# BIOSORPTION OF COLOUR IN LANDFILL LEACHATE USING ACID PRE-TREATED *HYDRILLA VERTICILLATA*

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BIOSORPTION OF COLOUR IN LANDFILL LEACHATE USING ACID PRE-

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| BET | Brunauer-Emmett-Teller |
| BOD | BioChemical Oxygen Demand |
| COD | Chemical Oxugen Demand |
| FT-IR | Fourier Transform Infrared Spectroscopy |
| HCL | Hydrochloride acid |
| PFO | Pseudo First Order |
| PSO | Pseudo Second Order |
| PZC | Point Zero Charge |
| SS | Suspended Solid |
| O—H | Carboxyl group |
| C=C | Alkene group |
| C—N | Amine group |
| ZP | Zeta Potential |

# ABSTRAK

Leachate atau larutan lesap dari tapak pelupusan adalah cecair kompleks dengan pelbagai jumlah dan struktur kandungan cecair, komposisi kimia, dan lain-lain. Ia mengandungi sejumlah besar sebatian terbiodegradasi dan tidak terbiodegradasi seperti bahan organik, fenol, nitrogen ammonia, fosfat, logam berat dan sulfida, serta warna yang kuat dan bau yang tidak menyenangkan. Terdapat beberapa sistem rawatan yang telah direkabentuk untuk merawat warna larut lesap, tetapi setiap sistem rawatan mempunyai hadnya yang tersendiri terutamanya dari segi kecekapan yang rendah, pengeluaran sisa sekunder dengan kos operasi yang tinggi. Satu kajian mengenai pelbagai biopenjerap dalam menggalakkan kelestarian alam sekitar dan ekonomi telah menjadi percubaan terkini oleh para penyelidik untuk menghilangkan warna larut lesap dari tapak pelupusan. Akibatnya, biosorpsi menggunakan biojisim kos rendah seperti *H. verticillata* telah menunjukkan hasil yang menjanjikan dalam penyingkiran warna tetapi kurang ditkaji dengan menggunakan spesies rumpput air tropika. Oleh itu, kajian ini bertujuan untuk menyiasat potensi *H. verticillata* untuk digunakan sebagai biosorben untuk penyingkiran warna, daripada larut resapan tapak pelupusan. Teknik ini melibatkan pencirian *H. verticillata* pada kapasiti biosorpsi maksimum (qmax) dan peratusan penyingkiran warna (R%). Kajian telah dibuat mengenai kesan pra-rawatan ke atas biosorben untuk menyiasat kapasiti biosorpsi. Pencirian biosorben ditentukan oleh Fourier Transform Infrared Spectrophotometer (FT-IR), Brunauer-Emmett-Teller (BET) dan cas sifar mata (pHpzc). Biosorpsi menggunakan mod kajian kelompok telah dikaji selanjutnya untuk kesan pelbagai parameter operasi seperti masa sentuhan (20-100min), pH (2-6), dan dos biosorben (1.0-5.0 g/L). Keputusan menunjukkan bahawa masa keseimbangan untuk semua spesies rumpai laut boleh dicapai dalam masa 60 minit pada

suhu bilik. *H. verticillata* dengan pra-rawatan dengan proses HCL telah digunakan untuk keseluruhan eksperimen tidak meningkatkan kapasiti pengambilan *H. verticillata* kerana peratusan penyingkiran warna yang diperolehi selepas merawat larut larut dengan ketara sangat rendah. Data isoterma penjerapan menunjukkan Langmuir lebih baik dipasang berbanding model isoterma Freundlich. Walau bagaimanapun, data kinetik lebih sesuai dengan model kinetik pseudo-tertib pertama. Kesimpulannya, rumpai laut merah *H. verticillata* dengan pra-rawatan dengan asid didapati mempunyai potensi yang rendah sebagai biopenjerap semula jadi alternatif khusus untuk warna larut resapan tapak pelupusan. Teknik pengaktifan selanjutnya, pada *H. verticillata* disyorkan meningkatkan penyingkiran warna daripada larutan larut resapan tapak pelupusan kerana ia berpotensi untuk menjadi biosorben lebih hijau yang mampan untuk kegunaan masa hadapan.

# ABSTRACT

Leachate from landfills is a complex fluid with a wide range of amounts and structures in fluid content, chemical composition, and others. It also contains high amounts of biodegradable and nonbiodegradable compounds such as organic matter, phenols, ammoniacal nitrogen, phosphate, heavy metals, and sulphide, as well as strong colour and unpleasant odour. Several treatment systems have been designed for leachate colour removal, but each treatment system has its own limitations, especially concerning low efficiency, production of secondary waste, and high operational cost. A study on various biosorbents in promoting environmental and economic sustainability has become a current attempt by researchers to remove the colour of leachate from landfills. Consequently, biosorption using low-cost biomass like *H. verticillata* had shown promising results in colour removal but somehow was less research for tropical aquatic plant species. Therefore, this study was conducted to evaluate the potential of *H. verticillata* to be used as a biosorbent for removing colour in landfill leachate. The techniques characterizing *H. verticillata* on their colour removal percentage (R%). Studies have been made on the effect of pre-treatment on the biosorbent in order to investigate the biosorption capacity. Characterization of biosorbent was determined by Fourier Transform Infrared Spectrophotometer (FT-IR), Brunauer-Emmett-Teller (BET) and Zeta Potential Measurement. Biosorption using batch study mode was further examined for the effect of various operational parameters such as contact time (20-100min), pH (2–6), and biosorbent dosage (1.0–5.0 g/L). The results reveal that the equilibrium time for *H. verticillata* can be achieved within 60min at room temperature. *H. verticillata* with pre-treatment with HCL process was used for the entire experiment did not enhance the uptake capacity of *H. verticillata* since the percentage removal of colour obtained after treatment leachate was significantly very low. The adsorption isotherm data show that the Langmuir was better fitted than the Freundlich isotherm model. The kinetic data, however, were better fitted to the pseudo-first-order kinetic model. In conclusion, red seaweed of *H. verticillata* with pre-treatment with acid was found to have a low potential as an alternative natural occurring biosorbent specifically for the colour of landfill leachate. Different activation techniques on *H. verticillata* are recommended to enhance the removal of colour from landfill leachate solution since it has the potential to become a sustainable, greener biosorbent for future applications.

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Landfilling is the engineered disposal method with the lowest possible environmental impact that involves the disposal, compression, and filling of rubbish embankments in suitable locations. Due to their simplicity, adaptability, and affordability relative to alternative disposal options, landfills are currently the most popular method of removing all waste products. It is most typically found in developing countries. In recent decades, municipal and industrial trash generation has significantly increased in many nations worldwide due to the consistent rise in industrial output and trade. Municipal solid waste (MSW) landfills' transportation of contaminated leachate and landfill gas is a substantial source of potential worry. As a result, it is impossible to overlook the effects of the various landfills that are present in the world.

Leachate from landfills is a complex fluid that appears in various sizes and shapes. High concentrations of organic matter, phenols, ammoniacal nitrogen, phosphate, heavy metals, and sulphide are among the biodegradable and nonbiodegradable substances it includes. It also has a vivid colour and an awful odour. Leachate from MSW dumps frequently went over the legal limits for effluent release. Biogas is a byproduct of biological activity in MSW landfills, also referred to as landfill gas. Organic materials that can be biologically decomposed produce biogas as a byproduct. The production of biogas from the fermentation of organic matter will increase the frequency of air pollution.

According to Jabatan Pengurusan Sisa Pepejal Negara (JPSPN, 2015), Malaysia has a total of 296 landfill sites, of which 165 are still in operation, along with 131 closed landfill sites and of the 166 operational landfills in Malaysia, only 11 are sanitary and capable of preventing environmental contamination from landfill leachate (LFL) and gas. These landfills produce leachate, which needs to be controlled and handled.

## 1.2 Problem Statement

Generally, Alor Pongsu Landfill (APLS) is a typical landfill classified as old/matured and anaerobic landfill leachate since it has been operated for more than ten years. Only the detention pond is provided with additional treatment on-site (Zakaria et al., 2018). Numerous studies comparing actual leachate discharge limits to allowed discharge limits reveal that most parameters were higher than these limits, which contributed to the pollution problem (Aziz et al., 2018).

A potential source of groundwater and surface water contamination is leachate. It's a dark shade of high-strength wastewater (Ramli et al., 2022). Leachate from landfills frequently contains colour as a by-product. Water appears colourless, and aesthetics is the primary factor in colours. Even though it is believed that colourless water is clean, it could harm people's health. Coloured water is dangerous and contains many poisonous contaminants that can harm aquatic ecosystems, human health, and the environment.

Physical/chemical, biological, and combination processes are a few of today's leachate treatment methods. Recently, techniques including enhanced oxidation, activated carbon adsorption, ion exchange, coagulation and flocculation have all been used to reduce the dangers of mature landfill leachate. Physical and chemical treatment techniques are frequently used in the leachate treatment process for their ease of use, low operational costs, and little secondary contamination.

Due to its straightforward operating setup that encourages cost-effectiveness, eco-friendliness, and eco-safety, sorption technology has recently attracted adequate attention for dye cleanup. Biosorption, also known as adsorption utilising biomass material, is a unique strategy that provides inexpensive material, efficient adsorption, and competition with commercial adsorbents (Torres, 2020). Integrating a pollutant ion (sorbent) into a biological substance is called biosorption (biosorbent). According to a prior study using the algae *E. spinosum*, modification techniques have been used to assess the adsorption capacity by physical and chemical pretreatment. The modification procedure may either boost or decrease the biosorption efficacy of algal biomass, according to the results of the previous study. In this study, *H. verticillata* was used as a biosorbent to remove the colour from landfill leachate. The perennial freshwater aquatic plant *H. verticillata* is widespread throughout the world. In freshwater bodies, it grows as a weed in most countries, including Malaysia. The biosorption in removing colour from landfill leachate using *H. verticillata* after being exposed to hydrochloric acid (HCL) was carried out to understand the capability of *H. verticillata* that had been treated with hydrochloric acid (HCL).

This research may be the first in Malaysia to use *H. verticillata* , which has been acid-pretreated to remove the colour from landfill leachate. This study should be made public because the use of *H. verticillata* for leachate colour removal or pretreatment and reusability tests has never been published. Therefore, the study's primary goal is to add to our understanding of *H. verticillata* treated with acid by evaluating the sorbent's ability to remove the colour of landfill leachate from the perspective of its economic viability for actual industrial use. Hopefully, all landfills in Malaysia will benefit from the study's practical usage of novel biosorbent.

## 1.3 Objectives

The objectives of this project are to evaluate the performance of *H. verticillata* as bio sorbent in removing colour from landfill leachate.

The specific objectives are as follows:

i. To characterize the bio sorbent made of *H. verticillata* treated with acid.
ii. To evaluate the impact of three variables (i.e., dosage, contact time and pH value) on the color removal efficiency from the leachate.
iii. To measure the biosorption mechanism based on adsorption isotherms and kinetic models.

## 1.4 Scope of Work

The leachate sample was collected APLS. The landfill leachate at APLS is classified as stabilised landfill leachate due to the $BOD_5$/COD<0.1, which is challenging to treat biologically (Ramli et al., 2022). The leachate sample was collected three times, and each was characterised for pH, BOD, COD colour, turbidity, total suspended solids, and ammoniacal nitrogen. Studies have been conducted into *H. verticillata* potential for biosorption. Previously, acid pre-treatment was investigated at 0.25M-1.25M of HCL on biosorption capability (Zakaria et al., 2018). The Braunauer-Emmett-Teller (BET), Fourier Transform Infrared Spectroscopy (FT-IR) spectra, and zeta potential measuring has been used to analyse the morphology, active functional group, surface structure, and chemical composition of *H. verticillata* . The biosorption isotherm model and biosorbent with particle sizes ranging from 0.6 to 1.18 mm were examined (equilibrium and kinetic study). For the biosorption experiment, the effect of dose, pH, and contact time was evaluated.

## 1.5 Dissertation Outcomes

The report is divided into the following 5 chapters:

Chapter 1: Introduction- This section describes and summarises the study that will be carried out. It discusses the history of treating leachate, the study's problem statement, the objectives, and the expected outcome.

Chapter 2: Literature Review- This chapter includes a detailed description of the study scientific terms, findings, fields of study, and conclusions, as well as references to previously published research articles. It might offer advice and recommendations to help researchers better comprehend the subject and carry out their research.

Chapter 3: Methodology- This chapter describes in detail the scientific method used to achieve the expected results as well as ways to meet the project objectives. This research specific equipment, techniques, or materials are specified.

Chapter 4: Results and Discussions- This chapter summarises all of the research findings. The data analysis, whether quantitative or qualitative, is meant to condense a large amount of information to answer research questions, test theories, and investigate challenges encountered. The results will be analysed and discussed in this chapter to answer the research objectives. The findings are expected to be consistent with past research in a similar environment. However, some variances are to be expected because the researchers use different approaches and data to attain their conclusions.

Chapter 5: Conclusion and Recommendations- This chapter summarizes the results and outcomes of the study. The research topic, as well as all objectives and expected outcomes, will be addressed. Recommendations for action are based on the findings, and the relevant literature, with limitations, are both considered.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction to Leachate

Leachate from landfills is a complex fluid that varies significantly in size and composition. The term "landfill leachate" describes the liquid that seeps through solid waste in a landfill and produces extractable, dissolved, or suspended elements, as well as precipitation, which seeps into the leachate collection system from the bottom of the landfill. It also describes the moisture present in solid waste dumped in landfills (Chen et al., 2020). Leachate from landfills has a high concentration and is complicated to remediate. It is frequently identified as having a black, dark brown colour (Ramli et al., 2022). Neighbouring ecosystems are at risk when leachate from landfills is discharged into water sources without first being treated, primarily when those water sources are located upstream of the landfill. By depositing MSW in landfills, enormous amounts of toxic leachate are created, endangering the soil, surface water, and public health. Raw leachate is directly disposed of in a natural setting without engineered liners. Leachate collection systems might pollute the liquid and negatively impact surface water and groundwater standards, with critical consequences for human and environmental health if adequately managed (Hussien et al., 2022). Concern about the safe disposal of municipal solid waste is developing as the environment becomes more polluted (MSW).

### 2.1.1 Characteristics of Leachate

Leachate is a byproduct of disposing of municipal solid waste that is produced by landfills, incinerators, composting facilities, and transfer stations. Various factors, such as age, precipitation, seasonal weather changes, waste type, and composition, affect the quality of these leachates (depending on the standard of living of the surrounding population structure of the tip). Pollutants make it challenging to manage. Leachate, also known as a water-based solution, is the term for the watery effluent created by the solid waste in landfills as a result of the physical, chemical, and biological changes caused by these materials. It contains a lot of dangerous chemicals, including ammonia, heavy metals, a diverse array of elements, and significant amounts of organic molecules. Thus, the neighbouring freshwater and groundwater are significantly impacted by hazardous leachate (Parvin et al., 2021). A dark-coloured liquid known as landfill leachate is mostly produced when rainwater seeps through the lid of a finished site or an open landfill.

Due to the features, composition, degree of degradation, and landfilling technology of the waste, the leachate components differ depending on the landfill. Inorganic macro components (calcium, magnesium, sodium, potassium, ammonium, iron, chloride, sulfate, and hydrogen carbonate), Heavy metals (cadmium, chromium, copper, lead, nickel, and zinc), and Xenobiotic organic compounds (benzene, toluene, and ethylbenzene) are the four groups that make up the composition of leachate produced at landfills (Iravanian et al., 2020). To describe the characteristics of landfill leachate, the basic metrics COD, BOD, the ratio $BOD_5/COD$, pH, suspended solids (SS), ammonium nitrogen ($NH_3$-N), be consistent on subscript and superscript, total Kjeldahl nitrogen (TKN), and heavy metals are frequently used. Leachate produced by an old landfill with low biodegradability ($BOD_5/COD<0.1$) is known as stabilized leachate.

The colour of stabilized leachate indicates that it has a high concentration of organic components such as humic and fulvic chemicals. In naturally occurring organic materials with complex structures, humic substances are polymerized organic acids, carboxylic acids, and polysaccharides. Similar to this, leachate should not be dumped directly into a stream because it harms the aquatic ecology and puts the lives of the creatures therein.

### 2.1.2 Leachate Treatment

Leachate treatment and management must be done with care to prevent possible negative effects such as groundwater contamination (Mishra et al., 2018). Leachate requires effective pollution-reduction techniques prior to final release. Leachate is treated using a variety of technologies, including chemical/physical, biological, and combined techniques (Bolan et al., 2017). In recent years, physical-chemical methods have been used to reduce chemical oxygen demand (COD), suspended solids (SS), colour, and heavy metals in stabilized leachate. One such method is the coagulation-flocculation approach. Considering the complicated makeup of leachate, handling and treating it can be exceedingly challenging. Multiple treatment techniques are typically needed, and these vary depending on the nature and age of the landfill (Aziz et al., 2022).

Lagooning, activated sludge treatment, aerobic treatment, and anaerobic treatment have all seen substantial study and application. Due to its dependability, simplicity, and high cost-effectiveness, biological treatment (suspended/attached growth) is frequently used for the removal of the majority of leachate with high concentrations of BOD (Koliopoulos et al., 2018). Biological mechanisms have been shown to be particularly effective at removing organic and nitrogenous components from immature leachates when the $BOD_5$/COD ratio is high (>0.5).

The completion of the process that started at the tip is made possible by anaerobic digestion of leachates, making it especially suitable for dealing with high-strength organic effluents like leachate streams from young tips. A fully mixed aeration reactor, where biodegradation takes place and clears the area where sludge settles, is the core of activated sludge systems. Pathogens, organic trash, and inorganic waste can all be effectively and affordably treated using aerated lagoons. They are a well-liked alternative for wastewater treatment because of their low operating and maintenance expenses, especially in developing countries where specialized skills are not needed to operate the system (Godini et al.., 2020).

Flotation, coagulation/flocculation, adsorption, chemical oxidation, and air stripping can remove suspended solids, colloidal particles, floating material, colour, and dangerous compounds (Aziz et al., 2018). In order to treat a specific contaminant or in conjunction with the treatment line (pre-treatment or final purification), physical/chemical treatments for landfill leachate are generally used (stripping for ammonia). However, because leachate has a variety of characteristics, it is challenging to completely cure it using a single technique. A blended process is typically employed. Numerous approaches, such as air stripping, adsorption, membrane treatment, and advanced oxidation technology, have already been employed for the treatment of municipal wastewater. Adsorption is regarded as one of the most effective strategies for treating wastewater among all others because of a number of qualities that make it less effective than other comparable procedures (Rashid et al., 2021).

The adsorption procedure has become more crucial in recent years for the treatment of wastewater and water. Due to its straightforward design and application, sensitivity to dangerous contaminants, reliance on sustainable resources, economic viability, harmless secondary by-products, and convenience of use, adsorption techniques have been proved to be preferable to alternative approaches (Torres., 2020). To put it another way, they have excellent levels of dependability, energy efficiency, design flexibility, technological maturity, and the capacity to regenerate, making them a good alternative option for water filtration. Adsorbent pores have a high adsorption capacity if their specific surface area is big. Because there are so many tiny pores between the adsorption surfaces, there is a huge interior surface area in a small volume. Adsorption is still subject to substantial limitations, such as the high cost of adsorbent and adsorbent replenishment, which could lead to losses. Furthermore, adsorbent pores may have issues due to the presence of fine material. The type of adsorbent utilized has an impact on adsorption performance as well.

## 2.2 Introduction to *H. verticillata*

*H. verticillata* is a prolific, rooted submerged macrophyte, that is native to the warmer regions (Asia) and is a submerged, perennial and vascular aquatic plant found in freshwater habitats native to Asia and Australia that can be found on every continent except Antarctica (Jain et al., 2018). It is highly invasive where it hinders navigation, impacts water intake and delivery systems, limits recreational uses, outcompetes native vegetation, acts as a breeding ground for mosquitoes, destroys fish and wildlife habitats, created significant ecological, and human-related problems in many aquatic systems worldwide (Matthew et al., 2019).

*H. verticillata*, also known as Hydrilla, is a monocotyledonous angiosperm (family Hydrocharitaceae) with a rooted submerged growth type that responds to environmental variables with great variability. *H. verticillata* is a submersed plant with stems branching above and rooting freely from the lower nodes depending on the water depth (Sangwijit et al., 2021). These species improve light acquisition by having grown tall, dense canopies with biomass heavily focused near the surface of the water. The content of dissolved nutrients, the active reaction and mineralization of water, the type of bottom sediments, illumination, and flow rate do not significantly limit *H. verticillata* growth and distribution (Efremov et al., 2020).

### 2.2.1 Structure and Species Description of *H. verticillata*

The shoot morphology of *H. verticillata* is very flexible, as is observed for most aquatic plants. The number of leaves in the node, shape, length, width of the leaf blade, type of branching of the shoot, and the length of the internodes are the factors that vary the most. *H. verticillata* monoecious and dioecious biotypes exhibit pronounced seasonal changes in turions production (Efremov et al., 2020). The in-depth analysis of hydrilla morphology are shown in **Figure 2.1**. The plant has long, slender stems that are terete (circular in cross-section) and can reach lengths of several meters. The stems can develop stoloniferously, with stolons growing in or just above the bottom sediments or developing upright in the water column. While upper and median leaves are grouped in whorls of three to eight or more, lower leaves alternate in opposite pairs (typically towards the plant's base). Smaller, somewhat oval leaves are found on the lower portions of the stem together with green, sessile, and oblong (5-15 mm long; 2-4 mm wide) leaves.

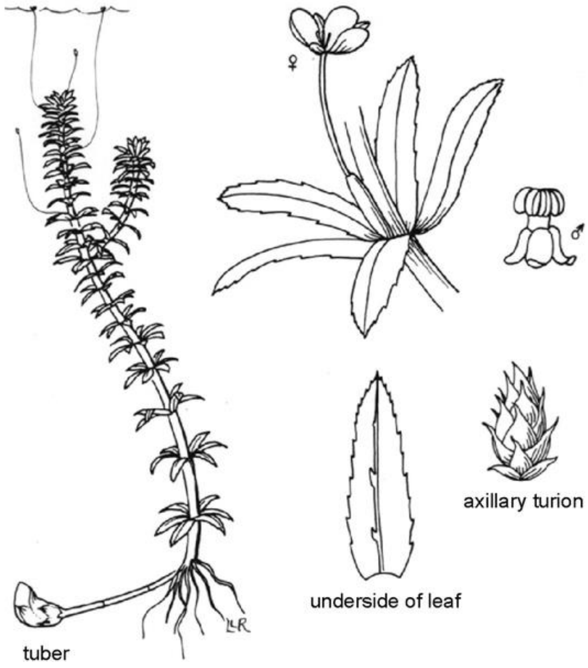


**Figure 2.1** *H. verticillata* Morphology (IFAS Centre for Aquatic Plants, University of Florida, Gainsville, 1990)

The leaves of young plants are thin and delicate. When the plant matures, the leaves become more uniform and fibrous, with serrations along the borders and a midrib with spines beneath. Hydrilla flowers are unisexual, solitary, and insignificant, measuring no more than 4–5 mm across the summit. Both staminate and pistillate flowers are whitish (occasionally with crimson streaks), with three petals and sepals.

### 2.2.2 *H. verticillata* Modification (Pre-treatment with Hydrochloric Acid (HCL))

The goal of seaweed alteration is to boost biosorption capacity. This is accomplished by increasing the accessibility of dye molecules to seaweed cell walls. With a high surface-to-volume ratio, high accessibility is possible. The seaweed biosorbent's accessibility is mostly governed by its specific surface area and pore size.

According to previous study, chemical pre-treatment with acid (hydrochloric acid, nitric acid, and phosphoric acid) reduced the removal effectiveness of MB dye due to a decrease in the electronegativity of the algal surface (Mokhtar et al., 2018). However, one study claimed that the alga was acid pre-treated in order to improve sorption performance and to strengthen it for Hexavalent Chromium(Cr(VI)) sorption processes (Husien et al., 2019). In general, numerous pre-treatments can be applied to improve the removal efficiency of metal ions by biomass. As a result, the impacts of specific surface area and pore size on biosorption performance should be studied.

## 2.3 Hydrilla ventricilata Charcteristics

### 2.3.1 Functional Groups of Biosorbent Surface (FT-IR)

Biosorption capability is highly influenced by functional groups. Fourier transform infrared spectroscopy (FT-IR) was utilised to identify useful functional groups in sorbents and to explore the variation in the vibration frequencies of these groups. It is an important analytical technique which detects the vibration characteristics of chemical functional groups present on adsorbent surfaces. (Samant et al., 2018).

The cell walls of various biosorbents contain a variety of different functional groups that contribute to the biosorption process (Redha, 2020). The variation of the functional group such as carboxylic, hydroxyl, phosphoryl, and sulfydryl on the surface of the cell wall is responsible for the mechanism differences (Mokhtar et al., 2018). The presence of several functional groups in biomaterial cell walls, such as carboxyl, sulphate, amino, hydroxyl, and phosphate groups, increases the occurrence of ion exchange (Bilal et al., 2018).

### 2.3.2 Brunauer-Emmett-Teller (BET)

The Brunauer-Emmett-Teller (BET) method is a widely used analysis technique for measuring surface areas of porous structures. The BET method is named after the last name of the scientists who developed the BET theory in 1938. The BET theory is based on generalization of the Langmuir theory to multi-layer 2 adsorption of gas molecules on a solid surface. The success of these theories lies in the fact that they can predict the number of adsorbate molecules present in the first layer covering the surface of the solid, also known as the monolayer loading capacity (Sinha, 2018). Some of the underlying assumptionsof the BET theory are (1) adsorption occurs on a uniform/homogeneous surface and all the gas molecules in the first adsorbed layer have equal energies of adsorption, (2) the uppermost molecules in adsorbed stacks are in dynamic equilibrium with the vapor, (3) the differential energy of physisorption for the first layer, E1 is higher than the heat of liquefaction, EL, (4) there is no lateral interaction between adsorbate molecules in the same layer, and (5) the second and subsequent layers formation start before the completion of the first layer.

### 2.3.3 Zeta Potential:Point Zero Charge (PZC)

Zeta potential is am electrical potential developd at the solid-liquid phase interference. The interference science that occur in colloin, suspension, composite, adhesive, paints, and coating, led to the applications.

Every particle of a material on its surface is charged. When this particles come in contct with a liquid at counter charge develop at the interference, and the particles acquired charge at the surface. This charge immediately compensated bycounter ions from the bulk. Such phenomenon originates a potential diffetrence between the particles and bulk. This is the zeta potential, the extent o which determines the degree of adherence of the two surface. zeta potential is a valuable tools to explain many phenomenal like lotus effect, stability of colloid and others (Kamble, et al., 2022).

## 2.4 Biosorption

Biosorption is a sort of sorption technology in which the sorbent is produced from biological sources. It is a variant of the sorption techniques in which the sorbent is a material of biological origin. Today, biosorption is a process that is used as an attractive alternative for removing pollutants. Within this context, biosorption is a general term that describes the removal of pollutants by their binding to the material of biological origin (biomass) (Torres, 2020). Biosorption is increasingly recognised as a simple, cost-effective, and ecologically acceptable method of pollution removal. Biomaterials for biosorption are often sourced from natural sources that are non-synthetic, low-cost, and environmentally beneficial; the biosorption technique is simple, easy to operate (Anuar, 2019), and energy-independent (Esmaeili & Aghababai Beni, 2014). The biomaterials create sludge-free effluents at the end of the procedure and can be reused for several cycles of treatment (Bada et al., 2017).

The biosorption process is multi-layered, involving ion exchange, chelation, surface complexation, physical adsorption, and surface microprecipitation (Mokhtar, 2018). Both living and non-living forms of biomaterial can be employed as biosorbents in biosorption, which is referred to as a metabolically-passive process. Taking this into account, the use of biological materials as sorbents has an important alternative: this biomass can be alive or dead (Torres, 2020). Bacteria, algae, fungi, animal and fruit skins, plant leftovers, active sludge, and biopolymers are examples of biosorbents. According to experts, the following conditions should be met by a commercial biosorbent: (1) A significant biosorption capacity as well as adequate kinetics (Wang et al.: 2017a). (2) Appropriate size, shape, and physical qualities (Praveen et al., 2021). (3) Separation of biosorbents from solutions should be cheap, fast, and efficient. (Xin et al., 2017). (4) High mechanical strength (Wang et al., 2017a), thermal stability (Wang et al., 2017a,d), and chemical resistance (Wang et al., 2017a,d) (Lingamdinne et al., 2017). (5) Biosorbents are widely available, as are low-cost preparation methods. (Praveen et al., 2021). (6) The ability to regenerate and reuse (Saha e al., 2017). Non-living bio sorbents are advantageous not only because they are less expensive but also because they are easy to handle, do not require food expenditure for cell growth, and are resistant to hazardous effects.

It is recommended to use biosorbents with relatively high biosorption capacities, as this suggests that a greater amount of sorbate can be biosorbed; biosorbents with low biosorption potentials will need to be replaced eventually (Torres, 2020). Other factors to consider when choosing a biosorbent include the degree of sustainability in terms of any negative environmental effects of using the biosorbent, the speed of biosorption of target species in terms of removal efficiency, and the possibility of regenerating and reusing the biosorbent.

Following that, biosorption has limits in its industrial applicability. The type of biosorbent utilised has a significant impact on biosorption performance. Because some biosorbents have poor biosorption performance, some chemical modifications are required to improve efficiency, which may incur additional costs in the process (Mokhtar et al., 2018). The selection of appropriate biosorbents should take into account not only their removal efficiency but also the overall raw material preparatory cost as a deciding factor (Bulgariu et al., 2019). Some sorbents also require an optimal pH to promote high pollutant absorption. However, it is impossible to change the pH of a large volume of industrial wastewater only to meet the pH requirement. The main downside of the biosorption process is the large amount of end-product biomass that contains high concentrations of contaminants (Torres, 2020). As a result, effective garbage disposal is critical.

### 2.4.1 Biosorption effective factor

Taking this into account, factors such as pH, contact time, and amount of biosorbent are evaluated to optimize the biosorption process (Torres, 2020).

#### 2.4.1(a) Dosage

The biosorbent dose is the quantity of biosorbent employed per volume of effluent. The potential of a certain biosorbent to adsorb dye is revealed by a study on the influence of biosorbent quantity. The number of sorption sites and the surface area generally increase as the amount of biosorbent increases (Verma et al., 2017). The removal efficiency will soar as a result. The ideal dosage for treatment processes is crucial for industrial-scale applications from an economic point of view. A crucial factor in the sorption process is frequently the biosorbent dosage. Diagrams based on biosorbent amount and biosorption capacities show that the proportion of biosorption frequently has a direct relationship with the amount of biosorbent. The previous researcher used the macroalgae Chaetomorpha sp., Polysiphonia sp., Ulva sp., and Cystoseira sp. to study the effects of biosorbent dosage on zinc biosorption (Deniz and Karabulut, 2017). According to the study, the biosorption capacity rose along with the amount of biosorbent material. In studies to optimize the amount of biosorbent dosage, the removal efficiency and biosorption capacity curves are often plotted along with the dose of biosorbent. The same point is where both curves peak, indicating that the ideal dosage has been established. It should be emphasized that researchers can take all possible steps to increase biosorbent capacity and reduce biosorbent dose; in other words, employing innovation in biosorbent modification, coming up with the shape and size, and constructing a suitable reactor can all help with this issue.

#### 2.4.1(b) pH

The biosorption process depends heavily on the pH of the solution. Therefore, it is crucial to look into how well biosorption works with respect to pH. As was previously mentioned, the pH at which biosorption takes place is crucial and directly affects the capacity for biosorption as well as, in some cases, the method by which it takes place. Because it affects the adsorbent surface charge, level of ionization, and adsorption type, the pH of the solution affects separation by hydrolysis, complexation, and oxidation-reduction (Dhanarani et al. 2016). The chemistry of metal ions and functional groups in bio sorbents are both influenced by pH. (Wei et al., 2016). In addition to being necessary for microbial growth and enzyme function, pH also has the capacity to separate bonding sites (Karthik et al., 2016). The biosorption process would be impacted by different species' affinities for the functional groups of the biosorbent.

#### 2.4.1(c) Contact Time

For a biosorption process to be successful, equilibrium contact time must be attained. A high rate of biosorption is one of the additional requirements for an excellent biosorbent (Zhou et al., 2019). Since the parameter is crucial for biosorption optimization, it is crucial to calculate such an equilibrium duration for the biosorption process (Rangabhashiyam and Balasubramanian, 2019). According to a prior study, extending the period before the system reaches equilibrium can lead to a rise in biosorption. Under test conditions, lengthening the contact duration would enable the biosorbent substance to reveal its highest biosorption capacity (Ali Redha, 2020). Increasing contact time would have no further impact once the biosorbent reaches its maximal biosorption capacity under specific conditions and its binding sites are fully saturated. In general, as contact duration lengthens, removal effectiveness grows. A longer contact time will enable the dye molecule to occupy the sorbent's accessible active site (Manna et al., 2017).

### 2.5 Biosorption Equilibrium (Isotherm modelling)

Adsorption isotherm models were employed to investigate the biosorption isotherm and determine the biosorption equilibrium (Lu et al., 2020). A proper understanding and interpretation of adsorption isotherms is critical for the overall improvement of adsorption mechanism pathways and effective design of adsorption system (Ayawei et al., 2017). The adsorption can be improved by supplying constant values. Isotherm expresses biosorbent surface attributes and clarifies the biosorbent-surface biosorbent dependence (Hasan et al., 2016). Among the criteria used to compare the amount of biosorption is the analysis of adsorption isotherms for each biosorption process (Nayak et al., 2017). The majority of academic adsorption studies used Langmuir and Freundlich isotherm models because they are the most accurate at forecasting experimental equilibrium biosorption data. (Gomez-Gonzalez et al., 2016). Langmuir adsorption which was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the adsorptive capacity of various adsorbents. Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered. The Langmuir equation can be written in the following linear form:

$$\frac{\mathbf{C_e}}{\mathbf{q_e}} = \frac{\mathbf{1}}{\mathbf{q_m K_e}} + \frac{\mathbf{C_e}}{\mathbf{q_m}}$$

(2.1)

Where, $C_e$ is the concentration of adsorbate at equilibrium (mg g$^{-1}$). $K_L$ is the Langmuir constant related to adsorption capacity (mg g$^{-1}$), which can be correlated with the variation of the suitable area and porosity of the adsorbent which implies that large surface area and pore volume will result in higher adsorption capacity. The empirical model calculates the maximum biosorption capacity based on three hypotheses: (1) monolayer coverage of the biomass surface, (2) homogeneous distribution of sorbate binding sites, and (3) no lateral contact between sorbate molecules (Tural et al., 2017).

Freundlich isotherm is applicable to adsorption processes that occur on heterogonous surfaces. This isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies. The linear form of the Freundlich isotherm is as follows:

$$\mathbf{\log q_e = \log K_F \frac{1}{n} \log C_e}$$

(2.2)

Where $K_F$ is the adsorption capacity (L/mg) and $1/n$ is adsorption intensity; it also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites (Ayawei et al., 2017). Freundlich, on the other hand, with the theories of (1) multilayer adsorption, (2) heterogeneous distribution, and (3) reversible adsorption, fits well with experimental data from most adsorption instances.

## 2.6 Kinetic Modelling

For the design of process equipment, the biosorption kinetics and time data are absolutely essential. (Wei et al., 2017) Understanding the metal ions removal process utilizing the biosorbents in terms of the rate constant is made easier by the biosorption kinetics. Given that the biosorption rate affects the solid-liquid interface, the residence period of the biosorbate is crucial (Rangabhashiyam, 2018). According to a study, extending the period before the system achieves equilibrium can result in a rise in biosorption (Redha, 2020). The experimental data can be utilized to analyze the processes of rate-governing phases in the biosorption process, such as mass transfer, using kinetic isotherm models. Experimental data can be determined using batch reactions for a variety of parameters, including initial concentration, contact time, dosage, pH, and temperature. After then, kinetic models are used to analyze the experimental results.

### 2.6.1 The Pseudo First Order (PFO)

The PFO model is frequently used to describe kinetic processes in non-equilibrium situations (Wang, 2019). The pseudo-first-order kinetic model may accurately anticipate the beginning of the reaction but is insufficient to forecast the biosorption kinetics of the entire biosorption process. (Daneshvar et al., 2017). According to the PFO hypothesis, during the initial phases of adsorption, the adsorbent's fraction of occupied active sites approaches zero.

### 2.6.2 Pseudo-Second-Order (PSO)

A pseudo-second-order (PSO) equation is used to describe chemisorption. The electron-sharing or transfer chemical adsorption that exists between the adsorbate and the adsorbent is assumed to be the control step of the adsorption process by the pseudo-second-order rate equation of the chemical reaction (Li et al,. 2018). A pseudo-second order equation has several advantages, including the ability to compute the equilibrium capacity and the initial adsorption rate.

## 2.7 Along Pongsu landfill site

APLS or Beriah Landfill as shown in **Figure 2.2** in Perak was constructed as open dumping, which started its operation since year 2000. It was organised and monitored under Majlis Daerah Kerian. As shown in **Figure 2.2**, APLS is located at 5° 05'14.20" N and 100° 36'10.53" E and approximately covers an area of 8 acres within palm oil plantation. Furthermore, the site is positioned on an area of alluvium deposits which consist of silt, clay, sand, and gravel. Moreover, it receives an average of 660000 metric tons of domestic solid waste per year which represents the daily average of 200 metric tons (Zakaria and Aziz, 2018). The climate of this region is classified as a typical Malaysian Peninsula (equatorial) with a uniform daily temperature of a minimum and maximum of 30° C-40° C and high humidity of 80%-90% (Hamidi et al ., 2019). The average value of rain might become one of the factors influences the production of landfill leachate(Hamidi et al., 2019). Therefore, at APLS, a detention pond was provided for leachate collection and also as a biological treatment (natural anaerobic process) before wastewater was discharge into the environment (Zainal et al., 2022).


**Figure 2.2** Alor Pongsu Landfill Site

## 2.8 Summary of Literature Review

According to the existing literature, biosorption with low-cost biomass from different sources, including organisms (fungi, yeast, etc.), natural earth resources (clay, bentonite, etc.), plants, agricultural waste, nanomaterial, and activated sludge, shows potential as a pollutant removal method. Due to this, biosorption research has been done on colour removal in landfill leachate.

Despite the fact that an extensive study on *H. verticillata* biosorption has been conducted, this review found few information gaps. The majority of research discussed the ability of seaweed to absorb dyes, but none of them used *H. verticillata* acid-treated as a case study for removing colour from landfill leachate. However, it has been noted that numerous pretreatment techniques for seaweed biosorbent have been proposed in numerous studies. Some techniques include a lot of extra processes and have substantial operational costs.

There appears to be a dearth of studies using actual landfill leachate wastewater, particularly in the areas of colour, COD, BOD, and pH. It is essential to do a feasibility study on the *H. verticillata* bio sorbents at the lab scale for the treatment of actual textile wastewater. This provides a more comprehensive picture of the bio sorbents' ability to function as a natural polishing agent in dirty wastewater that contains a diverse mixture of organic and inorganic compounds.