# THE EFFICIENCY OF LANDFILL LEACHATE TREATMENT BY ADSORPTION PROCESS WITH BIOCHAR

# NURUL NAJIHAH BINTI MOHD IDRIS

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By

# NURUL NAJIHAH BINTI MOHD IDRIS

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Name of Student: Nurul Na	ajihah binti Mohd Idris
I hereby declare that all conexaminer have been taken	rrections and comments made by the supervisor(s)and into consideration and rectified accordingly
Signature : Majihah	Approved by:
Date: 11/08/2022	(Signature of Supervisor) Name of Supervisor : Dr. Rosnani Alkarimiah Date : 12/08/2022
	Approved by: (Signature of Examiner)
	Name of Examiner : Dr. Nik Azimatolakma Awang

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#### ABSTRAK

Air larut lesapan mengandungi sejumlah besar bahan cemar organik dan bukan organik. Bahan cemar organik dan bukan organik adalah berbahaya dan membawa kesan negatif terhadap alam sekitar. Air larut lesapan mesti dikendalikan dengan sebaik mungkin untuk mengelakkan pencemaran komposisi berbahaya yang dihasilkan oleh proses larut lesap. Proses penjerapan kimia-fizikal merupakan kaedah rawatan yang disyorkan yang telah dibincangkan dalam penyelidikan ini. Penjerapan karbon teraktif (AC) adalah salah satu kaedah terbaik untuk merawat bahan larut lesapan. Kaedah ini, bagaimanapun, memerlukan komponen prekursor AC yang mahal dan terhad. Matlamat penyelidikan ini adalah untuk mengenal pasti penjerap alternatif yang boleh mengurangkan bahan cemar dalam larut Lesapan tapak pelupusan secara berkesan tetapi lebih murah. Biochar digunakan sebagai media karbon teraktif dalam kajian ini. Kecekapan penyingkiran COD, kekeruhan dan zink dalam lesapan tapak pelupusan dinilai oleh penjerap biochar. Dos penjerap dan pH adalah dua parameter yang menjadi tumpuan untuk penyelidikan makmal. Dos optimum biochar yang dicapai sepanjang penyelidikan ini ialah 1g untuk penyingkiran COD, 2g untuk penyingkiran kekeruhan, 2.5g untuk penyingkiran zink dan 3g untuk penyingkiran pepejal terampai. pH optimum yang dicapai ialah pH 4 untuk penyingkiran COD, zink dan pepejal terampai. Bagi penyingkiran kekeruhan, pH ideal ialah pH 12. pH optimum untuk potensi zeta menghampiri cas titik sifar ialah pH 4 dan saiz zarah paling kecil pada pH 12. Kekeruhan adalah dianggap sebagai kurang dirawat kerana saiz penjerap biochar. Saiznya memberi pengaruh besar terhadap nilai kekeruhan. Secara keseluruhannya, biochar yang telah digunakan adalah cekap untuk mengurangkan COD dan Zink.

#### ABSTRACT

Landfill leachate contains large amount of organic and inorganic contaminants. The organic and inorganic pollutants are hazardous and bring negative impact towards the environment. The landfill leachate must be handled in order to prevent contamination of these hazardous compositions generated by the leaching process. The chemical-physical adsorption process is the recommended treatment that has been discussed in this research. The adsorption of activated carbon (AC) is one of the best methods to treat stabilised landfill leachate. This method, however, needed expensive and limited AC precursor components. The goal of this research is to identify alternative adsorbents that could effectively lower the contaminants in landfill leachate but are less expensive. Biochar was used as an activated carbon media in this study. The removal efficiency of COD, turbidity and zinc in the landfill leachate was assessed by biochar adsorbent. Adsorbent dose and pH are the two parameters that are the focus of the approach for laboratory research The optimum dosage of biochar achieved throughout this research was 1g for removal COD, 2g for removal turbidity, 2.5g for removal zinc and 3g for removal suspended solids. The optimum pH achieved was pH 4 for removal COD, zinc and suspended solid. As for the removal of turbidity, the ideal pH was pH 12. The optimal pH for zeta potential to near the zero point charge is pH 4 and the particle size is smallest at pH 12. Overall, the biochar that been used was efficient to reduce COD and Zinc.

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## LIST OF SYMBOLS

Symbol	Caption	Unit
D1	DO of diluted sample immediately after preparation	mg/L
D2	DO of diluted sample after 5-day incubation	mg/L
Р	Fraction of wastewater sample volume to combined	-
	volume	
Р	Percentage of impurity removed	%
Co	Initial impurity concentration	mg/L
Ce	Final impurity concentration	mg/L

# LIST OF ABBREVIATIONS

BOD	Biochemical Oxygen Demand		
COD	Chemical Oxygen Demand		
DO	Dissolved Oxygen		
PBSL	Pulau Burung Sanitary Landfill		
SS	Suspended Solid		
NH3-N	Ammonia Nitrogen		
BC	Biochar		
ZP	Zeta Potential		
PS	Particle Size		

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#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 Research Background

Malaysia currently produces approximately 23,000 tons of waste each day and is expected to upward thrust to 30,000 tons by the year 2020 (Sreenivasan et al., 2012a). Due to the rising of population and development, the quantity of waste generated is increasing and only less than 5% of the waste is being recycled. The major sources of the waste are domestic waste, agriculture waste and commercial waste. This waste comes from the household, school, factories and agriculture. An unavoidable consequence of landfilling is the generation of leachate.

Leachate is described as any contaminated liquid that is produced when water from rain infiltrates the deposited waste. Leachate commonly contains dissolved contaminants, hazardous heavy element, volatile organic acids, and excessive concentrations of organic matter, biochemical oxygen demand (BOD5), chemical and ammonia nitrogen (Daud et al., 2017). If the high-level dissolved-contaminant leachate is discharged directly into the environment without any treatment, it able to contaminate water bodies and soil. Leachate also can cause harmful to the environment and public health. In order to prevent these negative effects of leachate on the environment, it is compulsory to comply with the discharge standard Environmental Quality Act (EQA) 2009, which is enforced by the Department of Environment Malaysia. As such, environmental professionals are determined to develop suitable treatments for quantity of polluted leachate. Physical, biological and chemical processes, as well as a combination of these processes, have been used in several leachate treatment techniques.

The adsorption technique has been generally considered as the most efficient and

cost-effective fundamental method to wastewater treatment. Adsorption is a process by which a substance is transported from the liquid phase to the surface of a solid and it bonds there through physical and chemical interactions (Li et al., 2010). Adsorbate and adsorbent are the two components of the adsorption process. Adsorbent is the substance on the surface of which adsorption occurs, and adsorbate is the substance that is being adsorbed onto it. There is force attraction between the adsorbent and the adsorbate. The conditions for choosing a good adsorbent for the leachate treatment process include high porosity, high surface area, high stability, and strong adsorption force (Er et al., 2018).

This study focused on the adsorption treatment method using low-cost adsorbent which is biochar. This study assessed three main characteristics of landfill leachate which are Chemical Oxygen Demand (COD), turbidity, zinc concentration, suspended solid (SS), zeta potential and particle size before and after the treatment.

#### **1.2 Problem Statement**

As the population grows, it tends to the generation of large amounts of municipal and industrial waste. These issues are leading to high generation of leachate from landfill activities, the potential of hazardous pollutants flowing into the surface water is high and become one of the most serious problems to human beings, aquatic life and environment. The landfill operators are having difficulty determining the best treatment technique to solve this issue. Mostly, landfill leachate contains of high toxicity due to excessive concentrations of organic and non-organic pollutants.

Various methods have been used for the treatment of landfill leachate such as biological treatment and physiochemical treatment. The example of biological treatment are aerated lagoon, activated sludge, sequencing batch reactors while for the physicochemical treatment are coagulation/flocculation, adsorption, chemical oxidation and membrane filtration (Mojiri et al., 2021). The selection of the preferred treatment method depends on the chemical composition of the leachate in addition to their susceptibility to biodegradation. Among these various methods, adsorption is also wellrecognized because the most efficient and fundamental method in the leachate treatment. The presence of organic and inorganic pollutants in landfill leachate needs the use of adsorbents that can remove a variety of pollutants. Activated carbons are generally known as the most effective and simplest adsorbents for removing organic contaminants from the aqueous or gaseous phases. However, activated carbon is expensive, making it potentially challenging for landfills to implement. A cheaper alternative to activated carbon would be desirable to increase landfill leachate treatment. One option to activated carbon is biochar, that which capable to adsorb contaminants to its surface. This study was carried out to analyses biochar as low-cost adsorbent to reduce pollutants in leachate.

#### 1.3 Objective

The primary goal of this study is to utilize a low-cost material as an adsorbent to reduce the pollutants in leachate. The parameters of leachate that will be tested are pH, BOD, COD, turbidity, zinc, suspended solids and zeta potential. Then, all the results for the treatment are analyses. Therefore, the following are the objectives of this study:

- i. To determine the effect of biochar dosage and pH on the adsorption process at constant contact time.
- ii. To evaluate the efficiency of adsorption performance of biochar (BC) to reduce contaminants of landfill leachate by assessing the removal of turbidity, COD, suspended solid and zinc values.

#### **1.4** Scope and limitation of study

The leachate sample used for this research from Pulau Burung Sanitary Landfill (PBSL). This experiment was conducted in the Environmental Laboratory 1, School of Civil Engineering USM Engineering Campus. The landfill leachate characteristics considered in this study are BOD, COD, turbidity, zinc, suspended solid and zeta potential. The overall performance was analyzed based on the parameter removals to determine the optimum operating conditions. Lastly, the biochar adsorbents effectiveness will be determined based on batch adsorption study in terms of adsorptive removal of COD, turbidity, zinc, suspended solids, zeta potential and particle size in landfill leachate.

#### **1.5** Thesis organization

There are several chapters in the thesis.

Chapter 1 briefly discuss all the outline of the thesis. Start with identify the problem statement and clarify why this research conducted. The goals of this study are then listed so that the desired work target can be determined.

Chapter 2 reviews the previous research that has been done on the treatment leachate by adsorption of biochar. It also briefly explains the properties of biochar.

Chapter 3 starts with the overall methodology applied in this research with details. The brief description of the experiments was carried out to determine the overall performance of the adsorption of biochar and their efficiency to treat COD, turbidity, zinc, suspended solid, zeta potential and particle size from landfill leachate.

Chapter 4 presents the results for the characterization of leachate after treatment and the process performance of biochar adsorption. It presents the optimization results based on the percentage of removal for COD, turbidity and zinc. Next, this chapter also discussed on the characterization and efficiency of biochar that have been used. In terms of parameter removal, a comparison is done between the addition of an adsorbent and the absence of an adsorbent.

Chapter 5 is the final chapter in the thesis. It consists of conclusions for this research based on the findings of the experimental work. This chapter also contains several recommendations for upcoming research.

#### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Overview

This chapter will briefly discuss the background information regarding waste disposal landfill, composition of leachate, leachate treatment by using batch adsorption study and adsorbent used.

#### 2.2 Landfills

A landfill is defined as a system that is designed and established to dispose of waste material via burying it in the ground in order to minimize the release of pollutants or contaminants to the environment. According to the type of waste disposed of, landfills can be divided into hazardous, municipal (solid waste and sewage sludge), and inert waste groups. There are various types of landfills, including sanitary landfills, hazardous waste landfills, construction and demolition landfills, MSW landfills and industrial waste landfill. The concept of sanitary landfill shown in Figure 2.1. From the figure, it clearly show the process of sanitary landfilling. The bottom liner that lined with synthetic liner to prevents the buried waste from coming in contact with underlying natural soils and groundwater. When the wastes are dumped into the landfill and properly compressed using specialized machines. The methane gas produced by layer of clay and top soil in order to prevent exposure to the air and foul smell.



Figure 2.1: The Concept of Sanitary Landfill (Google Image)

Due to demographic behaviour, landfills are chosen rather incinerators for waste disposal in Malaysia. Waste that cannot be recycled, reused, or reduced is managed at landfills. Disposal decisions depend on the cost, population characteristics, land availability, and proximity to waterbodies (Sreenivasan et al., 2012). Due to its technological viability, ease of operation, requirements for less technology, and minimal supervision requirements, landfilling is the most popular and recommended technique.

#### 2.3 Landfill leachate

Leachate is stated as a liquid mixture that is produced when water seeps into the waste layers and then goes through a variety of hydrological and biogeochemical reactions. (Kaur et al., 2016). Leachate contains large amounts of organic and inorganic contaminants which significantly impact soil permeability, surface water, groundwater, and air quality. Leachate characteristics may be influenced by several aspects, such as the composition of landfilled waste, temperature and precipitation (Ferraz & Yuan, 2020). The leachate composition varies most likely depending on the type of solid waste and the age of the landfill. Chemically bound water which is found in solid waste constituents, combined with water from external sources, causing it to produce a very high dissolved and suspended solid content, as well as organic and inorganic compounds. Leachate from landfill is typically described as a liquid in black colour with a pungent odour. The most typical characterisation of landfill includes Biochemical oxygen demand (BOD), Chemical oxygen demand (COD), BOD/COD ratio, total organic carbon (TOC), pH, suspended solids (SS), ammonium nitrogen (NH3-N), turbidity, bacterial count or heavy metals content. It is a soluble organic and mineral molecule that forms when water seeps into the waste layers, eliminates various contaminants, and begins a complicated interplay between the hydrological and biogeochemical reactions. The reactions act as a mass transfer mechanism for producing of moisture content sufficient to the liquid flow, induced by the gravity force, precipitation, irrigation, surface runoff, rainfall, snowmelt, recirculation, liquid waste co-disposal, refuse decomposition, groundwater intrusion and initial moisture content present within the landfills (Mukherjee et al., 2014). Figure 2.2 shows the collection pond of landfill leachate.



Figure 2.2: The Collection Pond of Landfill Leachate (OK, 2014)

#### 2.4 Composition of leachate

Leachate is the liquid that is formed mainly by the percolation of precipitation water through an open landfill or through the cap of a completed site. Commonly, leachate may contain huge amounts of pollutants such as organic substances measured as Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), ammonia, high concentrations of heavy metals, and inorganic salts, as well as strong colour and unpleasant odour (Kamaruddin et al., 2019). It also contains a high amount of phenol, nitrogen, and phosphorus. If the landfill leachate is not adequately treated and safely disposed of, it could cause surface and ground water contamination. It can lead to percolate throughout soils and subsoils, causing negative impacts to receiving waters (S. Q. Aziz et al., 2010). A presence of contaminants such as BOD<sub>5</sub>, COD, ammonia, inorganic salts and others in higher concentrations makes landfill leachate as potential source of contamination for both surface waters and ground. Hence, it must be treated before discharged to water resources. Table 2.1 shows the typical information on leachate composition from new to mature landfills.

Constituents	New Landfill (less than two years)		Mature landfill
(*mg/L)	Range	Typical	(greater than ten years)
BOD	2000-30000	10000	100-200
TOC	1500-20000	6000	80-160
COD	3000-60000	18000	100-500
Total Suspended	200-2000	500	100-400
Solids			
Organic Nitrogen	10-800	200	80-120

Table 2.1: Typical data on the composition of leachate from new to mature landfill

(H. A. Aziz & Hosseini	, 2012)
------------------------	---------

Ammonia Nitrogen	10-800	200	20-40
Nitrate	5-40	25	5-10
Total Phosphorus	5-100	30	5-10
Ortho Phosphorus	4-80	20	4-8
Alkalinity as	1000-10000	3000	200-1000
CaCO3			
pH	4.5-7.5	6	6.6-7.5
Total Hardness as	300-10000	3500	200-500
CaCO3			
Calcium	200-3000	1000	100-400
Magnesium	50-1500	250	50-200
Potassium	50-1000	300	50-400
Sodium	200-2500	500	100-200
Chloride	200-3000	500	100-400
Sulphate	50-1000	300	20-50
Total Iron	50-1200	60	20-200

#### 2.5 Leachate Effect to Environment and Health

If landfill leachate is released into these water bodies without being treated, the effects on the quality of the surface and groundwater would be the huge concern. A pollution incident's effects on a watercourse can have disastrous consequences for the local environment. When the oxygen content is low, an anaerobic situation develops, which kills all oxygen-dependent life forms, including flora and fauna.

Leachate release to the environment without any treatment also poses to the public health risk. In case of drinking water contamination, humic substances in leachate could deteriorate the water quality causing changes in odour, taste and also colour (Renou et al., 2008). Furthermore, humic substances in leachate may react with disinfectants like chlorine, forming carcinogenic by-products such as trihalomethanes. Leachate also contains xenobiotic compounds for example phenol, phthalates and pesticides. Depending on their concentration and availability, it might be hazardous to human health (Gao et al., 2015).

#### 2.6 Leachate Treatment Methods

Leachate treatment becomes a major consideration in wastewater treatment with various approaches present such as physical, biological and chemical treatment. The application of the most suitable technique for the treatment of leachate is directly influenced by the characteristics of the leachate. Biological treatment processes are effective for young or freshly produced leachate, but are ineffective for leachate from older landfills (more than 10 years old). The physical–chemical methods which are not recommended for young leachate treatment but recommended used for older leachate (Ahmad et al., 2018). Each treatment process has its own advantages as well as disadvantages.

There are a various of methods available for treating landfill leachate in different ways. Biological treatment is worldwide the most popular method for leachate treatment. This is usually the primary step in the treatment of landfill leachate. It involves using many different filters to remove or reduce nitrogen and other biological elements from the wastewater. Biological systems can be divided into two which is anaerobic and aerobic treatment processes (Stegmann et al., 2005). For the anaerobic biological treatment such as anaerobic lagoons and reactor while for the aerobic biological treatment likes aerated lagoons and activated sludge. Physical and chemical

process treatments normally used in the combination process. This process includes reduction of suspended solids, floating material, colloidal particles, colour, and hazardous chemicals by either flotation, chemical oxidation, coagulation/flocculation, adsorption and air stripping.

#### 2.7 Adsorbent

An adsorbent is a solid substance that used to remove contaminants from liquid or gases that can harm the environment. There are some different types of adsorbents that are commonly utilized in the adsorption. Most adsorbents are manufactured such as AC, silica gel and alumina and some occurred naturally such as coal and zeolite. Each substance has its unique properties such as porosity, activation sites, pore structure and nature of its adsorbent surfaces. Researchers are currently seeking for low-cost adsorbents since it requires less processing.

In adsorption processes, the adsorbents with high specific surface areas are required. Small pores, for examples mesopores and micropores, result in a large specific surface area responsible for adsorption. Pore size, surface area and pore distribution as well as pore surface chemistry, are the key factors in the adsorption process (Yaashikaa et al., 2020). Table 2.2 shows the literature reviews of different type of adsorbent used in adsorption treatment by another research.

Based from this literature review, it can be summarize most adsorbent can perform well to remove the pollutants in the landfill leachate. However, the efficient adsorbent from this table is activated cow dung ash. According to the Kaur et al. (2016), the results show that with a 2.0 g/L dosage, 79% COD removal was achieved at

the optimum pH 6.

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Type of Sample	Type of adsorbent	Parameter study	Summary of outcome	References
Leachate	Activated Cow Dung Ash	COD	The research indicates that cow dung ash is an effective adsorbent for removing COD from leachate. The results show that with a 2.0 g/L dosage, 79% COD removal was achieved at the optimum pH 6.	(Kaur et al., 2016)
Leachate	Cockle Shells	COD	The optimum shaking speed was determined at 150 rpm according to the adsorption of COD by the media. The optimum pH was 5.5, and the dosage was 35g/L.	(Daud et al., 2017)
Leachate	Activated Carbon obtained from coffee waste	Ammonia, COD, copper, Bromine and Chlorine	The study carried out using this AC in order to evaluate the effect of adsorption time and the dosage of adsorbent reveals that the concentration of ammonia suffers as a reduction agent from the beginning to minute 60 of the experiment. Furthermore, the removal of this pollutant increased with an increase in the adsorbent load. However, the dosage that maximizes the removal of ammonia per mass unit of adsorbent was 3 g/L.	(Chávez & Galiano, 2019a)
Leachate	Granular Activated Carbon and Green Mussel Adsorbent	COD and Ammoniacal Nitrogen	The potential of the GAC and GM adsorbent mixture was used for this research study in order to investigate the percentage removal of COD and ammoniacal nitrogen from stabilized leachate. The functional parameters that affect the reduction efficiency of adsorption mixing media include the optimum mix ratio, pH, shaken time, shaken speed, and dosage. The optimum parameters were found as shown in mixed media ratio 2:2, shaken speed 200 rpm, shaken duration 120 min, pH 7, and amount of dosage 32 g respectively.	(Detho et al., 2021a)
Leachate	Banana peels	Total	Banana peels were used as adsorbents in this study to treat the leachate. The	(Salami et al.,

Table 2.2: The literature review of different type of adsorbent used in adsorption treatment.

		dissolved solids (TDS)	findings of this study showed that as the dosage of the adsorbent was increased, the concentration of total dissolved solids (TDS) in the dumpsite leachate decreased.	2021)
Leachate	Oil palm frond- activated carbon (OPF-AC)	COD, Colour and Fe	This study used oil palm frond-activated carbon (OPF-AC) as an adsorbent to treat landfill leachate. It has the capability to remove COD, color, and Fe up to 70%.	(Yusoff et al., 2021a)
Leachate	Coir (Coconut Fiber)	DO and COD	In this research, the adsorbent for the treatment used activated carbon made from coconut fibre. This adsorbent is one of the most effective options, providing good results in the removal of DO and COD. The COD reduction was observed up to 76.56%.	(Kamble et al., 2020)

#### 2.8 Adsorbate

An adsorbate is a substance that has undergo adsorption on the surface. The adsorbate can be attached to the surface of the adsorbent by the physical or chemical attraction. The adsorbate is attracted to the surface of the adsorbent by van der Waals forces. The forces which are a reversible process that permits the adsorbent to be regenerated for future uses (de Gisi et al., 2016). Organic matter, ammonia nitrogen, phenols, heavy metals, phosphate and sulphide are among the biodegradable and non-biodegradable compounds found in landfill leachate. Table 2.3 shows the literature reviews on the treatment of landfill leachate and mining waste leachate using adsorption method.

From this table, it can be summarize that adsorption method has been widely considered as the most efficient and cost effective fundamental approach to wastewater treatment. According to Kani Kani & Mophin Kani, (2017), it stated that adsorption is efficient in decreasing COD and turbidity.

Type of Sample	Summary	References
Landfill Leachate	According to the study, adsorption is efficient in decreasing COD and turbidity. At the optimum dosage, contact time, speed, and pH, it was found that rice husk ash had a maximum COD removal efficiency of about 74%. It was found that chemical adsorbents such as powdered activated carbon was about 88% COD removal at optimum dosage, contact time, speed and pH whereas 86% in turbidity reduction.	(Kani Kani & Mophin Kani, 2017)
Landfill Leachate	A combination of two coagulation- adsorption treatments can give optimum results in removal of organic compounds leachate. According to the findings, a modified tea waste adsorbent with an optimum dose of 5 g/L can remove up to 88.7% of COD. Therefore, a combination of coagulation and absorption is sufficient for the treatment of this leachate, such as the application	(Bazrafshanp & Ahmadip, 2017a)

Table 2 3: Literatures Reviews on Treatment of Landfill Leachate and Mining WasteLeachate using Adsorption Method.

	of modified tea waste adsorption.	
Mining Waste Leachate	Mostly, mining activities discharge heavy metals into the environment. In this study, adsorption treatment is used to remove heavy metal ions from synthetic solutions and from mining waste leachate using spent coffee grounds was investigated. The percentage of metal removal gradually increases with the increasing dosage of adsorbent. Furthermore, the maximum Zn, Cd and Ni uptake values were calculated at 10.22 mg/g, 5.96 mg/g and 7.51 mg/g, respectively, while using unwashed coffee grounds (UCG) as adsorbent and 5.36 mg/g, 4.28 mg/g and 4.37 mg/g when employing washed coffee grounds (WCG) as adsorbent.	(Ayala & Fernández, 2019a)
Landfill Leachate	Adsorption is widely used to remove colour and organic matter. This research evaluated the effectiveness of spent coffee grounds (SCG) activated carbon in removing organic matter and colour from landfill leachate as well as its maximum adsorptive capacity. Batch tests for real landfill leachate shows great reductions for COD and colour (90%). Leachate from landfills has been effectively treated using SCG activated carbon.	(Ayala & Fernández, 2019b)

#### 2.9 Adsorption

Adsorption is defined as the adherence of a liquid to the surface of an adsorbent, resulting in the formation of an adsorbate film at the interfacial layers, where the progressive adsorptive process occurs. Adsorption is divided into two types based on the nature of the forces involved which is physisorption and chemisorption. Physisorption involves only weak Van der Waals contact without any redistribution of electron density. Chemisorption however incorporated creation of strong chemical or ionic bond and exhibit rearrangement of electron density due to the transformation of components in a chemical form. Adsorption is a popular technique for removing pollutants from wastewaters. For the design and efficient operation of adsorption processes, equilibrium adsorption data is necessary. Biochar adsorption is a physicochemical process that has been reported as low cost and effective method for removing

high molecular weight refractory organic matter from landfill leachate. The mechanism of adsorption process shown in Figure 2.3.



Figure 2.3: Mechanism of Adsorption Process (Ameri et al., 2020)

#### 2.10 Biochar as an adsorbents

The production of other sorbents to replace the expensive activated carbon has been intensified in recent years. Consideration has been focused on various natural solid for its ability to remove pollutants from contaminated water at low cost. Cost is truly a crucial factor for comparing the adsorbent materials.

Biochar (BC) is a carbon-rich solid substance made from biomass such as wood, dung, or leaves using a thermochemical process called pyrolysis which in a tightly enclosed container with little or no ventilation (Kamarudin et al., 2022). Biochar and charcoal are both made from organic parent materials that have been burned or pyrolyzed in the absence of sufficient oxygen. The term "biochar" is used when the material is burnt with the purpose of amending soils, using it as carbon sink or filtration of percolating soil water, whereas the term "charcoal" is used when the material is charged with the intent of being utilised as an energy source (Berger, 2012).

Biochar has been used in wide water and wastewater treatment due to the unique properties, for example, adsorption capacity, microporosity, specific surface area and ion exchange capacity. The considerable number of surface functional groups and the large surface area of the biochar, which efficiently absorbed and eliminated a significant amount of the organic compounds from the leachate (Yaashikaa et al., 2020).

Nowadays, incorporating activated carbon (AC) into leachate treatment involves a high cost. Biochar is less expensive than activated carbon because it does not require an additional activation process. In other research, the price of biochar was found to be nearly half than the price of activated carbon, and its adsorption capability was shown to be nearly equal. However, due to the low costs of its production the use of biochar seems to be an interesting alternative. The finding from other research that uses biochar as a adsorbent in adsorption treatment are displayed in Table 2.4 below.

Type of sample	Type of adsorbent	Parameter study	Summary of outcome	References
Leachate	Biochar	Lead, manganese, and copper	The study carried out using wood-derived biochar (BC) in removal of Pb, Mn and Cu from landfill leachate. To assess the impact of BC particle size on adsorption properties, BC was used in two forms which are pulverized (PWB) and crushed (CWB). The contact times of 200 and 150 min were sufficient to attain adsorption equilibrium condition, respectively for PWB and CWB. The removal efficiency of the heavy metals only slightly enhanced as BC dosage exceeded 20 g L- 1. PWB showed the highest experimental adsorption intensity of 1.58 mg g- 1 for the removal of Mn from the landfill leachate.	(Zand & Abyaneh, 2020a)
Produced Water (PW)	Tea Waste (TW) Biochar	COD	In this research, tea waste (TW) biochar was used for the removal of organic pollutants from produced water (PW). The removal of organic pollutants was measured in terms of COD. In a batch adsorption study, the performance of biochar was investigated at various biochar dosages, pH levels, and contact times. The modified tea waste biochar (MTWBC) was able to remove $90.5 \pm 0.5\%$ and $95.95 \pm 0.05\%$ of COD from the produced water in an acidic and alkaline condition, respectively. Whereas treated tea waste biochar (TWBC) removed $89.35 \pm 0.5\%$ COD at optimum conditions. It can be concluded that the biochar produced by tea waste offered a convenient and cost-effective means for the removal of COD in PW.	(Khurshid et al., 2021)
Landfill Leachate	Wood-Derived Biochar	Cadmium (Cd)	In this study, the results indicated that the wood-derived biochar is an effective adsorbent for the removal of Cd from landfill leachate. The contact time of 200 min was sufficient to reach adsorption equilibrium condition.	(Zand & Abyaneh, 2020b)

Table 2.4: Literature Reviews on the use of Biochar in Leachate and Wastewater Treatment.

			The removal rate of Cd only slightly enhanced as biochar dosage exceeded 20 g L-1 in leachate.	
Wastewater	Walnut Shell Biochar	Chromium	The use of walnut shell biochar (WSB) showed in this research. The result shows that the maximum removal efficiency of Cr(VI) is 93%. The maximum removal was attained at 110 mg/L Cr, 1.1 g/L WSB amount, with pH 5.5 and 2 hours contact time.	(Kokab et al., 2021)

#### 2.11 Critical Operation Parameter for Adsorption Process

Many influence of major parameters governing the efficiency of the adsorption process such as, solution pH, sorbent dose, initial concentration, and contact time. Table 2.5 below shows the summary of a few studies that were done to determine the optimum parameter which is pH, contact time, dosage and agitation speed for the adsorption process used for leachate treatment.

#### **2.11.1 Effect of Amount of Dosage**

Adsorbent dosage is one of the important operating factors to determine the capacity of an adsorbent for a given adsorbent amount under the operating conditions. Adsorbent dosage can also influence the efficiency of adsorption Generally, the higher amount of adsorbent dosage provides an increase in the adsorption removal efficiency due to greater available adsorption sites of the adsorbent and resulting in greater removal of pollutants (Mosoarca et al., 2020).

According to Chávez and Galiano, (2019b), mentioned that with an increase of adsorbent dosage, the available adsorption surface and availability of more adsorption sites also increase. It also resulted that more adsorbate attached to the surfaces. The results obtained at the end of the experimentation indicate that the removal percentage of ammonia increased with an increase in the adsorbent load from 3 to 9 g/L. and the ammonia removal percentage was 51.6%. Next, according to Bazrafshanp and Ahmadip, (2017b), mentioned that adsorbent dose significantly influences the amount of adsorbed. The results showed modify tea waste by Zncl<sub>2</sub> that the removal efficiency increased from 83.3% to 89%, with an increase in the biosorbent dose from 1 to 3 g/L. Table 2.5 below shows the summary of a few studies that were done to determine the optimum dosage for the adsorption process used for leachate treatment.

#### 2.11.2 Effect of pH

One of the most important factors affecting the capacity of adsorbents in wastewater treatment is pH. The pH value of the solution was an important controlling parameter in the adsorption process.

According to the study from Bazrafshanp and Ahmadip, (2017b), it shows that the removal of leachate onto modified tea waste ZnCl<sub>2</sub> increases significantly with decreasing pH. The maximum removals of leachate for a contact time 60 min were carried out at pH 12. The hydrogen ion and hydroxyl ions are adsorbed quite strongly; therefore, the adsorption of other ions is affected by the pH of the solution. The pH change affects the adsorptive process through dissociation of functional groups on the active adsorbent surface. Next, according to Padmavathy, Madhu and Haseena, (2016), the maximum removal efficiency of hexavalent chromium is higher at low pH. As the pH was increased from 3 to 10 efficiency decreased as. The optimum pH was at 3.0 and all other experiments were done at this pH. As pH increases the surface of magnetite nanoparticles becomes more negatively charged. This causes increased repulsion between Cr (VI) and magnetite nanoparticles. Hence the removal efficiency decreases with an increase in pH.

#### 2.11.3 Effect of Contact Time

Contact time is one of the main factors that affect the adsorption process. Contact time is crucial in the adsorption process, because contact time allows the diffusion and adhesion of adsorbate molecules to take place. Table 2.5 summarizes a few studies that were conducted to determine the contact time for the adsorption process used to treat leachate.

The summary of a few studies that were done to determine the optimum pH for the adsorption process used to treat leachate is shown in Table 2.5. From the table, the constant contact time and shaking speed are determined. Contact time and shaking speed in this study referred to the research from Daud et al. (2018). In this previous research, the parameters that removed were COD and NH<sub>3</sub>-N with using Mixed Granular as adsorbent. It able to remove of COD for effect shaking speed and shaking time for 40% and 55%, respectively.

				Working Range				
Type of Adsorbent	Sample	Researcher	Parameter	рН	Contact Time (min)	Dosage (g)	Speed (rpm)	Efficiency
Cockle Shells	Landfill Leachate	(Daud et al., 2017)	COD	2-10 (5.5)	105	8, 16, 24, 32, 48, 64 (35)	50, 100, 150, 200 (150)	The result from this study shows that the COD removal for effect shaking speed, pH and dosage are 28%, 53% and 55%, respectively.
Granular Activated Carbon and Green Mussel	Landfill Leachate	(Detho et al., 2021b)	COD and Ammoniacal Nirogen	4-12 (7)	5 to 360 (120)	3–80 (57)	50-200 (200)	The results revealed that the optimal reduction rate of COD for effect shaking speed, pH, dosage and contact time are 75%, 70%, 88% and 72%, respectively. Then, the ammoniacal nitrogen removal for effect shaking speed, pH, dosage and contact time are 65%, 65%, 82% and 63%, respectively.
Mixed Feldspar and Cockle Shells	Landfill Leachate	(Daud et al., 2018)	COD and Ammonia	2, 4, 6, 7, 8, and 9 (6)	60-360 (120)	4–56 (32)	50-150 (150)	From this study, the results shows that the optimum percentage removal of COD for effect shaking speed, pH, shaking time and dosage are 40%, 45%, 55% and 71%, respectively. Next, the optimum percentage removal of NH3-N for effect shaking speed, pH, shaking

# Table 2.5: Literature Review on The Optimum pH, Contact Time, Dosage and Agitation Speed for Leachate Treatment by Using Adsorption Process