

**BIOSORPTION of COLOUR in LANDFILL
LEACHATE by USING BASE PRE-TREATMENT
HYDRILLA Sp.**

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**SCHOOL OF CIVIL ENGINEERING
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BIOSORPTION of COLOUR in LANDFILL LEACHATE by USING
BASE PRE-TREATMENT HYDRILLA Sp.

By

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ABSTRAK

Biopenjerap adalah tumbuhan yang masih tidak digunakan secara meluas dalam rawatan air sisa. Penggunaannya dalam rawatan air larut lesap belum dilaporkan sehingga kini. Kajian ini mengkaji kecekapan tumbuhan *Hydrilla* terawat *base* dalam menyingkirkan warna daripada larut lesapan dari tapak pelupusan. Larut lesapan disampel dari Tapak Pelupusan Alor Pongsu (APLS) dan dicirikan. Saiz zarah 1.18 mm - 600 mm telah dipilih. Kepekatan penjerap, dos, pH dan nilai masa sentuhan dinilai secara ujian kelompok. Kepekatan penjerap optimum berlaku pada 1.0M. Asid humik dalam sampel larut lesap menjejaskan kecekapan penjerapan. Dos optimum didapati pada 1.0 g/L. Ia meningkat dengan peningkatan dos biopenjerap sehingga mencapai titik keseimbangan disebabkan peningkatan dalam bilangan tapak serapan dan luas permukaan penjerap. pH optimum biopenjerapan ialah 8. Interaksi antara cas kationik dan anionik meningkatkan kecekapan penjerapan, tetapi ia juga menjejaskan hidrolisis ikatan peptida jika $\text{pH} > 11$. Kajian mendapati masa sentuhan optimum 60 minit. Ini disebabkan oleh bilangan tapak pengikat yang lebih besar pada permukaan selular semasa proses biosorpsi awal. Analisis FTIR menunjukkan bahawa *hydrilla* mengandungi kumpulan -OH, -COOH dan -NH di mana tarikan elektrostatik berlaku. Kajian mendapati luas permukaan dan isipadu liang lebih tinggi selepas rawatan. Nilai potensi zeta maksimum (pH_{Zc}) adalah sebanyak -50.8 mV pada pH 10 sebelum rawatan dan -55.2 mV pada pH 8 selepas rawatan. Data keseimbangan menunjuk model isoterma Freundlich lebih baik daripada model Langmuir mengikut model tertib pseudo-second, mendedahkan kecekapan yang agak rendah dan tidak berkesan dalam penyiasatan ini. Penemuan semasa menunjukkan *hydrilla* bukanlah biopenjerap yang baik untuk penyingkiran warna dalam larut resapan tapak pelupusan kerana ia menyumbang warnanya sendiri kepada sampel. Penggunaannya untuk rawatan logam disyorkan dalam kajian akan datang.

ABSTRACT

Biosorbent from plant origin is still not widely applied in wastewater treatment. Its usage in leachate treatment has not been reported to date. This study examined the efficiency of Base Pre-treated Hydrilla in removing colour contaminants from landfill leachate. Leachate was collected at the Alor Pongsu Landfill Site (APLS), which was first characterised. A particle size range of 1.18 mm to 600 mm was chosen. Various adsorbent concentrations, dosage, pH and contact time values were evaluated in batch tests. The optimum concentration occurred at 1.0M. Humic acid in the leachate sample affected the adsorption efficiency. The optimum dosage was found at 1.0 g/L. It increased with increasing biosorbent dosage until it reached the equilibrium point due to the increase in the number of sorption sites and surface area. The optimum pH of the biosorption was 8. The interaction between cationic and anionic charges between sorbate and sorbent increases the adsorption efficiency, but it also affects the hydrolysis of peptide bonds if $\text{pH} > 11$. This study found the optimum of 60 min contact time. This is probably due to the larger number of binding sites on the cellular surface during the initial biosorption process. FTIR analysis shows that hydrilla contains -OH, -COOH and -NH groups where the attraction electrostatic occurred. This study found the surface area and pore volume slightly higher after treatment. The maximum zeta potential values (pH_{Zc}) determined was -50.8 mV at pH 10 and -55.2 mV at pH 8, before and after treatment, respectively. The equilibrium data were well fitted using the Freundlich is far superior to the Langmuir isotherm models followed the pseudo-second-order model, which revealed a relatively low and ineffective efficiency in this investigation. The current findings demonstrate that hydrilla was not a good biosorbent for colour removal in landfill leachate as it contributes its own colour to the sample. Its usage for metal treatment is recommended in future studies.

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CHAPTER 1

INTRODUCTION

1.1 Background

An engineered sanitary landfill is a well-managed facility that provides for municipal solid waste disposal that can preserve the environment from contamination caused by the waste stream. Solid waste typically has some moisture/liquid. Leachate forms when the liquid of solid waste flows through to the landfill. Rainfall infiltrates and percolates through decomposing garbage to produce landfill leachate, whereas landfill gas is produced by microbial decomposition in anaerobic environments (Encyclopedia of Ecology,2008).

In Malaysia, there are around 230 landfills; there are a large number of outdated and uncontrolled landfills of varying sizes that do not have suitable bottom liners or leachate collection systems in place to safeguard the environment from hazardous wastes. (Hussein et al., 2019). Due to the lack of facilities for collecting and treating leachate and infrastructure for capturing landfill gas, most landfills are not recognised as sanitary. For example, in Lawas town, located in Sarawak on the border of Sarawak and Sabah, there are no hygienic landfills. Leachate treatment and gas extraction are only available in a few of Malaysia's sanitary landfills (Hussein, 2019).

1.2 Problem Statement

The most significant threat that is posed by landfills for municipal solid waste is leachate that has not been treated (Hussein,2019). In addition, leachate that has not been handled poses a significant risk to human health as well as to groundwater and soil that has been polluted by toxins such as colour, heavy metal, and others. There are many chemical compositions of landfill leachate, and it depends on the pollutant concentrations

Besides, treatment of landfill leachate is complicated due to the complexity of the pollutants in the leachate, which usually necessitates multiple processes to reduce COD, nitrogen, and phosphorus, all of which make landfill leachate treatment expensive (Ren and Yuan, 2015). Many researchers implemented leachate treatment, including the removal of leachate colour with different techniques (Mojiri, 2020). One of the techniques is the adsorption process. Organic matter decomposition, such as humic acid, can turn water yellow, brown, or black.

Biosorption is one of the methods that can be used in wastewater treatment. When exposed to heavy metals, Ferhan and Gul (2010) discovered that adsorption was the predominant elimination method. The concentration of all metals reduced as the adsorbent content of mixed liquid suspended solids increased. We can conclude that increasing the adsorbent concentration increased metal uptake overall. Another study found that using plants (*Phanerocheate Sp.*) in the biosorption process removes organics, heavy metals, and toxicity from leachate (Ghosh and Thakur, 2016). COD decreased by 31%, lignin decreased by 19%, Fe decreased by 28%, and other components decreased by 28%. According to the use of a basic pretreatment weed for MB removal, modification of the adsorbent's surface tends to remove dyes with 77% of MD removal efficacy (Doctor of Philosophy, 2021). Unfortunately, the utilisation of biosorbent from plants for leachate treatment has received little attention among adsorption methods.

1.3 Objectives

This project's aims are to assess the efficacy of *Hydrilla Sp.* as a biosorbent for eliminating colour from landfill leachate. The specific objectives are as follows:

- i. To determine the capability of base pre-treatment *Hydrilla Sp.* to be a biosorbent
- ii. To evaluate the performance of base treatment *Hydrilla Sp.* as biosorbent to remove colour in landfill leachate
- iii. To evaluate the biosorption mechanism based on kinetic and isotherm study.

1.4 Scope of Work

The sample of leachate was collected at the Alor Pongsu landfill. The leachate sample was first characterised for COD, BOD, Colour, Ammonia Nitrogen, Suspended Solid and last but not least, pH. The raw *Hydrilla Sp.* was taken from a pond along Jalan Batu Sinar, Malim Nawar, Perak at coordinate 4°19'58.4"N 101°06'17.0"E. The adsorbent was washed and oven-dried at 105°C for 24 hr. 0.25 – 1.2 M Sodium hydroxide, NaOH solution was prepared, and the adsorbent was treated with the solution. The base-treated *Hydrilla Sp.* was then washed with distilled water, oven-dried, crushed and sieved according to size (1.18 mm – 600 µm). The performance (the effects on dosages, pH values and contact times) and the adsorption isotherm were determined in a batch study. Colour was taken as the targeted polluted due to its high level present at the APLS.

1.5 Dissertation Outlines

Introduction, methodology, findings and discussion and conclusion/recommendations are all included in the report's five sections.

Chapter 1: Introduction - This chapter provides an outline of the study's methodology and aims. In this section, you'll learn about the history of leachate treatment and the study's goals.

Chapter 2: Literature Review - With references to previously published research articles, this chapter provides a full description of technical terms, findings, subjects, and outcomes linked to the research. It can provide researchers with some suggestions and instructions to help them better comprehend the topic and conduct their research.

Chapter 3: Methodology - This chapter goes through the methods for obtaining the expected outcomes as well as ways to meet the project's objectives. The specific equipment, techniques, or materials employed in this study are specified fully.

Chapter 4: Results and Discussions- This chapter documents all of the research's findings and outcomes. Quantitative or qualitative data analysis is used to compress enormous amounts of data in order to answer research questions, test hypotheses, evaluate situations, and analyse concerns. In this chapter, the findings will be analysed and discussed in order to answer the study questions. The findings are likely to be similar to those of prior studies conducted in a similar situation. However, because the research employs diverse approaches and data to arrive at their conclusions, some discrepancies are to be expected.

Chapter 5: Conclusion and Recommendations - This chapter summarises all of the result obtained and findings. All objectives and expected outcomes will be covered, as well as the research question. Recommendations for action are made based on the findings and relevant literature, with the limits of both taken into account.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Landfill Leachate

Municipal, industrial, and commercial solid waste, as well as sludge deemed to be non-hazardous, are all routinely disposed of in landfills. Despite its possible harmful impact on the environment, sanitary landfilling is nevertheless used in waste management programs. The liquid that leaches or drains from a landfill is known as landfill leachate. Any discharged liquid that cannot be reused in future industrial processes is referred to as leachate. It could be a poisonous liquid, a chemical, or any other liquid material that is otherwise unfit for use. In landfill leachate, there are high quantities of organic contaminants, heavy metals, toxic chemicals, ammonia, and inorganic materials, as well as refractory compounds such as humic substances and contaminants of growing concern (Mojiri et al., 2020).

2.1.1 Characteristics of Leachate

Leachate quality and quantity are very dynamic and are strongly connected to variations in rainfall volume, waste composition/characteristics, age, and landfill operations patterns. The composition of landfill leachate changes dramatically depending on the season, leachate collection technology, and landfill age (Yusmartini and Setiabudidaya, 2013). Municipal landfill leachate contains a variety of substances, including organic pollutants and substrates, inorganic compounds, heavy metals, total dissolved solids (TDS), and colour. According to its age, landfill leachate is divided into three categories: young, middle, and elderly (Mojiri et al., 2020). Figure 2.1.1.1 shows the characteristic of landfill leachate in different periods.

Figure 2.1.1 The characteristics and treatability of leachate based on the age of the landfill (Mojiri et al.,2020)

Leachate type	Early	Medium-term	Old
Landfill useful life (years)	<5	5-10	>10
pH (-)	6.5-7.5 (7.0)	7.0-8.0 (7.5)	7.5-8.5 (8)
COD (g/L)	10-30 (15)	3-10 (5)	<3 (2)
BOD/COD (-)	0.5-0.7 (0.6)	0.3-0.5 (0.4)	<0.3 (0.2)
NH4 -N (mg/L)	500-1000 (700)	800-2000 (1000)	1000-3000 (2000)
COD/NH4 -N	5-10 (6)	3-4 (3)	<3 (1.5)

In the acid phase of a landfill, the leachate has a low pH, large quantities of volatile acids, and only degraded organic debris, according to this study. Most of the organic molecules in mature landfill leachate are humic and fulvic fractions, both of which contribute significantly to the landfill's methane generation and pH. Due to the

fact that waste properties vary from country to country, however, there is a little discrepancy in certain research. In comparison to Asian countries, The amount of contaminants in leachate in the U.S. and Europe is much lower than it is in Asia. Ammoniacal nitrogen in leachate from European and American countries, for example, is typically less than 1000 mg/L of $\text{NH}_3\text{-N}$, whereas it is typically greater than 1000 mg/L of $\text{NH}_3\text{-N}$ in Asian countries (Wang et al., 2018).

Furthermore, trash creation is expected to rise from 1.3 kg/capita/day in 2009 to 1.9 kg/day in 2025 (forecast) for Malaysia, which is the second-largest waste generator after Thailand. According to Tan al. et, 2020, food, paper, and plastics are the three main components of solid waste. Due to contact with rainwater, makes it looks like a lot of organic material will dissolve into the liquid phase as leachate. In landfill leachate, colour and TDS is a prevalent contaminant. The decomposition of certain organic molecules, such as humic acid (HA), can cause water to turn yellow to dark brown, highlighting the fact that colour and turbidity are created by substances and particles (Mojiri, 2020). Leachate is a strong-smelling liquid that is black or brown and smells bad. It has a lot of organic and inorganic materials in it, like aromatic compounds and humus. It also has a lot of inorganic salts like ammoniacal nitrogen, carbonate, and sulphate, as well as metal ions like chromium, lead, and copper. Leachate water has high levels of pollutants and, in some cases, is toxic to living things. This is because the waste is made up of many different things (Wang et al., 2018).

Furthermore, A water/total wastewater's dissolved solids (TDS) is a measure of the combined effect of various cations and anions on the water/chemistry. wastewater's Organic carbon decomposition can be slowed or halted by the addition of TDS, which can be generated from modest amounts of organic materials. TDS can be used to identify

dissolved organic and inorganic compounds in samples with high electrical conductivity (Mojiri et al., 2020).

Moreover, the composition of organic and inorganic pollutants is regularly in landfill leachate. Waste characteristics, landfill age, and climate affect the organic composition. The appearance of dissolved organic such as BOD₅ and COD in landfill leachate affects the percentage of total organic compounds and basically composed of volatile fatty acids and refractory humic substances that may not be efficiently degraded by conventional biological treatments, while inorganic macro components such as ammonia, aluminium and zinc comprise anions, and cations consist of low amounts of compounds compare to organics compound in landfill leachate (Mojiri et al., 2020). The presence of heavy metals in landfill leachate is the primary source of harmful pollutants. The most frequent heavy metals found in landfill leachate include chromium (Cr), manganese (Mn), cadmium (Cd), and others. Many scientists have found substantial quantities of heavy metals in landfill leachate.

2.1.2 Leachate Treatment

Leachate waste composition such as COD, BOD, pH, turbidity, suspended solids, colour, zinc, copper, manganese, cadmium and iron are the parameters of leachate that need to be investigated in the process of treatment leachate. This is because of the effects on the selection of technology for leachate treatment. Many researchers use various techniques to implement leachate treatment, including the removal of leachate colour and suspended solid (Mojiri, 2020). According (Mojiri et al., 2020), there are four types of methods most reported in landfill leachate treatment: co-treatment with wastewater, physicochemical, biological and combined methods. Adsorption, AOPs, membrane and lastly, coagulation or flocculation category as a physiochemical method in landfill leachate treatment.

Treating landfill leachate is an obstacle task. This is because landfill leachate contains a significant amount of organic matter and a large number of poisonous and organic compounds. A single biochemical or physicochemical procedure is insufficient to meet discharge limits; this requires a combination of physical and biological processing. The first problem is to select an acceptable, cost-effective, and efficient combination method. Besides, ammoniacal nitrogen levels are high in landfill leachate, making it difficult to find a nitrogen removal procedure for leachate that is both effective and comprehensive. That made the treatment process more complex and obviously affected the cost of treatment even high.

2.2 Biosorption and Adsorption

Biosorption is the economical alternative to treat wastewater, including landfill leachate treatment. For pollutant remediation, it is a significant feature of both living and dead microorganisms (and their components) (Michael, 2014). Biosorption can be done with seaweeds, plants, animals, and derived products like chitosan. Biosorption has been hailed as promising biotechnology for pollutant removal and/or recovery from solution due to its simplicity, similarity to classic ion exchange technology, apparent efficiency, and availability of biomass and waste bio-products. (Michael, 2014).

The adsorption method is the most widely used in landfill leachate treatment. Adsorption bonds gas or liquid components to a solid absorbent. According to Tan et al., 2020, Treatment uses standard and nonconventional adsorbents. Adsorbents or filters are selected based on pollutant affinity, adsorption capacity, and hydraulic characteristics.

Moreover, for the removal of both organic and inorganic pollutants, adsorption is a surface phenomenon commonly employed. So far adsorption treatment of landfill leachate (mostly with activated carbon) has yielded positive results particularly in the

removal of organic compounds and ammonia nitrogen, including removal of colour and suspended solid (Reshadi et al., 2020). Natural materials such as clays, sawdust, biosorbent, etc., improved natural materials (e.g., activated carbon from coal, wood, nutshells, etc.), synthetic materials like resins and zeolites, agricultural and industrial wastes and by-products such as ash, sludge, etc., biological adsorbents, and others can be used as adsorbents (Reshadi et al., 2020).

Basically, there are two types of biosorbent mechanisms. Firstly, physisorption is also known as physical adsorption. This particularly adsorption is a weak phenomenon due to occurs when the van der Waal forces of attraction between the adsorbate and the adsorbent are weak. Physical adsorption occurs when a multilayer of adsorbate forms on the adsorbent. It has a low adsorption enthalpy, i.e., H adsorption is 20-40 kJ/mol. It occurs at a low temperature, below the adsorbate's boiling point. The process of physisorption slows down as the temperature rises (Adsorption, n.d).

Next, chemisorption is also known as chemical adsorption. Chemical adsorption is a very strong process. Chemical adsorption begins when adsorbate and adsorbent have a chemical connection. A single layer of adsorbate formed during chemisorption. H adsorption is 200–400 kJ/mol. It's temperature-independent. Chemisorption increases with temperature and then declines (Adsorption, n.d).

2.3 *Hydrilla Sp.* as Biosorbent

Hydrilla is a submerged, perennial aquatic plant that has become the “worst invasive aquatic plant in the world.” This dreadful aquatic had been designated as a federal noxious weed. It has thrived in nearly every type of freshwater habitat, including rivers, streams, and lakes in Malaysia. It is commonly called water thyme.

Besides, *Hydrilla* has long stems (up to 25 feet) that branch at the surface and forms dense mats. They have originated on the Indian subcontinent, specifically on the island of Sri Lanka, while random DNA research suggests that India's southern mainland could also be a viable source. Freshwater lakes, ponds, rivers, impoundments, and canals are all infested with *Hydrilla*.

The plant (figure 2.3.1) has the ability to enter deep, dark waters, where most native plants are unable to thrive. The plant's strong growth can expand into shallow water locations, generating dense mats that block sunlight and displacing local flora. Lakes, ponds, rivers, impoundments, and canals were infested (*Hydrilla*, 2019).

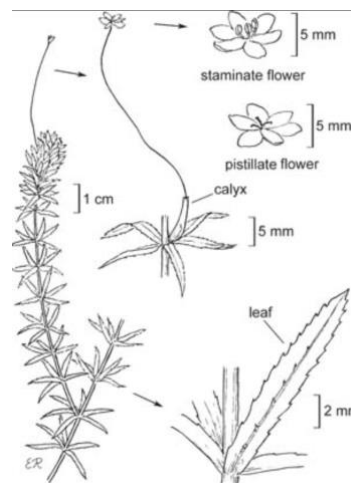


Figure 2.3.1 Illustration of *Hydrilla*

(Robert et. al.,2012)

The use of biosorbent from plants for pollutant removals has not been widely investigated. One of the studies used *Hydrilla verticillate* the biosorption and desorption work to remove Lead (II) (Dileepa et al., 2014). Pb (II) adsorption capacity of *Hydrilla verticillate* non-living biomass was evaluated in the presence of low Pb (II) concentrations in an aqueous solution. A steady increase in adsorbent dosage yielded the greatest percentage of removal of Pb (II) at the equilibrium point, according to these researchers. The biosorption's optimal pH was 4.0. When the pH was below 3.6, the