate, Khairul Ikhwan, Mohd Asyraf and Suhaila whom always guide and help me throughout my laboratory work. My appreciation goes to my roommates Aqilah, Aida Syazwani, Fatin Nadia, Liyana, Nur Afiqah and Jang Ki Yong who give me motivation and happiness. Last but not least, I really appreciate everyone who had been helping me directly and indirectly.

# ABSTRAK

Cecair larut resapan terjadi melalui proses penguraian bahan organik tapak pelupasan yang dibawa oleh air yang meresap melalui profil tanah. Cecair larut resapan mengandungi kepekatan bahan organik terlarut dan terampai yang tinggi, bahan kimia bukan organik dan logam berat serta permintaan oksigen kimia (COD) dan permintaan oksigen biologi (BOD) yang tinggi. Oleh itu, kajian ini dijalankan untuk menentukan rawatan optimum yang mempengaruhi kecekapan kaedah penjerapan untuk merawat cecair larut resap. Penyerapan adalah salah satu kaedah paling berkesan yang digunakan sebagai proses rawatan untuk penyingkiran bahan pencemar organik terlarut. Kaedah ini telah terbukti berkesan dalam merawat beberapa jenis air buangan seperti di tempat pembuangan sampah. Dalam kajian ini, arang dari sisa pembakaran untuk penghasilan gas acetilin digunakan sebagai penyerap kerana harganya murah dan mudah diperoleh. Ujian (batch study) yang telan dijalankan dalam kajian ini berdasarkan satu parameter satu ujian yang melibatkan dos bahan penjerap, kelajuan dan masa tahanan. Dos penjerap yang digunakan dalam eksperimen ini ialah 10 g, hingga 50 g. Manakala kelajuan adalah 50 rpm, 100 rpm, 150 rpm, 200 rpm dan 250 rpm dan masa adalah 20 minit, 40 minit, 60 minit, 80 minit dan 100 minit. Dos, kelajuan dan masa tahanan yang paling optimum untuk disingkirkan adalah COD, warna dan ferum adalah dengan menggunakan dos 30 g, kelajuan 150 rpm dan durasi 60 minit dengan hasil penyingkiran peratusan adalah 51%, 52%, 48%, 55% , 61%, 41%, 75%, 75%, dan 60% mengikut turutan.  Oleh itu, kaedah penjerapan dengan menggunakan arang untuk mengubati larut lesap adalah berkesan.

**ABSTRACT**

Landfill leachate forms via decomposition organic fractions in landfill by water percolating through the soil profile. Leachate contains high concentrations of dissolved and suspended organic matter, inorganic chemicals, and heavy metals as well as having both a high chemical oxygen demand (COD) and a high biological oxygen demand (BOD). The production of toxic leachates may pose a significant threat to the environment. Therefore, this study was conducted to determine the optimum treatment condition that influence the efficiency of adsorption process in treating landfill leachate. Adsorption is one of the most efficient ways used as high quality treatment processes for the removal of dissolved organic pollutants. In this study, charcoal from acetylene gas production (CAGP) was used as an adsorbent because it is a waste that can recycle and reuse. The CAGP was grind and sieve. The CAGP that passing 150um was used for adsorption study. The batch study was conducted based on one parameter at one time at different dose, shaking speed and contact time. Dosage used in this experiment is 10 g to 50 g. While speed is 50 rpm, 100 rpm, 150 rpm, 200 rpm and 250 rpm and time is 20 minutes, 40 minutes, 60 minutes, 80 minutes and 100 minutes. The optimum dose, speed and duration in order to remove are COD, colour and iron is 30 g of dose, 150 rpm of speed and 60 minutes of duration with the result of percentage removal is 51%, 52%, 48%, 55%, 61%, 41%, 75%, 75%, and 60% respectively. The preliminary results suggest that the performance of CAGP is acceptable as natural adsorbent for landfill leachate treatment. Further surface activation process might be required to enhance the capability of CAGP as an effective adsorbent. Therefore, the adsorption method by using CAGP to treat leachate is effective.

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| | |
|---|---|
| AC | Activated Carbon |
| APHA | American Public Health Association |
| BaO | Barium Oxide |
| BOD | Biological Oxygen Demand |
| CAGP | Charcoal From Acetylene Gas Production |
| $CeO_2$ | Cerium Oxide |
| COD | Chemical Oxygen Demand |
| Cu | Copper |
| CuO | Copper Oxide |
| DO | Dissolved Oxygen |
| DOC | Dissolved Organic Carbon |
| DOE | Department Of Environmental |
| DOM | Dissolved Organic Matter |
| EV | Evaporation Losses |
| Fe | Iron |
| GAC | Granular Activated Carbon |
| ICP-OES | Inductive Couple Plasma Optical Emission Spectrometry |
| Mg | Magnesium |
| MgO | Magnesium oxide |
| MSW | Municipal Solid Waste |
| $NH_3$-N | Ammonical Nitrogen |
| NTU | Nephelometric Turbidity Unit |
| PAC | powdered activated carbon |
| Pb | Lead |
| PBSL | Pulau Burung Sanitary Landfill |
| POM | Particulate Organic Matter |
| ppm | Part Per Million |
| $R^2$ | Correlation Coefficient |
| rpm | Rotation Per Minute |
| SBR | Sequencing Batch Reactor |

| | |
|---|---|
| SEM | Scanning Electron Microscopes |
| TDS | Total Dissolved Solid |
| TEM | Transmission Electron Microscopes |
| $TiO_2$ | Titanium Oxide |
| TKN | Total Kjeldahl Nitrogen |
| TSS | Total Suspended Solid |
| USM | Univerisity Sains Malaysia |
| $UV_{254}$ | Ultra Violet Ray Absorbance At 254 Wavelength |
| WHO | World Health Organization |
| WWT | Wastewater Treatment Facilities |
| XRD | X-Ray Diffraction |
| XRF | X-Ray Fluorescent |
| Zn | Zinc |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background Study

The materialistic lifestyle of the world is expanding population results in substantial waste production. The volume of solid waste collected annually on a global scale is expected to hit about 2.2 billion tonnes by 2025, according to literature. As a result of rising questions over how to dispose of such a large volume of waste, a variety of waste management practices has been implemented, including landfilling, recycling, composting, and incineration. Landfilling in sanitary landfills and open dumps is the dominant method of waste disposal in most countries, especially in developed countries where cheaper alternatives are generally favoured (Reshadi et al., 2020). Sometimes, a shortage of funding, the absence of or inadequate implementation of public laws, and a lack of concern about environmental emissions prevent the introduction of more appropriate solutions (Torretta et al., 2017).

One of the main challenges associated with a landfill, in addition to many other negatives, is the long-term production of polluted leachate. Water that has percolated into waste deposits that have undergone aerobic and anaerobic decomposition is known as leachate. The contaminated leachate that occurs has the ability to seep into the earth and contaminate soil and groundwater (Bashir et al., 2012). The detrimental implications of such a dilemma could be felt across the food chain. An analysis of the toxicity of 56 landfill leachate samples found 32 chemicals that can cause cancer, 10 chemicals that cause birth defects, and 21 chemicals that cause genetic harm. Besides that, some previously unknown fresh and evolving chemicals have now been found in leachates. These problems have received a lot of attention, and certain countries have enacted very strict laws as a result. More research on landfill leachate disposal has been prompted by tighter emission management requirements and revised discharge guidelines (Reshadi et al., 2020).

PBLS is located in the Byram Forest Reserve in Penang, Malaysia, at 5°240 N Latitude and 100°240 E Longitude, about 20km southeast of Penang Island. Although the landfill site is 63.4 ha in size, only 33 ha is now active, receiving 2200 tonnes of solid trash every day. Solid garbage is buried between 10 and 30 metres deep. As the landfill age exceeded ten years, this site was developed as a semi-aerobic sanitary landfill Level II by developing a regulated tipping technique in 1991 (Kamaruddin et al., 2016). By adopting controlled tipping and leachate recirculation, it was upgraded to a sanitary landfill Level III in 2001. A convection process can be used to create a semi-aerobic system. The latter entails the decomposition of organic materials within the landfill, which will result in a temperature rise. The temperature differential between the interior and outside of the landfill will cause a heat convection current to flow into the landfill via the leachate pipe (Aziz et al., 2004). A natural marine clay liner is developed at this site. It is one of only three locations of its sort in Malaysia and it is semi-aerobically developed. PBLS generates a dark black-green liquid with high COD and ammonium contents and a low BOD5/COD ratio that may be categorized as stabilised leachate (Aziz et al., 2010).

In aspects of an engineered landfill system, PBSL has adopted the Fukuoka method, which allows ambient air to flow into the waste body naturally through the leachate collecting pipes It improve the waste stability and increasing leachate quality by increasing microorganism activity in the waste. The Fukuoka technology that has been tested in countries such as Malaysia, Japan, China and Iran. In compared to aerobic landfills, this technique has numerous benefits, including improved aerobic biodegradation of organic waste, lower methane generation, reduced leachate pollution load, and cost effectiveness (Kamaruddin et al., 2016). Physicochemical methods are used in the PBSL leachate treatment system (Gujarati and Porter, 2010). Flotation, adsorption, coagulation-flocculation, air stripping or chemical oxidation are some of the physical and chemical procedures used to reduce, colloidal particles, suspended solids , floating material, hazardous chemicals and colour (Aziz and Ramli, 2018). Moreover, adsorption is also the most common treatment for removing recalcitrant organic compounds from landfills. Activated carbon in columns or powder form has a higher rate of pollutant adsorption and reduces COD levels more effectively than chemicals, regardless of the original organic matter content (Renou et al., 2008). When activated carbon adsorption and physicochemical treatment were combined, the efficiency of landfill leachate treatment improves because of its high adsorption capacity, microporous structure, wide surface area and natural physical characteristics. The surface reactivity powdered activated carbon is the most suitable adsorbent to apply in the treatment of contaminated wastewater to remove organic and inorganic pollutants (Aziz and Ramli, 2018).

## 1.2 Problem Statement

The heterogeneous mixture of organic and inorganic loads deposited within the waste layers in the landfill percolates with the heterogeneous mixture of organic and inorganic loads deposited within the waste layers in the landfill. Groundwater is typically contaminated by leachate percolation. Its transport from the soil surface via the unsaturated region, eventually reaching the water table and contaminating the groundwater, or by leachate migration via the bad liners of some sanitary landfills. This is due to gravity and the high density of the leachate (Halim et al., 2010). This contaminated substance contains elevated levels of nitrogen compounds, salts, heavy metals and other organic compounds, contaminating surface and groundwater (Azmi et al., 2015). With the landfill age, the properties and quality of the pollutants in landfill leachate change dramatically. The endogenous moisture of solid waste products, rainwater percolation into waste materials, and microbial decomposition of agricultural waste materials all contribute to the formation of leachates in landfills. (Ahmed and Lan, 2012; Bashir et al., 2012). Insoluble oils, such as oil and fats and fine particles, such as suspended solids and organic and inorganic matter, are the main constituents of leachates. Solid waste usually contains high concentrations of biodegradable and non-biodegradable materials, particularly volatile fatty acids, in the early settlement process, also known as the acinogenic phase. The leachate usually contains high molecular weight refractory compounds such as humic substances and fulvic-like fractions that are difficult to degrade in the later stages, the methanogenic process. The leachate has a strong chemical oxygen demand (COD) weight, ammonia, colour and a low 5-day biochemical oxygen demand (BOD5)/COD ratio of 0.1 in this step (Bashir et al., 2012). As a result, these methods will have an effect on turbidity, colour, pH, total dissolved solids, and heavy metals parameters that are used to evaluate leachate. Consequently, eliminating such contaminants from the leachate is important for the remediation of water sources. Biological or physicochemical techniques may be used to remediate the leachate in question (Naji et al., 2020).

Activated carbon (AC) adsorption is a physicochemical mechanism that has been shown to be useful in extracting high molecular weight refractory organic matter from landfill leachate. However, there are few studies on the use of AC to treat sanitary landfill leachates, either as a single step or in conjunction with other technologies (Aziz et al., 2010; Rivas et al., 2006). AC is one of the best filtration media in the world due to its high adsorption capability, microporous composition, expand surface area, high degree of surface reactivity, thermo-stability, low acid/base reactivity, and ability to remove a wide variety of contaminants. Chemically adapted AC materials can be used as a low-cost carbon adsorbent for landfill leachate application (Azmi et al., 2015). When it comes to designing and scaling up adsorption, isotherm data is a crucial tool. Similar, kinetic data is useful in determining the appropriateness and efficacy of an adsorption method (Rivas et al., 2006). Previous work have been conducted AC from different waste and most of them shows homogeneous monolayer by Langmuir adsorption model is perfectly for adsorption said because of the porous nature of AC allows for a longer diffusion path and a higher ability for adsorption. The Langmuir and Freundlich models were used in the isotherm research because both models had strong concordance with the experimental data and high coefficients of determination (Peres et al., 2018; Rivas et al., 2006). Therefore, it important to understand the adsorbent isotherm on the CAGP study.

## 1.3 Objectives

The objectives of this study are:

i. To identify the characteristics of leachate in Pulau Burung Sanitary Landfill.

ii. To determine the optimum dosage, pH, shaking speed and contact time for COD, colour and iron removal in leachate treatment.

iii. To determine the suitable adsorption isotherm model for COD, colour and iron.

## 1.4 Scope of Works

The thesis is only focus on prelimary work by using a batch study to determine the potential of charcoal waste from acetylene gas production (CAGP) as an adsorbent for COD, colour and iron in leachate treatment. The study begun with filter the leachate before conducting a sampling and characterisation of leachate that is from sanitary landfill located at the Pulau Burung Sanitary Landill, Nibong Tebal.

CAGP used supplied by MCB Sdn Bhd, Taiping, Perak. The CAGP was then grinded and sieved into the smallest size. Then, the CAGP were tested for XRD and XRF test to know the characteristic. Then, the mixture of CAGP and distilled water will be characterise by pH, colour, COD, turbidity, heavy metal and $UV_{254}$. Iron concentration were investigated using inductively coupled plasma (ICP) spectroscopy. This was followed by measurement of colour concentrations using the DR 2800 spectrophotometer.

Next, a set of batch study was carried out to determine the optimum dosage of CAGP from 10 g to 50g , shaking speed from 50 rpm, 100 rpm, 150 rpm, 200 rpm and 250 rpm and contact time from 20 minutes, 40 minutes, 60 minutes, 80 minutes and 100 minutes for COD, colour and iron removal in leachate. The pH was not adjusted in this study.

## 1.5 Structure of Thesis

This thesis consists of five chapters. The first chapter discusses background and problem statement of the treatment of leachate. This is followed by the objectives of the study which are the to determine the optimum dosage, pH, shaking speed and contact time for COD and colour removal in leachate using CAGP produce by acetylene gas as an adsorbent, the suitable adsorption isotherm model and kinetic behaviour for COD and colour and the determine the characteristic of CAGP in term of pore size, surface area, particle size and surface charge.

The second chapter is a literature review of leachate, colour, COD, CAGP, adsorption and finally CAGP as an adsorbent in leachate treatment. Reference to these literatures are made to further establish the scope of the study and to articulate methods demonstrated in the studies, as well as to acknowledge the gap in the previous studies.

The third chapter describes the methodology involved in the study. This includes leachate sampling method, leachate and CAGP characterisation. This chapter also illustrates the on-site data collection and laboratory experimental procedures, specifically batch study in determination of the removal of colour and COD in the leachate.

In the fourth chapter, findings obtained from this study including characterisation of leachate, removal of colour and COD in leachate, as well as data and figures from the study are discussed. All findings are then concluded in fifth chapter and finally, the recommendation for further studies are given.

## CHAPTER 2

## LITERATURE REVIEW

### 2.1 Introduction

The flow of literature in this chapter reflects the objectives of the study directly. The discussion will review on the topic of characteristics and the treatment of leachate, mainly adsorption and CAGP as an adsorbent.

### 2.2 Leachate at Sanitary Landfill

From a global perspective, concern about environmental conservation has evolved over time. The exponential population and social population growth, changes in efficiency and consumption habits, increasingly affluent lifestyles and resources use, and continuous growth of the industrial and technological systems have all been accompanied by the rapid generation of municipal and industrial solid wastes, creating the most obstructionist phenomenon around the world (Foo and Hameed, 2009). Addition to economic benefits, landfilling reduces environmental concerns and other inconveniences by allowing most solid wastes to decompose under controlled conditions before they are eventually transformed into relatively inert, stabilised materials (Nik Azimatolakma, 2011).

Landfill leachate is characterised as any polluted liquid effluent percolating from accumulated waste and discharged inside a landfill or dumpsite through external sources, the source of which is frequently uncertain, as well as its route of exposure and toxicity. (Foo and Hameed, 2009). It is a soluble organic and mineral compound that forms as water infiltrates through the refuse layers, absorbs a collection of contaminants, and sets off a complex interplay between hydrological and biogeochemical reactions that serves like an amass transfer mechanism. It is used to create a high enough moisture content to begin a liquid flow caused by gravity, precipitation, drainage, surface runoff, rainfall, snowmelt, recirculation, liquid waste co-disposal, waste decomposition, groundwater infiltration, and the original moisture content of landfills. (Foo and Hameed, 2009; Renou et al., 2008)

Water that has percolated into waste deposits that have undergone aerobic and anaerobic decomposition is known as leachate (Reshadi et al., 2020). Groundwater is usually contaminated by leachate percolation through its transport from the soil surface via the unsaturated zone, eventually reaching the water table and contaminating the groundwater or by migration of the leachate via the poor liners of some sanitary landfills. The contaminated leachate has the ability to seep into the earth and contaminate soil and freshwater (Naji et al., 2020).

Municipal solid waste landfills typically emit a variety of harmful product into the environment such as gas pollution, liquid leachate, and non-biodegradable solid waste. Leachate's ability to contaminate ground or surface water poses a significant threat to public health and habitats (Bashir et al., 2012). Furthermore, some previously undetected fresh and evolving chemicals have now been found in leachates (Reshadi et al., 2020).

As a result, in recent decades, pollutant reduction has been a major problem in leachate treatment. With the landfill age, the properties and quality of the pollutants in landfill leachate shift radically. The endogenous moisture of solid waste products, rainwater percolation into waste materials, and microbial decomposition of agricultural waste materials all contribute to the formation of leachates in landfills. Insoluble oils, such as oil and fats, and fine particles, such as suspended solids and organic and inorganic salts, are the main constituents of leachates (Bashir et al., 2012).

## 2.3 Leachate Generation

The materialistic lifestyle of the world's growing population leads in significant trash generation. According to estimations published in the literature, the volume of solid trash collected yearly on a global basis would reach around 2.2 billion tonnes by 2025. (Reshadi et al., 2020). Increasingly affluent lifestyles, as well as continued industrial and commercial expansion, have been followed by dramatic rises in urban and industrial solid waste production in many countries across the world over the last decade. In both per capita and total terms, municipal solid waste (MSW) generation continues to rise. In 1997, for example, waste production in Rio de Janeiro, Brazil, was 8042 tonnes per day-1, up from 6200 tonnes per day in 1994, despite essentially no population increase. Between 1992 and 1996, waste generation in Norway and the United States rose by 3% and 4.5 percent annually, respectively. Annual waste generation ranged from 300 to 800 kg per person in developed countries to less than 200 kg in developing countries in the late 1990s. In 2002, the French population produced 24 million tonnes of MSW, or 391 kilogrammes per human (Renou et al., 2008). The combined waste production in India's four major cities of Mumbai, Delhi, Chennai, and Kolkata is about 20,000 tonnes per day, with the majority of it being disposed of in landfills. The majority of landfill sites around the world are old and were not designed to prevent radioactive leachate from contaminating the surrounding soil and groundwater (Mukherjee et al., 2015).

Malaysia produces about 6.2 million tonnes of solid waste per year, or 17,000 tonnes per day. Because of rising population and per capita waste production, this number is projected to rise to more than 30,000 tonnes per day by 2020. In most developed nations, organic waste accounts for 40 percent to 60 percent of total waste weight (Aziz and Ramli, 2018). Despite the benefits of landfilling, the highly contaminated leachate that results has raised serious concerns, particularly because landfilling is a commonly used solid waste disposal method. When rainwater infiltrates the accumulated waste, leachate is produced. Many organic and inorganic contaminants, such as ammonia and heavy metals, are transported into leachate as water flows into a landfill. Leachate then travels to the top or bottom of a landfill cell, where it can pollute surface and groundwater, endangering human health and marine ecosystems. The consistency and quantity of leachate are influenced by a variety of influences, including seasonal weather variations, landfilling method, waste form and composition, and landfill structure. As a result, environmental experts are working hard to come up with innovative treatments for vast amounts of polluted leachate. Some leachate treatment techniques have been used, including biological, physical and chemical processes, as well as a combination of these processes (Aziz and Ramli, 2018).

Rainfall, groundwater level, surface drainage, landfill cover, and form of waste at the landfill all affect the rate of leachate production. In addition, the depth of the landfill reduces with time (Aziz and Ramli, 2018; Renou et al., 2008). As a consequence of rising issues over how to dispose of such a large volume of waste, a variety of waste management practises have been implemented, including landfilling, recycling, composting, and incineration. Landfilling in sanitary landfills and open dumps is the dominant method of waste disposal in most countries, especially in developed countries where cheaper alternatives are generally favoured. Usually, a shortage of funding, the lack of or inadequate implementation of public laws, and a lack of concern about environmental pollution prevent the introduction of more appropriate solutions (Reshadi et al., 2020; Torretta et al., 2017).

## 2.4 Characteristic and Composition of Leachate

Two important characteristics of leachate are its volume and composition (Mukherjee et al., 2015; Renou et al., 2008). The volumetric flow rate and the composition of a liquid effluent are two considerations that are associated in the case of leachate. The water cycle in a landfill is depicted in Figure 2.1. Precipitation (P), surface run-off (Rin,Rext), and penetration (I) or intrusion of groundwater percolating into the landfill are all closely related to leachate flow rate (E). Landfilling techniques, such as waterproof covers and liner standards, such as clay, geotextiles, and/or plastics, are important in controlling the amount of water entering the tip and thereby reducing the possibility of pollution (Renou et al., 2008; Reshadi et al., 2020). The atmosphere has a direct effect on leachate production because it impacts precipitation input (P) and evaporation losses (EV). Eventually, the production of leachates is determined by the composition of the waste, primarily its water content and degree of compaction in the tip. Since compaction lowers the filtration rate, performance is usually higher when the waste is less compacted (Nik Azimatolakma, 2011; Renou et al., 2008).

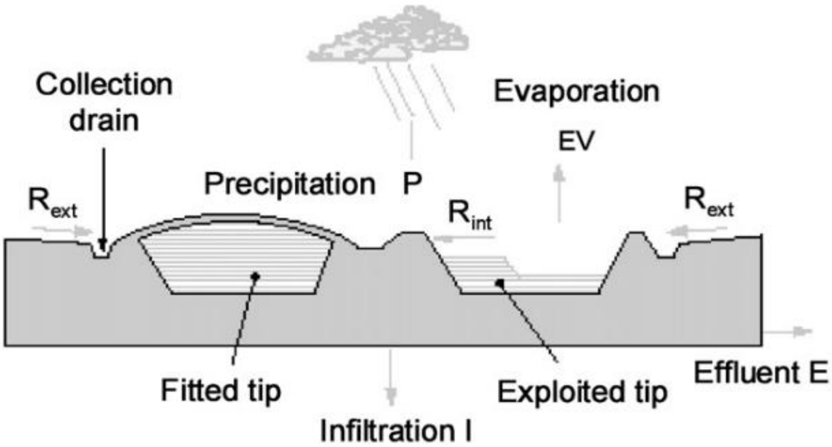


Figure 2.1: Water cycle in sanitary landfill (Renou et al., 2008)

Characteristics of deposited waste, soil properties, landfill age, temperature, liquid waste management, biochemical interactions both within the landfill and between the landfill and the environment, waste compaction, landfill design, and waste moisture content are all factors that can influence leachate composition (Mukherjee et al., 2015). The age of the landfill may be one of the most influential factors, because it can be used to make initial decisions since some factors can be difficult to predict immediately (Mukherjee et al., 2015; Reshadi et al., 2020). The evolution of waste at the stages of aerobic, acidogenic, methanogenic, and stabilisation (Mukherjee et al., 2015) will result in decomposition of waste. As a result of the inclusion of refractory compounds such as fulvic and humic acids and the drop in the $BOD_5$/COD ratio, ageing induces a decrease in $BOD_5$ content, hence the leachate becomes more stable (Ahmed and Lan, 2012; Reshadi et al., 2020).

The age of the leachate can be used to approximate its composition, which is categorized into four stages: new, intermediate, stabilised, and old (Mukherjee et al., 2015). The formation of fatty acids by anaerobic fermentation of the organic component of the waste results in a young leachate with a low pH and a high $BOD_5$. Although the pH level approaches neutral, bacteria transform anaerobically produced acids into methane and carbon dioxide during the methanogenic phase (Renou et al., 2008). When landfills age, the BOD5/COD ratio decreases, while non-biodegradable organic material increases in old leachate (Kjeldsen et al., 2002; Reshadi et al., 2020). As a result, biological treatment processes for old leachates are ineffective. BOD, COD, pH, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), total Kjeldahl Nitrogen (TKN), ammonia nitrogen, heavy metals, sulphur compounds, total organic carbon (TOC), BOD/COD ratio and dissolved organic matter (DOM) are the basic parameters that reflect leachate content (Kjeldsen et al., 2002; Reshadi et al., 2020). Composition is further complicated by the existence of complex pollutants such as PFCs, PAHs, alkaline earth metals, and phthalic esters (Silva et al., 2013). Table 2.1 shows some main characteristics of landfill leachate based on the age of the landfill (Renou et al., 2008; Reshadi et al., 2020). The existing relationship between landfill age and organic matter composition can provide a valuable criterion for choosing an appropriate treatment method (Renou et al., 2008).

Table 2.1: Landfill leachate classification vs age (Renou et al., 2008)

| | 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 | >0.3 | 0.1-03 | <0.1 |
| Organic compounds | 80% volatile fat acids (VFA) | 5-30% VFA + humic and fulvic acids | Humic and fulvic acids |
| Heavy metals | Low-medium | | Low |
| Biodegradibility | Important | Medium | Low |

## 2.5 Standard Treatment of Leachate

Biological, physical-chemical, and a mixture of physical-chemical and biological processes have all been classified as leachate treatment processes in previous reviews. There are many solutions used for landfill leachate disposal, many of which are dependent on biological method and physicochemical methods. Biological methods are activated sludge, aerobic and anaerobic stabilisation ponds, and biological filters. Examples of physicochemical methods are coagulation/flocculation, adsorption, chemical deposition, stripping, chemical oxidation, ion exchange and electrochemical treatment. Membrane filtration includes microfiltration/ultrafiltration, nanofiltration, and reverse osmosis, as well as modern oxidative processes (Fenton and ozonation) (wetlands). The relationship between landfill age and leachate composition, among other factors, should be considered when deciding on the best technology (Lebron et al., 2021). As seen in Table 2.2, only a few processes will work well irrespective of landfill age.

Table 2.2: Treatment applied to leachate treatment classified according to their effectiveness (Costa et al., 2019)

| Process | Landfill age (years) | | |
|---|---|---|---|
| | 0-5 | 5-10 | 10-20 |
| **Biological process** | | | |
| Aerobic | 🟩 | 🟨 | 🟥 |
| Anaerobic | 🟩 | 🟨 | 🟥 |
| Membrane bioreactors | 🟩 | 🟨 | 🟨 |
| **Physicochemical process** | | | |
| Coagulation - flocculation | 🟥 | 🟨 | 🟨 |
| Chemical precipitation | 🟥 | 🟨 | 🟥 |
| Adsorption | 🟥 | 🟨 | 🟩 |
| Oxidative process | 🟥 | 🟨 | 🟨 |
| Stripping | 🟥 | 🟨 | 🟨 |
| **Membranes** | | | |
| Ultrafiltration | 🟨 | 🟨 | 🟨 |
| | 🟥 | 🟥 | 🟥 |
| Nanofiltration | 🟩 | 🟩 | 🟩 |
| Reverse osmosis | 🟩 | 🟩 | 🟩 |

🟩 = good performace
🟨 = satisfactory performace
🟥 = inadequate

Even though biological processes are recognised for their operational simplicity and favourable cost-benefit ratio, their effectiveness would be limited to landfills with a biodegradable fraction greater than 10,000 mg/L, which corresponds to landfills operating for 0–2 years in tropical regions and 0–10 years in temperate regions. Nonetheless, high concentrations of cyanide, chromium, nickel, and zinc can inhibit the microorganisms that remove ammonia. As landfills mature and ammoniacal nitrogen concentrations rise, biological treatment processes can become ineffective in meeting the legislatively mandated threshold values for discharge into water bodies. Thus, combining biological and physicochemical processes appears to be an intriguing option for reaping the benefits of both technologies. In general, physical and chemical technologies are used to remove ammonia in situations where they are used as pre-treatment, and to remove recalcitrant compounds in post-treatment periods (Lebron et al., 2021; Renou et al., 2008).

### 2.5.1 Physical/Chemical Treatment

Examples of physical and chemical process are flotation, coagulation/flocculation, adsorption, chemical oxidation, and air stripping for reducing suspended solids, colloidal particles, floating material, colour, and toxic compounds. In addition, physical/chemical treatments for landfill leachate are used at the treatment line (pre-treatment or final purification) or to treat a particular pollutant (stripping for ammonia) (Renou et al., 2008). Coagulation/flocculation, chemical precipitation, and chemical and electrochemical oxidation are all common chemical methods for treating leachate. Meanwhile, adsorption, air-stripping, and membrane filtration are the most popular physical leachate treatment methods (Aziz & Ramli, 2018). Not only are physiochemical procedures used to remove refractory compounds from leachate, but they are often used as a refining method prior to biological therapy. Furthermore, for treating older leachates with reduced biodegradability and high ammonia concentrations, physical-chemical approaches are favoured (Reshadi et al., 2020). These procedures are similar to those used to lower COD, suspended solids, colloidal particles, floating material, heavy metals, suspended solids, and colour (Agamuthu and AI-Abdali, 2009).

### 2.5.2 Chemical Oxygen Demand

Emissions from landfills are generated over long periods of time, sometimes longer than a human lifespan. Leachate is the longest-lasting discharge. Co-treatment of urban wastewater has long been the most popular leachate treatment method. The pattern, on the other hand, is obviously going toward treatment at local treatment plants, where COD (chemical oxygen demand) and other variables are set as discharge limits. Obtaining low effluent COD values is difficult in general, particularly at plants that rely on biological degradation. COD has long been used as a measurement of organic matter. This can be seen in a variety of standard approaches. COD on the other hand, is no longer regarded strictly as a metric of organic matter and many other substances may affect the COD value. Both the organic and inorganic elements of a sample are vulnerable to oxidation, according to an American standard from 1998, but in most instances the organic portion predominates and is the one of greater importance. Inorganic compounds that can influence the COD value include iron, sulphide, manganous, manganese, ammonia nitrogen, nitrite and chloride. Many of the elements of water, air, and soil in landfill leachates, pollution contaminants are present in high concentrations (Kylefors et al., 2003).

The removal of the mixture of organic and inorganic contaminants that make up the main components of landfill leachate necessitates the use of an adsorbent that can eliminate a variety of organic and inorganic contaminants. Activated carbons are well known for being the most efficient adsorbents for removing organic contaminants from aqueous and gaseous phases (Halim et al., 2010). The only literature found was by (Azmi et al., 2015), who researched the preparation conditions of AC made from sugarcane bagasse for adsorptive COD removal from leachate, including activation temperature, activation time, and IR. They discovered that 687 °C activation temperature, 2 hour activation time and 2.59 IR were the best conditions for preparing AC and treating leachate using central composite design, resulting in a higher contaminant removal percentage COD (77.8%) (Ghani et al., 2017).

### 2.5.3 Colour

In several nations, the dark colour of leachate produced by organic dyes or biological compounds is a serious issue. As a consequence, colour reduction is crucial in environmental remediation. Since colour is typically the first pollutant to be discriminated against by the population, the presence of a dark brownish colour from landfill leachate can cause them discomfort. Untreated coloured leachate discharged into receiving waters imparts pigment, which prevents aquatic life development by reducing sunlight penetration and disrupting photosynthetic activity (Ibrahim and Yaser, 2019). The organic fraction in leachate from old landfills is dominated by refractory compounds that are barely biodegradable. Refractory compounds in the leachate, such as humic acids, fulvic acids, and the hydrophilic fraction, add a clear yellowy-brown or dark colour to the leachate, which is produced by high concentrations of organic matter. At pH values greater than 4, humic compounds in the aqueous system are negatively charged (Ibrahim and Yaser, 2019; Tzoupanos et al., 2008; Zouboulis et al., 2004). True colour is determined on samples which have low turbidity or have been filtered. There is a guideline being introduced in the Environmental Quality Act 1974 provided by the Department of Environment Malaysia (DOE). The standard for the discharge of leachate is 100 ADMI (DOE Malaysia, 2009).

### 2.5.4 Iron

The earth's crust, soils, streams, and groundwater all contain iron. Infiltration of precipitation via soils, rocks, and mineral deposits dissolves iron into groundwater (Sapingi, 2018). One of the most significant challenges associated with the deployment of sanitary landfill technologies is the control of leachate. The presence of heavy metals in leachate, in particular, can cause a variety of issues when it is combined with municipal wastewater in wastewater treatment facilities (WWTPs). This is one of the most often used solutions across the world. Biological treatment has little effect on heavy metals, unlike nitrogen and biodegradable organic contaminants. They are transferred to the surplus sludge produced by the treatment, prohibiting its direct or indirect use in agriculture. The disadvantages of leachate co-treatment in municipal WWTPs might be reduced if landfill leachate could be pretreated to remove heavy metals at a low cost (Bilardi et al., 2020). Iron, zinc, manganese, chromium, lead, cadmium, and copper are heavy metals that are often detected in high quantities in landfill leachate. They pose a threat to groundwater, surface water, and reservoirs by polluting them. Iron base material waste such as, paints, pigments, electrical components, building materials, polishing agents, and colour compounds usually contribute to the iron content in leachate (Aziz et al., 2004). The average content of iron in leachate is 2.00-2.95 mg/L (Aziz et al., 2010) The limitation of iron in with acceptable condition for discharge of leachate Second Schedule (Regulation 13) is 5.0 mg/L (DOE Malaysia, 2009).

## 2.6 Adsorption

Adsorption process technology is commonly apply in environmental engineering solutions (Sahu and Singh, 2018). It involves the attachment of one or more adsorbates to an adsorbent via physical or chemical connections (Weber et al., 2016). Adsorption is the process of a compound accumulating on the surface of another material, resulting in a higher concentration of molecular species on the surface than in the bulk. When a solid surface is exposed to a gas or a solvent, ions from the gas or solution phase collect or concentrate on it. Adsorption is the process of a gas or liquid's molecules concentrating on a solid surface (Sahu and Singh, 2018). It is commonly employed in the leachate treatment process to remove pollutants from leachate because adsorption is simple, socially acceptable, economically viable and efficient. Activated carbons are often used adsorbents because they have a thermo-stability, high porous surface area, interesting acid/base properties, a controlled pore structure, and a low cost if the preparation is made from byproducts (Weber et al., 2016). Adsorbates adhere to the adsorbent's surface in the shape of a film. An adsorbent is a substance that allows for adsorption to occur. (Foo and Hameed, 2009; Sahu and Singh, 2018).

### 2.6.1 Type of Adsorption

Physical adsorption or the physisorption occurs as a result of intermolecular attraction between adsorbate and adsorbent. The poor Van-der Waal forces are thought to tie the adsorbent and adsorbate together. Though new equilibrium adjustments occur without losing the original interaction of electrons with their respective interacting species, there is no transfer or sharing of electrons. Low heat of adsorption, typically less than 10 Kcal/mole, indicates the presence of these weak bonds. This adsorption is only noticeable at temperatures below the adsorbate's boiling point. It has a reversible existence and is non-specific to the adsorbent. According to the theory that physical adsorption can contribute to the creation of multilayers, the nature of the adsorbate is more important than the nature of the solid adsorbent (However, 2014). Chemisorption involves the formation of chemical bonds between the adsorbate and adsorbent due to transfer or sharing of electron. It can occur at high temperatures and is marked by a high degree of heat of adsorption of more than 20-150 Kcal/mole. In both adsorbate and adsorbent, it is normally irreversible and nonspecific. Due to the strong initial heat, which causes a significant volume of adsorption, chemical adsorption occurs, resulting in the forming of a monolayer, followed by the formation of multilayers bound by physical forces (However, 2014). Table 2.3 shows a differences between physical and chemical sorption.

Table 2.3: Physical and chemical sorption (Sahu and Singh, 2018)

| | Chemisorption | Physisorption |
|---|---|---|
| Temperature range over which adsorption occurs | Virtually unlimited; however, a given molecule may be effectively adsorbed only over a small range | Near or below the condensation point of the gas (eg. $CO_2$) |
| Adsorption enthalpy | Wide range, related to the chemical bond strength typically 40-800 kJ/mol | Related to factors like molecular mass and polarity but typically 5-40 kJ/mol (ie. Heat of liquefaction) Nondissociative and reversible |
| Nature of adsorption | Often dissociative and may be irreversible | Nondissociative and reversible |
| Saturation uptake | Limited to one monolayer | Multilayer uptake is possible |
| Kinetics of adsorption | Very variable; often is an activated process | Fast, because it is a nonactivated process |

The effectiveness of the adsorption process is determined by a number of variables, including the initial concentration, adsorbent dosage, shaking speed and contact time. In most studies, the effect of adsorbent dose is the most investigated factor. In this component, researchers have the option to choose their own study's range and interval. Because there are more accessible sites for adsorption, the elimination of pollutants increases as the amount of adsorbent mass adds. Nevertheless, as the mass of adsorbent increased, the amount of adsorbate adsorbed per unit mass of adsorbent decreased. This is due to adsorption sites overlapping or aggregating. As a result, increasing the adsorbent mass after reaching the optimal dose reduces the adsorption effectiveness (Sapingi, 2018).

Adsorption efficiency is mostly determined by contact time. Due to the availability of adsorption, the adsorption rate often increases with time, first being fast and then gradually decreasing. The higher the pollutant removal, the longer the adsorbate solution is in contact with the adsorbent. This criterion, however, is restricted when the adsorption and desorption rates have achieved equilibrium or the adsorption site has reached saturation (Ali et al., 2016).

The shaking speed is another key component in adsorption research. Normally, an orbital shaker with a unit revolution per minute controls the shaking speed (rpm). In adsorption, shaking speed is crucial since it determines how effectively the adsorbent and adsorbate mixture combined. Therefore, after reaching the optimal rate, increasing the shaking speed will not result in a substantial increase in adsorption efficiency (Shavandi et al., 2012). In this study, only dosage, shaking speed and contact time are the parameters that will be evaluated. The study will use leachate, thus the initial concentration will not be chosen. Because changes in pH might impact natural organic matter speciation, pH is not included in this analysis.

Adsorption, a surface phenomenon used to remove organic and inorganic pollutants in which gas or liquids from a mixture are attracted to solid sorbent surfaces and attachments are formed through physical and chemical bonds, has emerged as a promising and efficient fundamental approach in the wastewater treatment industries over the last decade. The table 2.4 below summarises the study on landfill leachate treatment utilising the activated carbon adsorption technique that has been done by various researchers and scientists. To deal with the temporal variations in the intensity and composition of landfill leachate, researchers have focused on developing collaborative multistage treatments that combine adsorption processes with a variety of complimentary methods (Norashiddin et al., 2019).

Table 2.4: Study on landfill leachate treatment utilising the activated carbon adsorption (Norashiddin et al., 2019)

| Researcher | Activated carbon | Type of adsorption | Leachate type | Pollutant removal | Dosage, speed, contact time |
|---|---|---|---|---|---|
| (Azmi et al., 2015) | Sugarcane bagasse | Physisorption | Stabilised | Colour, COD, $NH_3$-N | Dosage: 5g<br>Speed: 300rpm<br>Time: 180 min |
| (Ghani et al., 2017) | Banana pseudo-stem | Physisorption | Landfill leachate | Colour, COD | Impregnation ratio: 4.5g/g<br>Activation temperature: 761°C<br>Activation time: 87 min |
| (Detho et al., 2021) | Granular activated carbon and zeolite | Physisorption | Stabilised | COD, $NH_3$-N | Dosage: 15g<br>Speed: 200rpm<br>Time: 120min |
| (Aziz et al., 2011) | PAC-SBR | Physisorption | Stabilised | Colour, COD, $NH_3$-N, TDS | Dosage: 10g<br>Speed: 60 min<br>Time: 5.5h |

### 2.6.2 Adsorption Application in Leachate Treatment

Adsorption trials for the removal of colour and COD are being performed all over the world. Despite the fact that adsorption rate is influenced by a number of factors, the variety of outcomes reported in this study focused on cost, adsorbent efficacy, availability and feasibility in the removal of colour and COD (Kounou et al., 2015). Adsorption is also adaptable in terms of design and function. So far, adsorption treatment of landfill leachate has yielded positive results, especially in the removal of organic compounds and ammonia nitrogen (Reshadi et al., 2020). Activated charcoal, granular activated carbon, sodium aluminium silicate, activated aluminium oxide, zeolite, microporous polymer crystals, and silica gel are some of the most widely used adsorbents. Colorless, odourless, and highly recyclable by-products are typically encountered when adsorption is used as a treatment process (William et al., 2008)

## 2.7 Charcoal as adsorbent and its characterisation

Excess waste generation and environmental protection have been the most pressing societal concerns of the last decade and one of the most difficult issues for scientists and researchers to address. Despite these flaws, research has been undertaken to determine the suitability of raw, organic, and low-cost materials as alternative precursors. Activated carbon (AC) adsorption is a physical/chemical mechanism that has been shown to be useful in extracting refractory organic matter with a high molecular weight from landfill leachate (Azmi et al., 2015). A broad variety of techniques, including physical, chemical, and biological technology, have been applied and are receiving excellent feedback and high priority (Norashiddin et al., 2019). Granular activated carbon (GAC) and powdered activated carbon (PAC) are two types of activated carbon (PAC). As a catalyst for producing activated carbon, almost any substance with a high carbon content may be used. Coal, ash, peat, nutshells, tobacco, and lignite are some examples (Torretta et al., 2017).

According to one report, coal contributes for N40% which equal to 560.2680 g/mol of industrial activated carbon. Activated carbons are typically made using a continuous two-stage carbonization and activation process. The first step, which involves pyrolysis at high temperatures, produces the original porosity, while the second stage