PHYSICOCHEMICAL TREATMENT OF STABILIZED LANDFILL LEACHATE USING ELECTROFLOTATION AND IRON OXIDE NANOPARTICLES COAGULATION

ABDUBAKI MOHAMED HUSSEN SHADI

UNIVERSITI SAINS MALAYSIA

2022

PHYSICOCHEMICAL TREATMENT OF STABILIZED LANDFILL LEACHATE USING ELECTROFLOTATION AND IRON OXIDE NANOPARTICLES COAGULATION

by

ABDUBAKI MOHAMED HUSSEN SHADI

**Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy**

October 2022

ACKNOWLEDGEMENT

First and foremost, I would like to express my gratitude to Allah SWT for giving me the opportunity and blessing me endlessly in finishing this work. I would like to express my sincere gratitude to my supervisor, Dr. Mohamad Anuar Kamaruddin, for providing me with an interesting topic and helping me to overcome all challenges during my candidature. I am indebted to him for his valuable guidance and his utmost support to make this research process smoother. I also would like to thank my co-supervisors, Dr. Md Sohrab Hossain and Prof. Dr. Norli Ismail for their mentor support and useful comments on this dissertation. I gratefully acknowledge the Libyan Government for awarding me the Libyan Awards Scholarship. The financial support from the Ministry of Higher Education and Scientific Research, Libya is highly appreciated.

This project would not have been possible without substantial help from Prof. Dr. Mohd Omar Ab Kadir from School of Industrial Technology, USM. Thank you very much for providing me with nanoparticles in the treatment of landfill leachate wastewater for use in my experiments. I appreciate Pulau Burung Sanitary Landfill (PBSL) management for providing the necessary permissions to collect the samples and monitor the landfill area. I am very grateful to Ms. Nona Kartina Francis for her sincere help with binding this thesis.

My heartfelt thanks go to all my family members and friends in Libya and Malaysia for their love, support and encouragement, which contributed in various ways to the completion of this thesis. Thank you all for making my Ph.D, study at USM, and my stay in Malaysia a wonderful and enjoyable experience!

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF PLATES

LIST OF SYMBOLS

α	Alpha
β	Beta
γ	Gamma
q_e	The amount of solute adsorbed per unit weight of adsorbent
C_i	The initial adsorbate concentration
C_e	The equilibrium adsorbate concentration
V	The volume of solution
M	The mass of adsorbent
a	The Langmuir constant
b	The maximum adsorption value
C	The concentration of adsorbate in solution after adsorption complete
$\Delta G°$	Gibbs free energy
$\Delta H°$	Enthalpy
$\Delta S°$	Entropy
R	The universal gas constant, 8.314 (J/ mol K)
T	The absolute temperature
K	Kelvin
K_f	The Freundlich affinity coefficient (Lmg^{-1})
n	The Freundlich exponential constant
C_e	The final concentration (mgL^{-1}) of pollutants
C_i	The initial pollutants concentration (mgL^{-1})
A	The BET constant
Xm	The amount of pollutants adsorbed by the adsorbents
k_1	The equilibrium rate constants of pseudo-first-order
K_2	The equilibrium rate constants of pseudo-second-order models

ER	The efficiency removal.
C_i	The initial pollutant concentration
Cf	The final pollutant concentration
L	The losses ratio of the nanoparticles
W_o	The weight of the nanoparticles before regeneration
Wg	The weight of the nanoparticles after regeneration

LIST OF ABBREVIATIONS

MSW	Municipal solid waste
LFL	Landfill leachate
PBSL	Pulau Burong Sanitary Landfill
COD	Chemical oxygen demand
AN	Ammoniacal nitrogen
BOD	Biological oxygen demand
DoE	Department of environment
TOC	Total Organic Carbon
IOMNs	Iron oxide magnetic nanoparticles
DO	Dissolved oxygen
SW	Solid waste
VFA	Volatile fatty acids
USM	Universiti Sains Malaysia
UV	Ultraviolet light
TSS	Total suspended solid
TDS	Total dissolved solids
DSA	Dimensionally stable anodes
DC	Direct current
EF	Electroflotation
NPs	Nanoparticles
IONPs	Iron oxide nanoparticles
TEM	Transmission electron microscopy
XRD	X-Ray Diffraction
FTIR	Fourier-transform infrared spectroscopy
SEM	Scan electron microscope
EDX	Energy Dispersive X-Ray
BET	Brunauer-Emmett-Teller
HCl	Hydrochloric acid
PZC	Point of zero charge
SBR	Sequencing batch reactor
MF	Microfiltration

OH•	Hydroxyl radicals
R^2	Coefficient of determination
UF	Ultrafiltration
PVP	Polyvinylpyrrolidone
TDIW	Textile dyeing industry wastewater
UASB	Up flow anaerobic sludge blanket reactor
RBC	Rotating biological contactor
MBBR	Moving bed biofilm reactor
MFCs	Microbial fuel cells
GAC	Granular activated carbon
PAC	Polyaluminum Chloride
DLS	Dynamic Light Scattering

LIST OF APPENDICES

RAWATAN FIZIKO-KIMIA BAGI LARUT LESAPAAN STABIL MENGGUNAKAN ELEKTRO FLOTASI DAN PENGGUMPALAN NANOPARTIKEL BESI

ABSTRAK

Larut lesapan dari tapak pelupusan sampah merupakan sumber bahan pencemar organik dan bukan organik utama disebabkan jumlah sisa buangan yang sangat tinggi serta kadar bahan-bahan berbahaya yang rendah. Kajian ini mengkaji kebolehrawatan air larut lesapan dengan menyingkirkan permintaan oksigen kimia (COD), ammonia nitrogen (NH_3-N) dan warna melalui proses elektroflotasi dan nanozarah oksida besi (Fe_2O_3). Sampel-sampel larut lesapan yang telah distabilkan dikumpul dari Tapak Pelupusan Pulau Burung, Pulau Pinang, Malaysia yang kemudiannya telah dicirikan. Penyediaan nanozarah ferum oksida adalah melalui kaedah pengisaran mekanikal kepada nanozarah. Lima langkah telah dilaksanakan dalam proses penyediaan nanozarah ferum oksida. Kajian-kajian penjerapan menggunakan satu faktor pada sesuatu masa untuk menentukan keadaan-keadaan maksimum parameter-parameter operasi. Kesemua eksperimen dijalankan pada skala makmal menggunakan kelalang Erlenmeyer 250 mL sebagai reaktor kelompok. pH, dos, masa sentuhan dan suhu telah digunakan sebagai faktor-faktor individu dengan nilai pH (2-10), dos (5-30 g/L), masa sentuhan (10-60 minit) dan suhu (RT-80 ℃). Proses elektroflotasi sebaliknya disediakan untuk rawatan pos air larut lesapan. Sepasang titanium dan elektrod anod dimensi stabil telah digunakan sebagai katod dan anod. Elektrod tersebut mempunyai permukaan dengan ukuran 18 cm^2 pada setiap bahagian. Ini diikuti dengan penentuan kecekapan penyingkiran COD, NH_3-N dan warna dengan tiga parameter operasi dengan mengaplikasikan pH (2-10), masa sentuhan (15-60 minit) dan ketumpatan arus (10-50 Am^2). Dapatan nanozarah menunjukkan yang nanozarah oksida besi mencapai peratus penyingkiran yang tinggi untuk warna di antara ketiga-tiga bahan pencemar. Penyingkiran penjerapan maksimum untuk COD ialah >67.8, NH_3-N (>35), dan warna (97%). Data isoterma adalah paling bersesuaian dengan model isoterma Langmuir manakala data kinetik diterangkan dengan baik melalui model tertib Pseudo-second, menunjukkan yang kadar tindak balas penjerapan dikawal oleh mekanisma tertib kedua (penjerapan kimia). Keputusan termodinamik menunjukkan penjerapan adalah dapat dilaksanakan, spontan, dan endotermik. Penyah jerapan, penjanaan semula dan penggunaan semula berjaya dicapai dengan 0.4 M HCl dan 0.5 M HCl. Sebaliknya, NaOH telah menunjukkan kesan rendah pada proses penjanaan semula ke atas (Fe_2O_3). Untuk rawatan pengapungan elektrik, eksperimen yang dijalankan telah mencapai kecekapan penyingkiran maksimum COD, NH_3-N dan warna pada >75, >60 dan 97% dengan pembolehubah maksimum ketumpatan arus 40 Am^2, pH 4.0, dan masa sentuhan 60 minit. Kajian ini mendapati kadar COD, NH_3-N dan penyingkiran warna meningkat dengan penurunan kepekatan pH kepada fasa berasid. Manakala ketumpatan arus mencapai penyingkiran yang signifikan pada 40 Am^2. Untuk menyiasat kesan jujukan gabungan nanozarah besi oksida dan proses elektroflotasi ke atas air larut resapan, keadaan parameter maksimum (dos, pH, ketumpatan arus dan masa sentuhan) telah dipilih. Dalam tempoh percubaan selama 120 minit, 96% COD, 99% NH_3-N dan 100% warna telah dikeluarkan pada pH 4.0, dan 20 g/L dos Fe_2O_3, manakala ketumpatan arus ialah 40 Am^2.

PHYSICOCHEMICAL TREATMENT OF STABILIZED LANDFILL LEACHATE USING ELECTROFLOTATION AND IRON OXIDE NANOPARTICLES COAGULATION

ABSTRACT

Landfill leachate is a significant source of organic and inorganic pollutants due to extremely high volumes of waste and low levels of hazardous substances. This study investigates the treatability of removing Chemical oxygen demand (COD), Ammoniacal Nitrogen (NH_3-N) and color from landfill leachate by iron oxide nanoparticles (Fe_2O_3) coupled electroflotation process. Stabilized landfill leachate samples were collected from Pulau Burung Landfill Site (PBLS), Penang, Malaysia and characterized. The preparation of iron oxide nanoparticle was through a simple method of mechanical milling process into nanoparticles. Five steps were used for the preparation of iron oxide nanoparticles. Adsorption studies were used one factor at a time to determine the maximum conditions of the operational parameters. All the experiments were carried out at laboratory scale using 250 mL Erlenmeyer flask as batch reactors. pH, dose, contact time and temperature were used as individual factors with pH (2-10), dose (5-30 g/L), contact time (10-60 min) and temperature (RT- 80 °C). In contrast, the electroflotation process was prepared for the post treatment of landfill leachate. A pair of titanium and dimensional stable anodes electrodes was used as cathodes and anodes, respectively. The electrodes had a surface area of 18 cm^2 each. The determination of removal efficiency of COD, NH_3-N and color by three operational parameters with pH (2-10), contact time (15-60 min) and current density (10-50 Am^2) were applied. The results of nanoparticles indicated that iron oxide nanoparticles achieved high percentage removal for the color as the best among the three pollutants. The best adsorption removal were 67.8, 35, and 97 % of COD, NH_3-N and color; respectively, under the maximum condition of dose 20 g/L, pH 4.0. and time 60 min. Isotherm data was best fitted by Langmuir isotherm model while kinetic data was satisfactorily described by Pseudo-second order model, indicating that the rate of the sorption reaction was controlled by the second-order mechanism (chemical sorption). Thermodynamic results revealed that the adsorption was feasible, spontaneous, and endothermic. Successful desorption, regeneration and reuse were achieved with 0.4 M HCl and 0.5 M HCl, respectively. On the other hand, NaOH showed low effect of the regeneration process on (Fe_2O_3). For electroflotation treatment, the experiments achieved maximum removal efficiency of COD, NH_3-N and color that were 75, 60 and 97 %, respectively, with best variables of current density 40 Am^2, pH 4.0, and contact time 60 min. It was found that the COD, NH_3-N and color removal rates increased with the decrease of pH concentration to the acidic phase. Meanwhile, the current density achieved great removal at 40 Am^2. To investigate the sequence effect of combined iron oxide nanoparticles and electroflotation process on landfill leachate, best parameter conditions of (dose, pH, current density and contact time) were selected. In a 120-min trial, 96 % of COD, 99% of NH_3-N and 100% of color were removed at pH 4.0, and 20 g/L of Fe_2O_3 dose, while current density was 40 Am^2.

CHAPTER 1

INTRODUCTION

1.1 Background

Municipal solid waste (MSW) is the residuals of daily practices from different sectors such as domestic, commercial, industrial, and institutional activities in urban areas (Lunag et al., 2019). The management of MSW is considered as the biggest challenge to the authorities of both small and large cities in developing countries. This is mainly due to the increasing generation of such solid waste and the burden that follows up this increase; for instance, the collection ways of disposal putting in mind the high cost (Abdel-Shafy et al., 2018). The current MSW removal in Malaysia is mainly focused on landfilling, which has been a common practice for years, that cause hazardous environmental and social issues overall (Li et al., 2017). However, due to their popularity, these landfills are becoming limited as they are filling up rapidly, and factors such as high land prices and limited space, especially in cities that are also increasing in population, make it more challenging for industries to build new dumping sites to get rid of these wastes (Abdel-Shafy et al., 2018).

The high amount of wastes in these landfills are now bringing about another issue. When excess rainwater percolates through the layers of waste in the landfills, landfill leachate (LFL) occurs (Fazeli et al., 2016). The percolating water receives contaminants from the waste materials through a mixture of physical, chemical, and microbial processes (Mukherjee et al., 2015). Landfill leachate is a runny fluid which moves through or leaches from a landfill. This liquid is either already presents in the landfill or it may be produced after rainwater, picking up dissolved materials from the decomposing wastes and mixes with them. If this leachate is not dealt with through appropriate treatment, not only the environment, but also the health of the general public will be affected due to the varying levels of soluble contaminations such as organic and inorganic elements that contain several toxic materials (Pereira et al., 2018).

Landfill leachate is a mixture of toxic and both organic and inorganic contaminants. Leachate production mainly depends on certain factors, such as the composition of solid wastes, particle size, hydrology of the site, the degree of compaction, temperature and moisture conditions, oxygen availability, as well as the age of the landfill (Ragazzet al., 2016). Leachate which produced from landfills is characterized by high concentration of pollutants such as (COD, BOD_5, NH_3-N, high BOD_5/COD ratio, heavy metals and bad odor and strong color concentrations. Thus, all these pollutants contaminate the surface and groundwater through leachate, soil contamination through direct waste contact or leachate, air pollution through burning of wastes, spreading of diseases by different vectors such as birds, insects and rodents, odor and uncontrolled release of methane by anaerobic decomposition of waste are among the major disadvantages associated with this method of MSW disposal. Unfortunately, the generation of landfill leachate is rapid in tropical countries in general because the rainfall generally exceeds the amount that can be evaporated during the rainy season (Kamaruddin et al., 2017).

1.2 Problem Statement

Landfilling is considered as the most popular means of waste management compared to other methods such as incineration, composting, or recycling (Tulebayeva et al., 2020). Landfill leachates are characterized by moderately high concentrations of pollutants such as COD, BOD, NH_3–N, and color (Moody et al., 2017; Zamri et al., 2017; Azme et al., 2018). Leachate from landfills faces the challenge of balancing environmental protection, economic viability, and sustainable development (Kamaruddin et al., 2015). Therefore, there is an urgent need to find an efficient approach to preserve the environment.

In recent years, treatment techniques are widely applied for the treatment of landfill leachate such as physicochemical treatment processes. There is an increasing concern on the current conventional adsorption leachate treatments due to long precipitation time, difficulty of separation from treated water, higher hazardous sludge production and limited purifying efficiency (Verma et al., 2016). So far, nanomaterial-based technologies have emerged as promising alternatives to current water treatment techniques at high efficiencies to meet the increasingly stringent water quality standards.

The existing iron oxide nanoparticles used for the treatment of wastewater are mostly synthesised. However, the existing synthesised technologies have several limitations, including the need for high energy, high temperature and pressure, usage of toxic chemical and release of harmful by-products. Conversely, the natural iron oxide magnetic nanoparticles is effective technology in treating wastewater due to a high surface area to volume ratio, fast kinetics, strong adsorption capacities, high reactivity, and easy separation (Gutierrezet al., 2017; Lai et al., 2016). Iron oxide, which can be found naturally in the environment, is most abundant as rock form. The method of obtaining and utilizing the iron oxide nanoparticles is highly compatible with the environment, since it widely exist (Xu et al., 2017). Therefore, the production of nanoparticles from iron oxide rocks uses only one source, which is the milling process. An analysis of the current researches in treating landfill leachate by different type of synthesised nanoparticles has been reported (Azadi et al., 2020); however, iron oxide nanoparticles rocks has not been clearly observed in the treatment of landfill leachate.

The electroflotation as physical treatment process and one of many electrolysis treatments is viewed as an attractive method in water and wastewater treatment. This method has great advantages, such as separating trace elements, removing oil and emulsions, treating low concentrate suspended solids, increasing the level of dissolved oxygen DO, pH adjustment, no secondary waste generation and water pollution, low sediment moisture, easy for dewatering and easy to operate (Mohtashami et al., 2019), yet has not been fully covered in treating stabilized landfill leachate.

This study proposed to evaluate a batch iron oxide nanoparticles with electroflotation unit in treating stabilized landfill leachate from Pulau Burung Sanitary Landfill. Also, followed by electroflotation, as treatment to supply a high level of DO in the wastewater. The performance of both treatments on stabilized landfill leachate separately and combined was applied. Other than its performance, this study contributed to the comprehensive understanding on the role and the impact of Fe_2O_3 nanoparticles during the landfill leachate treatment by investigating surface modelling, kinetic and thermodynamic studies.

1.3 Research Aims and Objectives

The purpose of the present study is to improve residual organic and inorganic concentration in stabilized landfill leachate in particular COD, NH_3-N, and color removal with the stringent discharge limits set by DoE, Malaysia, 2009. The main objectives of the present study include the followings:

1. To evaluate magnetic iron oxide nanoparticles (Fe_2O_3) in the removal of COD, NH_3-N and color from landfill leachate effluent.
2. To design a batch electroflotation unit and evaluate the removal of COD, NH_3-N and color from landfill leachate effluent.
3. To determine the efficiency of combining (Fe_2O_3) nanoparticles and electroflotation process for the treatment of landfill leachate towards the complying standards discharge limits for landfill effluent set by DoE, Malaysia.
4. To determine the adsorption capacity of (Fe_2O_3) nanoparticles using the best-fit isotherm model, kinetics and thermodynamic studies for the removal of the COD, NH_3-N and color pollutants from the landfill leachate.
5. To investigate the regeneration and reuse capability of iron oxide nanoparticles on COD, NH_3-N and Color, removal from landfill leachate.

1.4 Scope of the Study

The scope of the study can be demonstrated by focusing on the applications of iron oxide magnetic nanoparticles (IOMNs) for the treatment of landfill leachate as an alternative to the conventional adsorbents. Electroflotation is applied for the treatment stabilized landfill leachate, since electroflotation can be an alternative to other electrochemical treatment methods.

- An extensive review of characteristics of landfill leachate as baseline has been provided. It provided a detailed insight on the concentration of the existence of parameters in landfill leachate. The experiments were performed on a laboratory scale at room temperature. Research studies were carried out to select important variables and process parameters range for both iron oxide magnetic nanoparticles (IOMNs) and electroflotation For instance (pH, dose, contact time ,current density and temperature).

- Multivariable analyses were used; for instance, of OriginPro and excel analyser. The experimental data were analysed based on the removal efficiency of the pollutants. Graphical designs were carried out for all parameters to illustrate the highest efficiency level of removal. Additionally, the investigation of parameter effects and interaction among variable was essential for understanding the actual process mechanism for both techniques.
- An extensive study of isotherm modelling, kinetics modelling and thermodynamic behaviour assessment has given a better understanding on the mechanism of iron oxide magnetic nanoparticles (IOMNs) in COD, NH_3-N and color removal.

1.5 Organization of the Thesis

The thesis is prepared and organized in five chapters outlined as follows:

Chapter 2 **Literature review.** A comprehensive review of literature of landfills, landfill leachate, and landfill leachate treatments. Fundamentals of electroflotation process, application of electroflotation in treating water and wastewaters. In addition, nanoparticles technology in particular iron oxide magnetic nanoparticles (IOMNs) and the role of treating wastewater were mentioned and discussed. Isotherm models, regeneration studies were extensively discoursed.

Chapter 3 **Materials and Methods.** Leachate sampling, experimentations, chemical analysis, preparation and characterizations of iron oxide nanoparticles, characterizations of electroflotation unit were obtained.

The statistical methods and isotherm model, kinetics and thermodynamic studies were explained in this chapter as well.

Chapter 4 **Results and Discussion.** In the first section, characteristics of leachate were analysed in detail. In addition, characterization of iron oxide nanoparticles were discussed. In the second section, the performance of all experimental techniques were applied and demonstrated. Subsequently, the assessment of isotherm modelling, kinetics modelling and thermodynamic behaviour for the removal of COD, NH_3-N and color from the stabilized landfill leachate using iron oxide nanoparticles were discussed. The electroflotation and iron oxide magnetic nanoparticles (IOMNs) pre-treatment and post-treatment results were presented. Finally, regeneration and reuse of iron oxide nanoparticle experiments were mentioned in the last part of this chapter.

Chapter 5 **Conclusions and Recommendations.** The findings from the current studies were concluded. Furthermore, recommendations were presented for future studies in the related field, made from the understanding and information generated in this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Municipal Solid Waste (MSW)

Substances that are no longer usable or consumed coming from the activities by society are known as solid waste or refuse. While based on technical operational procedures of urban waste management, solid waste refers to organic materials and inorganic materials that are considered not useful anymore and must be managed in order not to harm the environment and protect development investment (Brunner et al., 2015). Based on the environmental terminology, municipal solid waste is a waste material or discharged from sources of human activities and natural processes that have no economic value. Thus, municipal solid waste is the waste/yield of human activities, which is in the form of organic and inorganic that can harm the environment, so it requires good management and processing (Kaushika et al., 2016).

According to Sadef et al. (2016), refuse is generally derived from domestic and commercial origins. These wastes are an exception of hazardous chemicals (El-Haggar, 2010). Plastics of the organic type are recyclable only for the definition, but MSW are significantly differentiated by most jurisdictions. This definition of MSW works with a legal prohibition of this type that is found in this way as the material of the landfills. Materials do not prohibit elimination and process systems by alternative methods; typically recycle, reutilize or compost (Hoang et al., 2020; Arıkan et al., 2017).

2.2 Municipal Solid Waste Composition

Classifying domestic waste is essential for selecting appropriate methods for handling them. Municipal solid wastes are classified into several groups depending on the constitution of material such as organic, inorganic, putrescible and non-putrescible. Moreover, it is categorized based on the heat content and moistures (Mallak et al., 2015).

In Malaysia, the available data regarding the composition of municipal solid wastes are based on the combination of commercial, residential and non-hazardous wastes that were collected for disposal. Solid waste composition from these sources consists of 55% food wastes, 19% plastic wastes, 13% paper wastes, 3% metal, 1% wood wastes, and 4% glass and textile wastes Figure 2.1. Approximately 80- 95% of them are sent to landfills (Mallak et al., 2015).

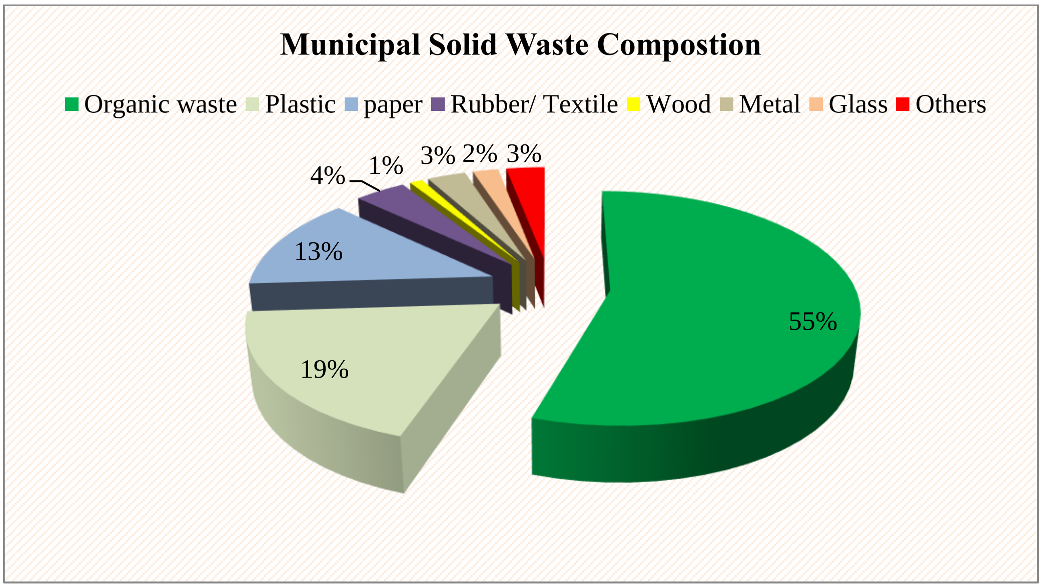

Figure 2.1 Municipal solid waste composition in Malaysia (Yatim et al., 2019)

2.3 Disposal of Municipal Solid Waste in Landfills

In Malaysia, a lot of the waste collected domestically is immediately sent to landfills. Such is also practiced in most other developing countries. Landfills are seen as a huge bin for disposal (Hoque and Rahman. 2020). This practice has been the most preferred method of dealing with waste over several decades. Undoubtedly, open disposal of solid waste in large capacities eventually causes detrimental environmental contamination hazardous to health. Environmental pollution occurs when surface water runs over the solid wastes and carries with it chemical, organic, and inorganic compounds (Vahabian et al., 2019). There are approximately 296 landfills in Malaysia of which 166 are still active until today, and in particular, only 11 are considered clean and competent in avoiding environmental pollution caused by landfill leachate and gas. Table 2.1 shows several sanitary landfills in Peninsular (West) Malaysia (Zakaria et al 2018).

Table 2.1 List of sanitary landfills in West Malaysia

Name of sanitary landfills	**Location**	**In operation**
Air Hitam Sanitary Landfill	Selangor	closed
Kulim Sanitary Landfill	Kedah	1996
Matang Sanitary Landfill	Perak	1997
Pulau Burung Sanitary Landfill	Penang	2001
Pulai Sanitary Landfill	Kedah	2001
Alor Pongsu Landfill Site	Perak	2000
Seelong Sanitary Landfill	Johor	2004
Tanjung Langsat Sanitary Landfill	Johor	2005
Bukit Tagar Sanitary Landfill	Selangor	2006
Jeram Sanitary Landfill	Selangor	2008
Tanjung 12 Sanitary Landfill	Selangor	2010
Kg Tertak Batu Sanitary Landfill	Terengganu	2014
Belengu Sanitary Landfill	Pahang	2017
Rimba Mas Sanitary Landfill	Perlis	2017
Teluk Mengkudu Sanitary Landfill	Perak	2022
Bukit Payong Sanitary Landfill	Johor	2022
Pagoh Sanitary Landfill	Johor	Proposed
Pekan Nenas Sanitary Landfill	Johor	Proposed
Sg Udang Sanitary Landfill	Melaka	Proposed
Teluk Mengkudu Sanitary Landfill	Perak	Proposed

Adopted from (Ghani et al., 2020; Moh, et al., 2017; Aziz et al., 2018; Hussein et al., 2019)

In many countries, sanitary landfilling is the commonest solid waste disposal method. In 2006, waste disposal in sanitary landfills reached 30.9% in Malaysia; however, this is estimated to reach about 45% by 2025, and this is considered the highest percentage compared to other methods of waste disposal (Fazeli et al., 2016). Landfills are considered the most economical and eco-friendly method of solid waste management compared to the other waste disposal methods like incineration, gasification, and composting. Sanitary landfills can be classified into three types: Anaerobic, Aerobic and Semi-aerobic (Hussein et al., 2019). Table 2.2 presents types of landfill decomposition process.

Table 2.2 Types of landfill decomposition process

Type	Mechanism	°C	pH	Timescale	Emissions	References
Anaerobic	five stages: aerobic, fermentation, acetogenesis, methanogenesis, oxidation	30–65	7–8	decades to millennia	CO_2, CH_4, H_2O, trace pollutants	(Adam et al., 2017; Pan et al., 2021; Pan et al., 2021)
Aerobic	Aerobic conditions achieved by forcing air into waste mass.	54-66	7.5–8	2–5 years	CO_2, H_2O, trace pollutants	(Cossu et al 2016; Morello et al., 2017; Slezak et al., 2015)
Semi-aerobic	Passive drawing of air into waste mass due to temperature Gradient.	40–50	>8	above >30	CO_2, H_2O, trace pollutants	(Matsuto et al., 2015; Huy et al., 2020; Yusoff et al., 2016)

2.4 Decomposition Process in Landfills

Landfill sites receive different kinds of municipal solid waste daily and the process of decomposition is highly distinct from one site to another. This method is very complicated and depends of several factors such as the structure of solid waste, climate change, landfill operation, age of landfill, moisture content, and pH. These changes play an important role in design, operation, and leachate treatment method (Kamaruddin et al., 2015).

Complex biological and chemical reactions happen when the decomposition process starts at the landfill site in Figure 2.2 (Faitli et al., 2015). Consequently, five stages can occur:

initial phase (Phase I), transition phase (Phase II), acidogenic phase (Phase III), methane fermentation phase (Phase IV), and finally maturation phase (Phase V). Decomposition rates in each phase are dependent on physical, chemical, and microbiology factors at the landfill site.

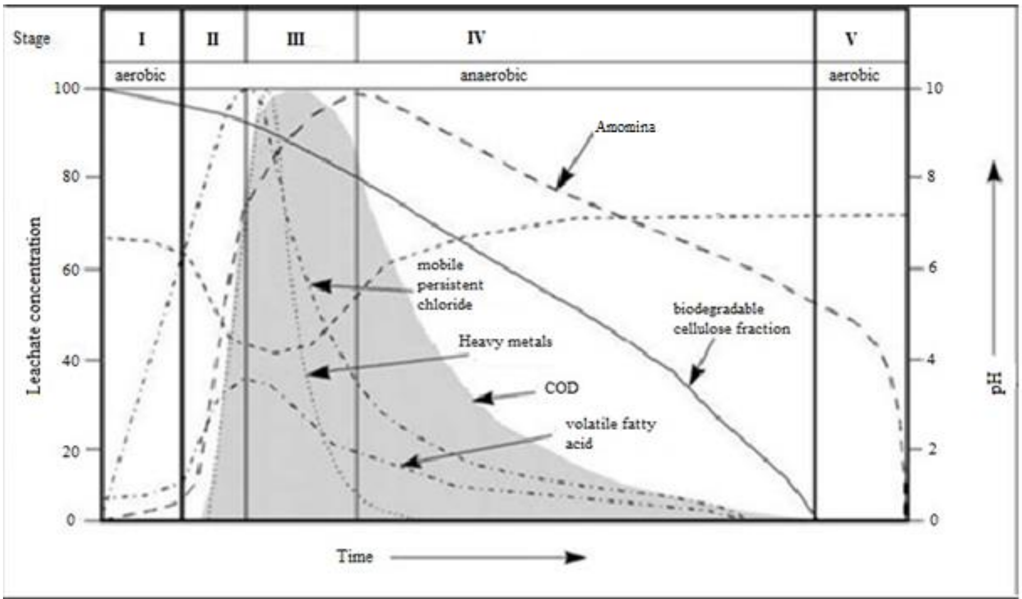

Figure 2.2 The decomposition process in landfill (Zhilina et al., 2017)

2.4.1 Initial and Transition Phase

The air that is confined inside a landfill creates a microbial decomposition of biodegradable organic matters, which usually happens at an aerobic state of the first adjustment point. The production of leachate at this point is slight (Japperi et al., 2021). Organic biodegradable matters go through a process of microbial decomposition. At the initial point, a complex solution is produced by the leachate created under aerobic states, with a pH level almost similar to that of neutral. As soon as the discarded waste is closed off in the landfill, it is cut off from any oxygen supply, which makes the microbial decomposition phase continue to occur until the oxygen within is depleted. With the heat produced through aerobic degradation, the heat level of leachate can go up to approximately 80-90°C, and in the case of maintained heat, this temperature is able to magnify the leachate production at a later phase.

The leachate processing at this point occurs when the covered waste causes moisture to be discharged while being compacted and short circuited of rainfall (Nanda, and Berruti. 2021)

2.4.2 Acidogenic Phase

The anaerobic phase occurs when the oxygen in the covered landfill is depleted. At the initial stage of this phase (acidogenic phase), a significant level of concentrations of soluble degradable organic matters and a slight to strong acidic pH level are produced. The presence of CO_2 causes the acidic pH to be stronger. The production of organic acids and acidic leachate causes the pH reduction of the leachate to 5.0 or below, and this decrease in pH level results in the removal of important nutrients in the leachate as well as the disintegration of heavy metals. On the other hand, this stage sees an increase in ammonium and metal concentrations while complex molecules are reduced. The completion of the whole process occurs within approximately four months, while it takes between one and two years for the stabilization of landfill gas generation level (He et al., 2017).

2.4.3 Methane Maturation Fermentation Phase

Leachate reaches a neutral or slightly alkaline state in methanogenic conditions, which usually occurs within the span of a few months or even years Figure 2.3. Methane and CO_2 are generated by methanogens, and gas present in landfills comprises of between 55 and 60% of methane, and between 40 and 45% of CO_2 (with hints of other gases) when the methanogenic state is stabilized (Bove et al., 2015). Mesophilic bacteria, which thrives in temperatures of around 30-35˚C, and thermophilic bacteria, which grows in temperatures of around 45-65˚C, are two kinds of bacteria that consume CO_2 and acetate. Albeit the slow and time-consuming reaction process, a benefit is an established leachate pH level of between 7.0 and 8.0. This reduces the heavy metals in leachate. Once the biodegradable refuse has been turned to CO_2 and methane, the aerobic states may reappear with the growth of new aerobic microorganisms, which will take the place of anaerobic forms; hence, the re-establishment of aerobic states (Feng et al., 2019).

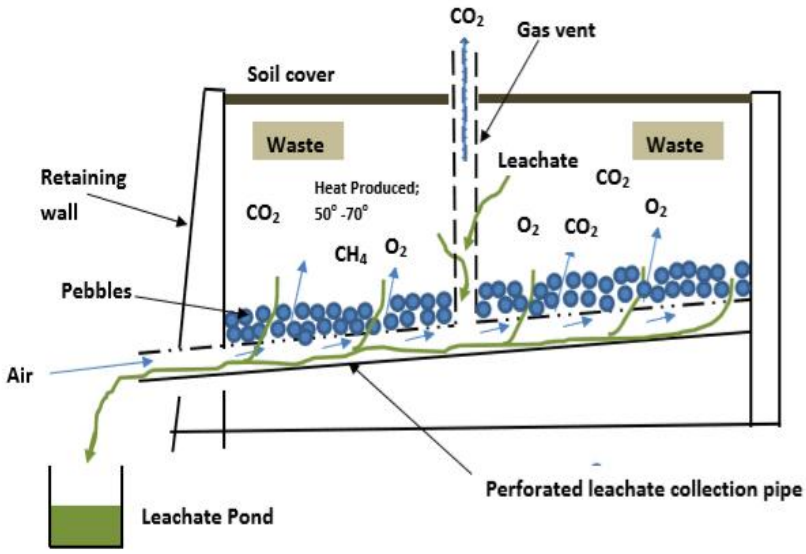

Figure 2.3 Semi-aerobic landfill mechanism (Kamaruddin et al., 2017)

2.5 Landfill Leachate Formation and Composition

Normally, solid waste in dumping grounds discharges a variety of pollutants into the area around it, which includes gas releases, liquid leachate, and non-compostable solid components. Landfill leachate is a mixture of toxic and both organic and inorganic contaminants. Leachate production mainly depends on certain factors, such as rainfall, the composition of solid wastes, particle size, hydrology of the site, degree of compaction, temperature and moisture conditions, oxygen availability, and the age of the landfill (Wdowczyk and Szymańska. 2020). If left unmonitored, leachate can cause serious surface and groundwater pollution as shown in Figure 2.4.

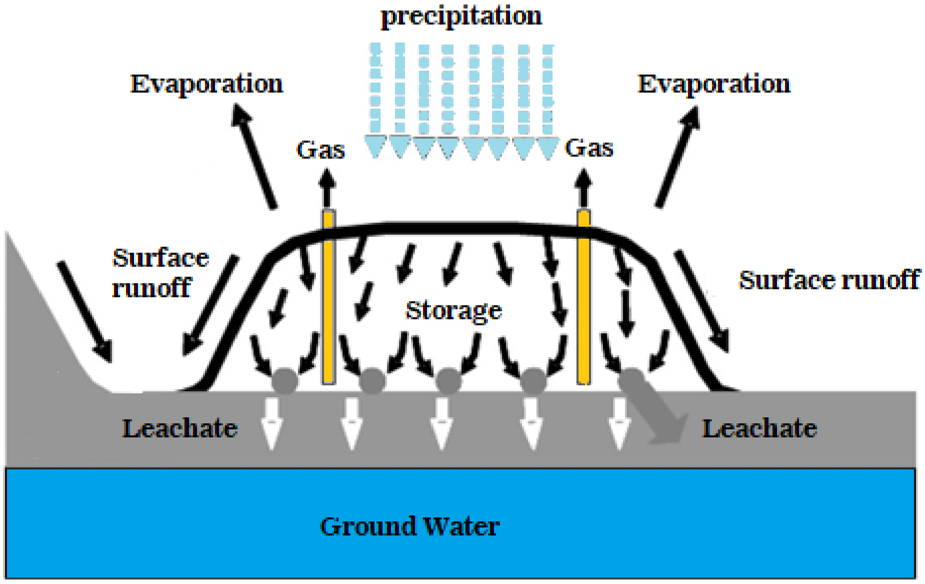

Figure 2.4 Water movements in the landfill

Understanding the age of a landfill determines the type of leachate (Kamaruddin et al., 2017) as demonstrated in Table 2.3; less than a year (aerobic phase), from 2 to 10 years medium (acidic phase), and more than a decade old (methane phase). The older that landfill, the more varied are the leachate parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), BOD_5/COD ration and pH. In newer landfills that contain a large amount of biodegradable organic substances that stimulates faster anaerobic fermentation which encourages the creation of volatile fatty acids (VFA) (Adhikari et al., 2015), it has been observed that the proportion of organic pollutants as COD is over 10,000 mg/l, whereas landfills that are more than 10 years only amounts to 3,000 mg/l. Older landfills exhibit lower degrees of COD and a higher level of ammonia nitrogen (AN), and the latter pollutant occurs because of the hydrolysis and fermentation of nitrogen of biodegradable refusubstrates. As the degree rises, it becomes more hazardous to the environment (Kamaruddin et al., 2017).

Table 2.3 Characterization of landfill leachate based on age

Landfill age (years)	**< 2**	**2–10**	**> 10**
Stabilisation status	**Young (fresh)**	**Intermediate**	**Mature (stabilized)**
BOD_5	2000 – 30,000	N.A	100 – 200
COD	3000 – 60,000	3000 – 15,000	100 – 2800
TOC	1500 – 20,000	N.A	80 – 160
BOD_5/COD	0.5 – 1.0	0.06 – 0.5	< 0.1
TOC/COD	< 0.3	0.3 – 0.5	> 0.5
Total Kjeldahl nitrogen	100 – 2000	N.A	N.A
Ammoniacal-nitrogen	10 – 800	30 – 1800	20 – 900
Organic nitrogen	10 – 800	N.A	80 – 120
Nitrate	5 – 40	N.A	5 – 10
pH	4.5 – 7.5	6.5 – 7.5	6.6 – 7.5
Alkalinity as $CaCO_3$	1000 – 10,000	N.A	200 – 1000
Total hardness as $CaCO_3$	300 – 10,000	N.A	200 – 500
Total suspended solids	200 – 2000	N.A	100 – 400
Heavy metals	> 2.0	< 2.0	< 2.0
Total phosphorus	5 – 100	N.A	5 – 10
Orthophosphate	4 – 80	N.A	4 – 8
Calcium	200 – 3000	N.A	100 – 400
Magnesium	50 – 1500	N.A	50 – 200
Potassium	200 – 1000	N.A	50 – 400
Sodium	200 – 2500	N.A	100 – 200
Chloride	200 – 3000	N.A	100 – 400
Sulphate	50 – 1000	N.A	20 – 50
Total iron	50 – 1200	N.A	20 – 200

All the parameter units in (mg/L) except pH, BOD_5/COD and TOC/COD has no unit
N.A Not Available
Adopted from (Kamaruddin et al., 2017)

2.5.1 Leachate Formation Mechanism

A landfill can only hold up to a certain amount of moisture via its porous medium that does not cause a downward percolation. Once the limit of moisture level is reached, it produces leachate. Surface tension and capillary pressure are the holding forces ascribed to moisture retention. As gravitational agents go above the limit of the holding forces, percolation happens. In a homogeneous soil, the field capacity seldom exceeds 50 % of total porosity. This value is more suitable for a homogenous soil than it is solid waste in which leachate is often released prior to reaching field capacity. Therefore, it is more appropriate to characterize the refuse by its absorptive capacity. Determinants such as climatic and hydrogeological, site operation and organization, waste classifications, and inner landfill operation affect the construction of leachate. These determinants are classified into two separate groups which are ones that have direct effect on landfill moisture (rainfall, ground water intrusion, initial moisture content, irrigation, recirculation, liquid waste, disposal, and composition) and others that influence the dissemination of leachate or moisture within the landfill (age of landfill, compaction, permeability, particle size, density, settlement, cover, sidewall, gas and heat generation). Even though leachate is believed to emerge with a rise in moisture levels, it is also usually connected to intense biodegradation activity within the landfills. Consequently, increased biodegrading is encouraged with the more favoured design of a landfill cover that receives water for higher filtration, which eventually brings about speedy stabilization and shortens the amount of time needed to use the landfill for more advantageous purposes.

2.5.2 Significance of COD, NH_3-N and Color at PBLS

The current research mainly concentrates on the effluent produced from Pulau Burung Landfill Site (PBLS). Leachate from Pulau Burung Landfill site has several characteristic parameters like COD, NH_3-N and color. These parameters are high concern due to the higher concentration level in the leachate. Various studies have been reported on the COD, NH_3-N and color (Zakaria et al., 2015; Aziz et al., 2015).

Concentrations of NH_3-N in leachate, which have been demonstrated through results of several previous researches, contributes highly to algal development that hampers biological management procedures, encourages eutrophication, and declines dissolved oxygen. Hence, ammoniacal nitrogen is fatal to microbes (Azme et al., 2018). Akinbile et al., (2012) described

PBSL as containing an excessive concentration of NH_3-N evaluated at (1810 – 1070 mg/l). Furthermore, results of a research study done by (Aziz et al., 2015) at separate occasions on the same landfill demonstrated that the collection and long durations of raw leachate caused excessive concentrations of NH_3-N. The NH_3-N value in PBSL (5 mg/L) still did not comply with the level suggested by DoE even though it is classified as an aged landfill.

Chemical oxygen demand levels are between 1302 and 1830 mg/L with an average of 1566 mg/L were found in other leachate studies of PBSL. The COD levels from this leachate classifies PBSL at the methanogenic stage since the common COD levels at this stage are between 500 and 4500 mg/L. Nevertheless, some results of past researches of this stage have suggested lower COD levels (Zakaria et al., 2018), whereas some were higher (Budi et al., 2016; Jumaah et al., 2016) in the acidic phase. Another result recorded by (Azme et al., 2018) showed a COD level of more than 2000 mg/l. Elements such as landfill age, abnormalities of site, landfill structure, geographical climate, and solid waste qualities may contribute to the different levels of COD. Before a leachate is eliminated into the environment, it is usually at a COD value of lower than 400 mg/L. The colouring of the leachate, which is usually dark brown, is brought about by the oxidation of ferrous to ferric form and the following generation of ferric hydroxide colloids and complexes with fulvic and humic substance. The color concentration at PBSL in the past few years was from 2310 to 4790, according to (Aziz et al., 2015).

2.6 Landfill Leachate Treatments

Developing an efficient treatment either for high or small quantity of leachate is one of the critical issues facing landfill management. Different biological, physicochemical, chemical, and physical methods have been applied for the management of landfill leachate. However, the procedure has to go through several stages that can be costly and complex. High loading, complex chemical composition, and seasonally variable volume cause challenges in managing leachate (Bu et al., 2010). Integrating several techniques ensures efficient leachate management since this integration allows each process to work to its maximum advantage (Bove et al., 2015); however, not all the methods can be combined due to several reasons such as the cost effectiveness, chemical usage, time processing and large sludge production. Liu et al., (2015), as an example, incorporated agitation, coagulation, sequencing batch reactor (SBR) technique, and filtration for managing landfill leachate. In this research, a technique of eliminating ammonia through stripping and adding poly ferric sulfate in coagulation was used to manage SBR and dispose of COD. Consequently, 99.2% NH_3-N and 97.4% COD were eradicated. This data validates the significance of incorporating different techniques for generating successful results in managing leachate. The most suitable procedure and actual leachate management are established by the qualities of leachate. Nonetheless, these treatments are complex and expensive. Figure 2.5 shows several techniques that are frequently used for managing landfill leachate.

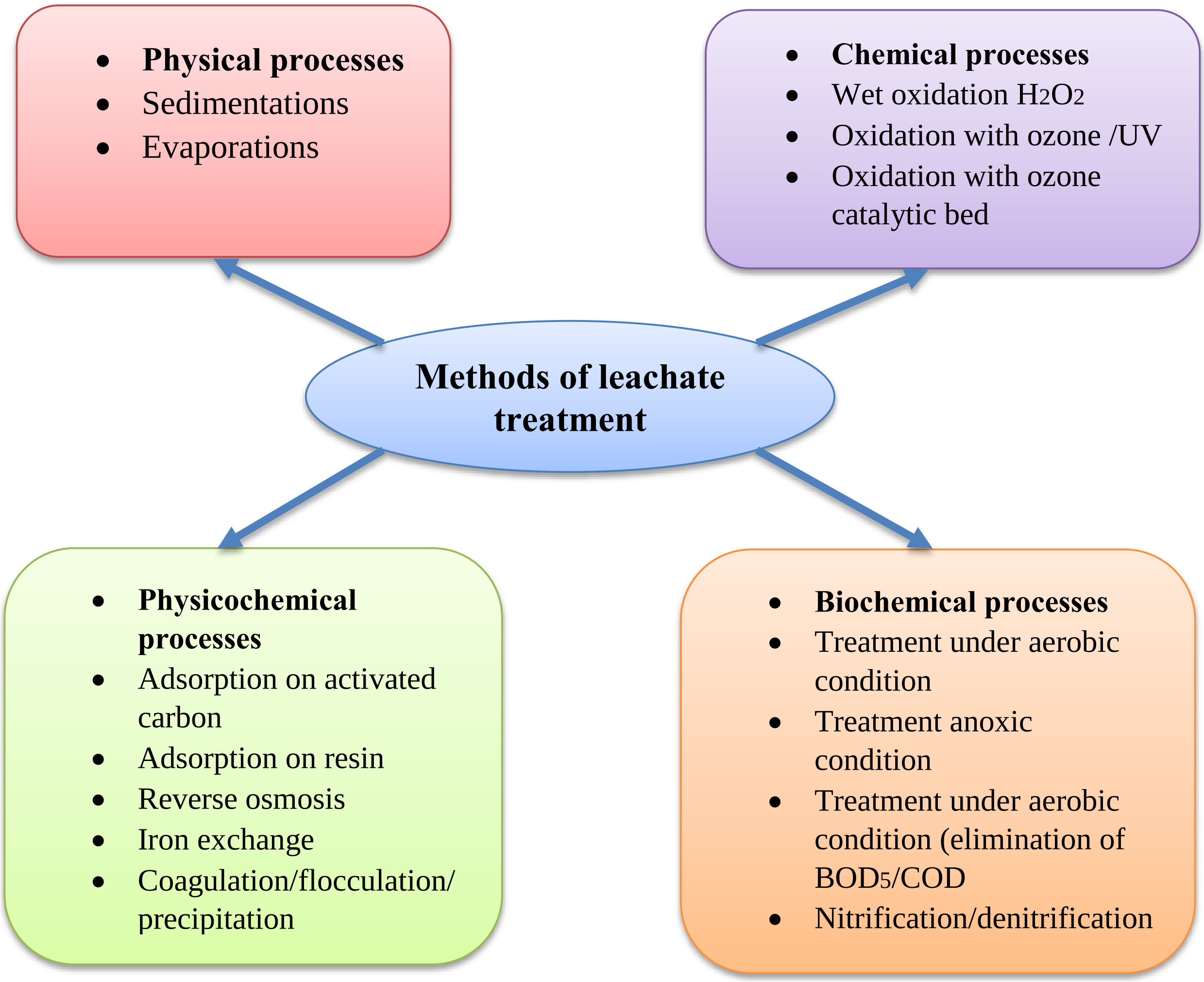

Figure 2.5 Applied methods for landfill leachate treatments

2.6.1 Biological Treatments

The biological treatment processes (aerobic or anaerobic) have been well known for successfully managing municipal wastewater. Biological treatment (suspended/attached growth) is usually applied to the bulk of leachate when removing high concentrations of COD due to its accuracy, clarity, and is very economical (Harb et al., 2016). Biological techniques are efficient for the elimination of organic and nitrogenous substances from young leachates (BOD_5/COD ratio > 0.5). For mature leachates, the process efficiency tends to be limited because of the existence of refractory elements, in particular the humic and fulvic acids (Akkaya et al., 2010).

2.6.1(a) Aerobic and Anaerobic Treatment

Aerobic decomposition can be defined as the destruction of degradable organic matters through aerobic biological mechanism. Suspended-growth biomass such as aerated lagoons, conventional activated sludge processes and SBR as the basis of aerobic biological methods have been researched and utilized. According to Lindamulla et al (2022), it is generally common for much simpler treatments being applied to landfill leachates that are fairly new compared to landfill leachates that are more stabilized. This is an indication that the choice of treatment methods depends on the leachate's characteristics.

Aerated lagoons have commonly been observed as an efficient and cheap process in the elimination of pathogens, inorganic as well as organic elements. It is the most popular wastewater treatment option in developing nations because its operation and maintenance is quite economical (Payandeh et al., 2017). In addition, administering the system does not require professional abilities. However, even with the good economic value, it may not be the best leachate treatment option. The main disadvantages of this method include the large area requirements, odor and aerosol formation and problems of maintaining it (Malovanyy et al., 2018). Sequencing batch reactor system is idyllically appropriate for nitrification–denitrification processes as it offers an operation system well-matched with concurrent organic carbon oxidation and nitrification. Meena et al. (2022) reported that the SBR technique might be considered appropriate for biologically managing nitrogen from landfill leachate.

The oldest method in managing wastewater is anaerobic digestion. This method involves biological decomposition of organic substances mainly to methane and carbon dioxide when oxygen is unavailable. Omar et al., (2015) reported that anaerobic degradation of complex organic substances follows a sequential process that includes the steps of hydrolysis, acidogenesis, acetogenesis and methanogenesis. Different reactors such as anaerobic filters

(AF), anaerobic sequencing batch reactor (ASBR) or up flow anaerobic sludge blanket (UASB) and fluidized bed reactor can be used to accomplish anaerobic digestion.

Anaerobic sequencing batch reactor (SBR) shows good capability for organics removal and solid capture in one vessel. Yuan et al., (2016) conducted a research by applying a lab-scale SBR by sequential anaerobic-aerobic operations to study nutrient reduction from pre-treated leachate, and the research brought about 62%, 31% and 19% of COD, NH_4^+-N and PO_4^{3-}-P removal, respectively, at the end of cycle time 21 h. The biological treatment of landfill leachate using a simultaneous aerobic-anaerobic bioreactor system investigated by Yang and Zhou (2008) indicated that 35% COD elimination was obtained in the anaerobic stage. However, the COD and BOD_5 removals were around 75% and 99%, respectively, in the combined process.

Upflow Anaerobic Sludge Blanket Reactor (UASB). Typically, UASB can achieve good treatment effectiveness in short hydraulic retention times. According to Wu et al. (2019), UASB was efficient in managing landfill leachate with the Chemical Oxygen Demand (COD) concentration, ammonium nitrogen (NH_3-N) concentration, and total nitrogen (TN) concentration of the basal leachate was 2200–2500 mg/L, 1200–1300 mg/L, and 1300–1400 mg/L, respectively. After treatment, the final COD, NH_4^+N, and TN were decreased to 90–100 mg/L, 13–14 mg/L, and 35–38 mg/L, respectively. A number of limitations are faced when applying biological treatment for stabilized landfill leachate. The stabilized leachate is indicated by a high molecular weight or refractory compounds which do not degrade simply. The high strength of NH_3-N that is available is recognized as being a hazardous substance to the microorganisms which inhibits the biological degradation process (Koliopoulos et al., 2018). As such, substrate such as phosphorus may be added at low concentration to encourage microorganism activities. Currently, physico-chemical treatment methods are satisfactory for eliminating refractory matters from stabilized leachate. Furthermore, physico-chemical processes as a refining step for biological treatment is a possible application.

2.6.2 Physicochemical Treatment

In managing stabilized landfill leachate, a number of physico-chemical treatment processes have been used including coagulation-flocculation, flotation, air stripping, chemical precipitation, adsorption, chemical oxidation, electrochemical, membrane filtration and ion exchange.

2.6.2(a) Coagulation-Flocculation

Coagulation-flocculation method has been extensively studied as a simple physico-chemical technique in managing landfill leachate with a variety of coagulants (GilPavas et al., 2017). The stability of colloidal particles is influenced when the leachate is mixed with coagulants in the coagulation method. As a consequence, the colloidal particles flocculate and form large flocs that is eliminated from the leachate by settlement within a duration of time. According to Bakraouy et al. (2017), the principal behind the elimination mechanism of this method is charge neutralization of negatively charged colloids by cationic hydrolysis products followed by integrating impurities in an amorphous hydroxide precipitate through flocculation. Most of the studies aimed to investigate the maximum performance including choosing the utmost suitable coagulant, deciding on experimental conditions, testing of pH effect and analyzing flocculant addition. The most applied coagulants were aluminium (alum) sulphate, ferrous sulphate, ferric chloride and ferric chlorosulphate. Furthermore, coagulation and flocculation can be utilized as a pre-treatment method for removing non-biodegradable organic materials.

According to Ronke et al. (2016), the effectiveness of tamarind seed powder as a coagulant for treating detergent wastewater using coagulation-flocculation process has been evaluated by varying pH, mixing time and coagulant dosage, which were the selected operating parameters for the treatment process. The best pH of the process was found to be 7.25 with turbidity and COD removal of 97.01% and 24.86% respectively; the best mixing time was obtained to be 3 minutes of rapid mixing and 15 minutes of slow mixing with turbidity and COD removal of 97.78% and43.50% respectively while the best dosage was given to be 400 mg/L with turbidity and COD removal of 97.72% and 39.55% respectively. Another study by Rasool et al., (2016) reported that by an active natural coagulant to be used in combination with alum for leachate pre-treatment. Leachate samples were collected from a municipal solid waste open dumping site. The effect of three parameters including contact time, pH, and alum–O. basilicum ratio on the color and COD reduction were analyzed. At the optimal conditions of 15 min, pH 7 and alum–O. Basilicum ratio of 1:1, 64.4% COD and 77.8% color removal were obtained in the pretreatment stage. Ozonation process was applied to leachate after coagulation. The optimal reaction time for the post-Ozonation by 0.2 g O_3 $^{1-}$1 h^{-1} was 30 min. The integrated technique consisted of CF and Ozonation was proved to be an efficient process for the treatment of leachate with 92% color removal and 87% COD reduction. Another study successfully done and tested an alternative coagulant.

Coagulation–flocculation process using the combination of PACl as coagulant and Tamarindus indica seed (TiS) as coagulant aid was used in treating the landfill leachate from the Alor Pongsu Landfill Site in Malaysia by Aziz et al., (2018). Some of the operational conditions determined were the pH and dosage of the coagulant aid, and their effect was considered on parameters, such as suspended solids (SS), color, and COD, using standard jar test procedures. The combination of (TiS) flocculant reduced the dosage of PACl coagulant from 5,000 mg/L to 2,750 mg/L with removal efficiencies of 99.3%, 97.3%, and 67.4% for SS, color, and COD, respectively.