Appendix A8

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

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LEACHATE TREATMENT: REMOVAL OF ORGANIC MATTER USING ULTRASONIC-ASSISTED ELECTROCOAGULATION METHOD

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By

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ABSTRAK

Projek penyelidikan ini bertujuan untuk mengkaji penyingkiran bahan organik menggunakan kaedah elektrokoagulasi berbantukan ultrasonik. Penggunaan teknologi rawatan hibrid telah diiktiraf sebagai salah satu kaedah rawatan yang dijalankan untuk meningkatkan keberkesanan rawatan larut lesap disebabkan oleh pelbagai halangan, seperti kepekatan bahan pencemar yang tinggi dan keupayaan terhad bagi satu proses rawatan. Ini adalah salah satu kaedah rawatan yang telah dijalankan untuk meningkatkan keberkesanan rawatan larut lesap. Sampel larut resapan diambil dari Tapak Pelupusan Alor Pongsu. Faktor yang digunakan dalam eksperimen ini ialah voltan (V) dan masa rawatan (minit). Dalam kajian ini, kaedah elektrokoagulasi berbantukan ultrasonik telah dijalankan untuk membandingkan keputusan dengan kaedah elektrokoagulasi. Selain itu, tujuan kajian ini adalah untuk menilai kecekapan kedua-dua rawatan dalam penyingkiran bahan organik daripada larut resapan tapak pelupusan dari segi COD serta minyak dan gris. Dengan menggunakan elektrod Al-Al, pengurangan COD maksimum adalah daripada rawatan EC-US menggunakan 9 V, masa rawatan 10 min dengan 81.7 %. Manakala, penyingkiran minyak dan gris pengurangan maksimum ialah 98.1 % semasa masa rawatan 6 V dan 10 min menggunakan proses EC-US.

ABSTRACT

This research project aimed to study the removal of organic matter using the ultrasonic-assisted electrocoagulation method. The utilisation of hybrid treatment technologies has been recognised as one of the treatment methods conducted to enhance the efficacy of leachate treatment due to the numerous obstacles, such as the high concentration of pollutants and the limited ability of a single treatment process. EC-US is one of the treatment methods that has been conducted to enhance the efficacy of leachate treatment. The leachate sample was collected from Alor Pongsu Landfill. The factors used in this experiment are voltage (V) and treatment time (minutes). In this study, an ultrasonic-assisted electrocoagulation method was conducted to compare the result with the electrocoagulation method. Additionally, the purpose of this study is to assess the efficiency of both treatments in removing organic matter from landfill leachate in terms of COD and oil and grease. Using the Al-Al electrode, the maximum COD reduction is from EC-US treatment using 9 V, treatment time 10 min with 81.7 %. Meanwhile, for the oil and grease removal, the maximum reduction is 98.1 % during 6 V and 10 min treatment time using the EC-US process.

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LIST OF ABBREVIATIONS

Al	Aluminum
AN	Nitrate-Nitrogen
AOP	Advanced Oxidation Process
COD	Chemical Oxygen Demand
Cu	Copper
DC	Direct Current
EC	Electrocoagulation
EC-US	Electocoagulation-Ultrasonic
EO	Electrooxidation
EPA	Environmental Protection Agency
Fe	Iron
HAOPs	Hybrid Advanced Oxidation Processes
HR	High Range
MSW	Municipal Solid Waste
OM	Organic Matter
RCRA	Resource Conservation and Recovery Act
RPM	Revolutions Per Minute
SS	Suspended solid
TN	Total Nitrogen

US	Ultrasound
USEPA	United State Environmental Protection Agency

LIST OF SYMBOL

%	Percent
Φ	Faradaic Yield

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Waste materials are produced by human activities and are frequently discarded because they are deemed worthless. These waste products are usually solid, and the word waste implies that they are unusable and undesired (Tchobanoglous et al., 2002). Malaysians create around 38,699 tonnes of solid garbage daily, or at least 1.17 kg per person. While Malaysia has a huge number of landfills, they cannot absorb the vast quantity of rubbish produced, and the amount of solid waste is predicted to continue to rise as the country's population expands. In Malaysia, there are now 141 solid waste dumps. There are 116 open dumpsites, 21 sanitary landfills (built with anti-pollution characteristics to facilitate safe decomposition), and four residual waste dumps (The Star Online, 2021).

Landfilling describes the process by which solid waste and solid waste residuals are disposed of at a landfill facility. Prior to the advent of the phrase "sanitary landfill," a landfill in which the rubbish dumped there was covered after each day's operations was referred to as a "sanitary landfill". Currently, a *sanitary landfill* is defined as an engineered facility for the disposal of municipal solid waste (MSW) that is planned and managed with the goal of minimising adverse effects on public health and the environment. Organic and inorganic pollutants are found in high leachate concentrations from municipal landfills. The leachate composition may vary based on several variables, including the degree of compaction, the makeup of the waste, the environment, and the amount of moisture present in the waste stream. Overall, leachate exhibits significant levels of chemical oxygen demand (COD), acidity (pH), nitrate-nitrogen (AN), heavy metals, and other contaminants, as well as intense colour and odour. Meanwhile, the properties of leachate fluctuate in terms of its composition and volume, as well as the number of biodegradable materials present in the leachate with time, depending on the circumstances (Raghab et al., 2013).

The chemical oxygen demand (COD) of a sample is one of the factors used to determine the pollutant strength (organic and inorganic materials) contained within it. COD concentrations in young, intermediate, and matured leachates are in the range of 10,000 mg/L and above, 4000 – 10,000 mg/L, and less than 4000 mg/L, according to the EPA. 'Leachate' is a poisonous substance that is harmful to both the environment and human health (Zakaria and Aziz, 2017). Leachate may be discharged into the environment or disposed of via the municipal sewage system. It may be processed before being disposed of, or it may be dumped straight from a landfill. All these solutions include dangers to the environment and human health. When leachate is not handled and disposed of through diffusion into ground or surface water, the ecosystem may suffer; as a result, depending on the amount and kind of leachate present. If the leachate is delivered to municipal sewage treatment facilities, methane explosions are at risk (Bricken, 2003).

Leachate from landfills may be handled biologically, physically, or chemically. Aerobic and anaerobic treatment strategies are used in biological therapy. Biological treatment, on the other hand, has certain limits. For example, when treating old landfill leachate with poor biodegradability, the biological process may fail to provide satisfactory results owing to the leachate's organic pollutants carbon. Simultaneously, the old landfill's high concentration of ammonia nitrogen and heavy metals exerts a severe suppressive impact on microorganisms. As a result, physical and chemical treatment techniques such as physical adsorption, chemical coagulation, nanofiltration, and reverse osmosis have received increased attention. A mix of biological and physical approaches is often utilised to remediate old landfill leachate. However, physical and chemical treatment has several limits, such as the production of a significant volume of sludge and the need for a considerable amount of coagulant. Electrochemical techniques offer the benefits of producing less sludge, being easy to operate, having a short operating period, and being very efficient. It has been shown to be effective in removing COD, ammonia nitrogen, and heavy metal pollutants, and chroma is frequently used in landfill leachate treatment. Among these, electrocoagulation (EC) and electrooxidation (EO) are the most often employed techniques. For EC, condensed ions (mostly aluminium and iron) are generated primarily by the electrolytic reaction on the electrode, and in the meanwhile, a gas beneficial to the flotation process may be generated to facilitate the removal of contaminants by precipitation and flotation. The material of the electrodes, their spacing, and the current density all have an influence on the EC (Guo et al., 2022).

In medicine, ultrasound (US) is defined as a longitudinal wave having a frequency greater than 20 kHz. These frequencies are both above the sonic range (20Hz to 20kHz) at which humans are capable of hearing as well as below the megasonic range (>600 kHz). The energy conveyed by the vibration of the molecules in the environment where the wave is being propagated is known as the United States wave (US wave). The United States could generate electricity using two techniques: first, “magnetostrictive” electrical energy is converted to mechanical energy (or vibration) with a magnetic coil attached to a vibrating piece such as nickel or Terfenol-D, and second, “thermostrictive” electrical energy is converted to mechanical energy (or vibration) with a magnetic coil attached to a vibrating piece such as nickel or Terfenol-D. Second, in the case of the piezoelectric approach, electrical energy is transformed into high-frequency electric energy by attaching piezoelectric crystals (which depend on material strain) to the vibrating item and allowing them to vibrate (sonotrode, probe, or horn). The United States improves the transfer of tiny molecules in a liquid solution by boosting the convection in a fluid that would otherwise be stagnant or flowing at a relatively sluggish rate. Increasing convection in liquids may also be accomplished using acoustic streaming, in which the momentum of directed propagating sound waves is transmitted to the liquid, resulting in the liquid flowing in the direction of sound propagation. Acoustic cavitation occurs in a liquid because of US irradiation applications, causing various mechanical, acoustical, chemical, and biological changes (Doosti et al., 2012).

In this particular study, ultrasound was utilised to evaluate the efficacy of a hybrid treatment process in landfill leachate treatment of organic matter removal in terms of chemical oxygen demand (COD) and oil and grease removal in comparison to a single treatment using varying levels of voltage and treatment times. This research project proposes using a method from the US because it has been used extensively to degrade organic components from wastewater and is one of the advanced oxidation processes that is able to oxidise almost all organic pollutants. This will allow for the efficient removal of organic matter from leachate, which is one of the goals of this research project (Mahvi et al., 2012).

1.2 Problem Statement

Landfill leachate is known to contain a specific chemical that is harmful to the environment. As a consequence, leachate must be cleaned before it may be released into the environment or transported to a municipal wastewater treatment plant (WWTP). A WWTP must collect and treat point sources, such as toxic landfill leachate, in order to improve the quality of the sludge produced by the plant.

It is investigated in this research if the electrocoagulation (EC) technique is effective in treating leachate. EC is a type of electrochemical process that has gained increasing attention in recent years and is addressed in this study. The EC approach has emerged as a viable option for the treatment of contaminated aqueous water. The effective and low-cost landfill leachate treatment technology is characterised by its ease of operation and short operating duration. Aside from all its benefits, this process has some downsides, including high energy consumption, electrode requirements, electrode passivation, and the creation of vast amounts of sludge. Attempts have been made to solve these drawbacks by combining the electrocoagulation approach with additional treatment methods such as sonolysis, photolysis, adsorption, ozonation, and others. The elimination of COD, as well as the removal of oil and grease, has been the primary emphasis of the therapy. According to findings, studies have shown that a hybrid strategy increases treatment efficacy while also outperforming the constraints of standard physico-chemical, biological, and AOPs procedures. Methods based on the ultrasonic mechanism have been used to eliminate a variety of contaminants and improve the treatment's effectiveness (Khoramipour et al., 2021).

This study used the ultrasonic-assisted electrocoagulation technique to treat leachate from the Alor Pongsu Inert Waste Landfill. The purpose is to learn more about this way of treating leachate. Several characteristics must be investigated, and the fundamental processes occurring inside a landfill must be understood in order to conduct a more thorough evaluation and discussion of the treatment possibilities. First and foremost, the treatment effectiveness of the electrocoagulation technique was evaluated in terms of COD removal as well as oil and grease removal. The results achieved by the ultrasonic-assisted electrocoagulation technique were compared to the results obtained by the electrocoagulation method. The ultrasonic-assisted electrocoagulation approach yielded significantly better results. Using the findings acquired, we can estimate the efficacy of the ultrasonic-assisted electrocoagulation technique by comparing them to one another.

Due to their low level of soluble in water, fat, oil, and grease (also known as FOG) are singled out for particular attention. In order to prevent interfaces in water treatment units, decrease fouling in process equipment, avoid issues in biological treatment stages, and comply with water discharge criteria, oil that is present in wastewaters has to be eliminated. Because of this, the removal of leftover oil from the process or waste effluent has become an essential environmental factor (Siang, 2006). The organic substances with the highest degree of stability are oils and greases. Because of their uniformity, they cannot be readily broken down physiologically and cannot be treated using any other method that is considered to be standard. On the other hand, the disposal of trash by incineration entails significant expenditures owing to the large amount of energy that is necessary to be input in order to evaporate the water content of the waste. Because of their viscous nature, oil and grease have a propensity to block drain pipes and sewage lines. This, in addition to producing an offensive odour and contributing to the corrosion of sewer systems in anaerobic environments (Stoll, 1997). FOG has a greasy consistency and may take the form of either a liquid or a solid. It may also arise. FOG, in its purest form, lacks colour, odour, and taste. It also has no discernible smell. In addition to this, FOG is not soluble in water but is soluble in organic solvents including hexane, ether, and chloroform. Because FOG is less dense than water (specific gravity < 1), it is able to float on the surface of the water. However, in the presence of soap or other emulsifying agents, FOG will form emulsions with aqueous media to create a stable mixture. In general, FOG has a higher viscosity than OG due to the structure having less closely packed molecules (Husain et al., 2014).

1.3 Objectives

The primary purpose of this research project is to evaluate and contrast the efficacy of two treatments for eliminating OM from Alor Pongsu leachate. The study also has a number of specific objectives, which are as follows:

- To study the efficiency of the electrocoagulation (EC) technique in removing landfill leachate organic matter (OM).
- To compare the effectiveness of the electrocoagulation (EC) technique and ultrasonic-assisted electrocoagulation technique.
- To determine the effectiveness of removing oil and grease when adding interval time for every 10 minutes.

1.4 Scope of Research

To achieve the objectives above, the scope of the study is as follows

- The study was focused on removing the chemical oxygen demand (COD) and oil and grease from leachate using two different methods.
- The electrocoagulation and ultrasonic-assisted electrocoagulation techniques were discussed based on data collected from the experiment.

1.5 Dissertation Outline

The thesis is categorised into five chapters: introduction, literature review, methodology, results and discussion, and conclusion and recommendations.

CHAPTER 1: Introduction – This chapter provides an explanation of the research study and a summary of the results that have been obtained so far. This section focuses on the background of leachate, the issue description, the study's goals, and the investigation's scope.

CHAPTER 2: Literature Review – This chapter gives a comprehensive discussion of technical terminology, results, subjects, and consequences connected to the study. It does so by referencing previously published research publications. It can provide researchers with some recommendations and instructions that will assist researchers in better comprehending the subject matter and carrying out their investigation.

CHAPTER 3: Methodology – This chapter focuses mainly on the approach for getting the intended results as well as methods for specifically meeting the programme goals. The tools, approaches, and resources used in this investigation are explained in great detail.

CHAPTER 4: Results and Discussion – This chapter provides a concise overview of all of the research's results and findings. In order to answer research questions, put ideas to the test, analyse problems, and study hypotheses, one must first condense a massive quantity of data via data analysis, which may be quantitative or qualitative. In order to respond to the issues posed by the research, this chapter will provide an analysis and discussion of the results. The results will probably line up with those of other research carried out in environments that were analogous to this one. To arrive at their conclusions, the studies use various research approaches and types of data; as a result, it is reasonable to anticipate that the results may vary to be expected.

CHAPTER 5: Conclusion and Recommendations – This chapter summarises all of the research's findings and outcomes. In addition to addressing the study question, we will go through all the anticipated goals and results. On the basis of the results and the relevant literature, recommendations for action are given, with the limitations of both sets of sources taken into consideration.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter is broken down into multiple subsections. The first subject provides general information on landfills covered in the second item. The second topic provides an overview of the solid waste disposal facility and goes into further detail on the subject of landfill leachate. The third item focuses on the specifics of leachate treatment, which is accomplished via the use of two different strategies. The last topic focuses on the electrocoagulation idea and method used to remediate leachate-containing organic waste.

2.2 Landfills

Undeniably, the generation of municipal solid waste (MSW) is directly proportional to the expansion of human activities. Worldwide, increased technical advancements and urbanisation have resulted in a rise in product consumption by the population, resulting in a growth in the expressive volume of garbage disposed of each year. About one billion tonnes of trash are being created globally, and this number is predicted to rise over time, reaching around 2.2 billion tonnes by 2025, according to Hoornweg and Bhada-Tata (2012). Leachate is produced because of the disposal of waste in landfills, and it is a highly polluting effluent due to the complexity of its composition, which includes a high concentration of organic material (both biodegradable and refractory), among which the humic compounds are an essential group of compounds, as well as nitrogenous compounds, heavy metals, and inorganic salts (Costa et al., 2019).

According to Cerbato and Argolo (2012), managed landfills are a middle ground between open dumping and sanitary landfills. They are based on the isolation process of the previous open dump sites but with the addition of leachate and gas drainage systems, residue compaction, and cell coverage at the conclusion of the working day. However, the lack of foundation waterproofing and the treatment of leachate in regulated landfills results in localised contamination, compromising the quality of surface and groundwater.

Land disposal facilities are often risky since dumping hazardous wastes on or on land invariably releases hazardous elements into the environment. Although modern landfills are highly constructed structures meant to avoid or reduce the negative consequences of waste, the development of leachates remains a severe issue for MSW landfills since these leachates may represent a considerable hazard to the soil, and surface water, and groundwater. Among leachate features, the age of the landfill is regarded as a determining factor regulating leachate composition since various metrics (for example, COD, BOD/COD ratio, and ammonia nitrogen) vary substantially as the landfill ages and stabilises (Luo et al., 2020).

2.2.1 Generation Of Landfill Leachate

Landfill leachate is described as the liquid effluents produced by rainfall percolation through solid waste disposed of in a landfill, as well as the moisture in the trash and residual degradation products. Degradation of waste matrix typically happens in landfills through four pathways: (1) early aerobic phase; (2) anaerobic acidogenic phase; (3) methanogenic phase; and (4) stabilising phase. Precipitation, rainfall, evapotranspiration, surface runoff, groundwater penetration, and the degree of compaction inside the landfill all have an impact on the number of leachates produced. Linings, waterproofing layers, and cover layers are measures used to restrict water entrance into the landfill to reduce the amount of leachate. The quality of landfill leachates is generally characterised by several physical-chemical parameters such as pH, suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia (NH_3), total nitrogen (TN), chloride, phosphorus, heavy metals, and alkalinity (Luo et al., 2020).

Each tonne of municipal solid waste (MSW) in Malaysia creates 150 litres of leachate. According to the publication TheStar (2021), Malaysians create around 38,699 tonnes of solid garbage per day, or at least 1.17kg per person. Every day in Malaysia, it is anticipated that about 3.9 million litres of leachate are generated, according to current estimates. Estimating the amount of leachate produced throughout the course of a landfill's life period is critical for environmental monitoring and possible risk management purposes. The production of leachate is influenced by the water balance at the landfill site. When considering the fluctuation in moisture content in landfills over time because of water inputs and outputs, the phrase "water balance" is used to describe the phenomenon. Leachate production occurs when the moisture content in a waste cell surpasses its field capacity, which is the maximum amount of moisture that a porous media can retain (Kamaruddin et al., 2017).

2.2.2 Factor Affecting Leachate Quantity

Waste compaction, operation method, daily cover material, waste/landfill age, superficial drainage, site hydrology, infiltration, and solid waste characteristics (such as type and original moisture content, water-holding capacity) are all factors that contribute to leachate generation and composition (rainfall, humidity, ambient temperature, evaporation, evapotranspiration) (Aziz et al., 2004).

2.2.2.1 Precipitation

The amount of rain and snow that falls on the landfill considerably impacts the amount of leachate produced. The meteorological conditions in developing nations are quite variable; in some areas, the quantity of precipitation exceeds 3,000 mm, while in others, the amount of precipitation does not even approach 500 mm (JICA, 2007). All landfills in Malaysia, a nation with a high rainfall rate, produce a substantial quantity of leachate. Organic and inorganic components are removed and dissolved in rainwater when it passes through a waste layer using the penetration method of filtering (Mukherjee et al., 2014).

2.2.2.2 Groundwater Intrusion

Occasionally, a landfill's foundation may be built below the water table. In this situation, leakage production at unlined landfills may be impacted by groundwater intrusion. As part of the natural process, landfills are often built below the groundwater table. Since landfills that are not adequately lined or handled might lead to groundwater intrusion, this is a possible consequence. There is a chance that leachate might occur in this situation (Ibrahim et al., 2017).

2.2.2.3 Moisture Content of Waste

The amount of moisture in waste and how quickly moisture moves through a waste bed are two separate things that affect how quickly MSW breaks down. Moisture flow is crucial for nutrient mobilisation and microorganism distribution in a waste bed, both of which are dependent on a wet environment. Improved mass transfer and the avoidance of stagnant zones are both made possible by the circulation of moisture through a waste bed. The microbes can't function without water to carry substrate and waste products back and forth. Waste products would build up around the microbes in the absence of flushing, resulting in dangerous concentrations. In addition to transporting nutrients and transferring heat, water is essential. Microorganisms may more easily access insoluble substrate and soluble nutrients when moisture is flowing through a landfill; therefore, this might be predicted to increase microbial activity (Chugh et al., 1998).

2.2.2.4 Final Cover/Daily Cover

Waste is covered with soil (usually 6 inches deep) at the conclusion of each working day, or it might be covered with soil on a regular basis (such as textiles, geomembrane, carpet, foam, or other proprietary materials). The daily cover is essential to prevent disease vectors and rodents, as well as to limit odour, litter, and air emissions, as well as to reduce the danger of fire and leachate development, and to reduce the risk of fire (Worrell et al., 2002).

2.2.3 Factors Affecting Leachate Quality

In general, it is considered that representative leachate samples are difficult to collect because 1) leachate composition varies greatly across landfills based on waste content, waste age, landfilling technique, and location (weather conditions); and 2) sampling sites, sampling methods, and sample processing protocols all have an impact on leachate composition. In cases when leachate is discharged into groundwater, such as in the case of older landfills that did not have liners, the geographical distribution of leachate quality is critical (Kejldsen et al., 2002).

Although the United States Environmental Protection Agency (USEPA) (2010) classified landfill leachate as an excluded hazardous waste that is not subject to the principal hazardous waste regulations under the Resource Conservation and Recovery

Act (RCRA), it is still widely regarded as a complex naturally occurring hazardous liquid. The pollutants produced depend on the processes mediated by physical, chemical, and biological agents, notably the waste biodegradation process. As a result, the quality of leachate fluctuates over time depending on the stage of waste biodegradation that it is in. Colloidal, heavy metals, non-organic salts like sodium, calcium, sulphate, ammonia, and high concentrations of toxics can be found within leachate. Inorganic materials such as humic and fulvic acids can be found within leachate and organic materials (including biodegradable and non-biodegradable carbon) (Kamaruddin et al., 2017).

2.2.4 Landfill Leachate Treatments

Regarding wastewater treatment, leachate treatment has become a severe problem, with various treatments available, including physical, chemical, and biological treatment. With landfilling being the most frequent method of solid waste disposal, sanitary landfill leachate, a highly contaminated industrial effluent, has long been a source of substantial concern. The properties of the leachate have the most impact on the use of the most appropriate approach for the treatment of leachate. Biological treatment procedures are successful for leachate from new or newly created landfills, but they are ineffective for leachate from landfills that have been in operation for more than ten years. Physical-chemical approaches, on the other hand, which are not recommended for young leachate treatment, are recommended for older leachate treatment (Ghafari et al., 2009).

2.3 Crutial Operational Parameters in Electrocoagulation (EC) Treatment

The efficiency of the EC processes is dependent on a number of operational elements, such as the current density, the amount of time spent in electrolysis, the distance between the electrodes, and the electrode material.

2.3.1 Applied Current

In the design of EC processes, the current density is often used to represent current intensity. Due to its impact on coagulant dose and bubble creation rate, as well as EC process energy consumption, the current density plays a vital role in managing reaction rate in the EC technique. The current density controls the cathodic reaction rate and anodic reaction rate. As a result, it is critical to explain how Faraday's law relates to the concentration of dissolved metals in solution. Cathode and anode ions are exchanged in an electrolyte solution, which might be water or salt solution. The current is carried between the electrodes by ions existing in the solution. At the anode, electrons from the external circuit are transported to the electrode, resulting in the oxidation of metal atoms in the electrode to produce metal ions. At the cathode, external circuit electrons are transferred to aqueous substances, causing a reduction process, such as the formation of hydrogen gas and hydroxide ions, from water (Mousazadeh et al., 2021).

According to Faraday's rule, the flow of electric current results in the transfer of electric charge, which is precisely proportional to the number of metal ions coagulated at the anode (assuming that no other chemical or electrochemical reactions are occurring). Therefore, the electrical current is the essential component in the process of pollutant elimination. Equation 2.1 may be used to determine, using Faraday's law as a guide, how much mass of metal ions is created (Mousazadeh et al., 2021).

$$m = \Phi \frac{It}{zF} M \qquad (2.1)$$

Where M is the atomic mass of the electrode material, F is Faraday's constant (1F = 96.486C), m is the mass in grams of metal (e.g. Al) generated at a specific current, and z is the number of electrons transferred per metal atom, which are three. However, for Faraday's law ($\Phi = 1$) to be valid, every electron in the system must take part in the metal-dissolution process at the anode. When parallel reactions take place, a correction factor called the current efficiency or faradaic yield (Φ) is employed to account for the difference in the theoretical and experimental dissolution of the sacrificial anode. This factor is utilised to account for the gap. This value is usually lower than 1, but Φ may be higher than 1 when the metal's chemical and electrochemical oxidation mechanisms proceed simultaneously. The metal cations that are liberated in bulk go through a variety of equilibrium processes in water. These reactions relate to acid/base, precipitation, complexation, and redox reactions. In accordance with the predictions made by Faraday's law, which is written as Equation 2.1, it is possible to create a range of varied aluminium concentrations by adjusting either the generation time or the current. As was discussed previously, the amount of metal ion produced from the metal anode's electrochemical oxidation is controlled by the current density. This results in an increased rate of production of metal hydroxide flocs that are formed in the solution for the purpose of contaminant removal. In addition, the bubble production rate may be enhanced by raising the current density, while bubble size can be lowered, which further improves the solid-liquid separation achieved by flotation. As a result, the current density range needs to be optimised with regard to the other variables of operation, taking into account the EC and EC-US processes (Mousazadeh et al., 2021).

2.3.2 Electrolysis Time

The amount of time spent in the EC is a significant factor that determines how well pollutants are removed. Because more extended periods result in producing more metal coagulants and flocs at a fixed current density, these conditions allow for a greater pollutant removal rate to be accomplished. On the other hand, the effectiveness of the EC reaches a plateau after a certain amount of time because the pollutant removal rates become stable due to the occupied active sites that create coagulant pollutant flocs.

Because the electrolysis time affects the rate at which pollutants are removed, optimising that time is essential to prevent the waste of energy and resources (Tahreen et al., 2020).

2.3.3 Inter-Electrode Distance

The amount of time spent in the EC is a significant factor that determines how well pollutants are removed. Because more extended periods result in the production of more metal coagulants and flocs at a fixed current density, these conditions allow for a greater rate of pollutant removal to be accomplished. On the other hand, the effectiveness of the EC reaches a plateau after a certain amount of time because the rates of pollutant removal become stable as a result of the occupied active sites that create coagulant pollutant flocs. Because the electrolysis time has an effect on the rate at which pollutants are removed, optimising that time is essential in order to prevent the waste of energy and resources.

On the other hand, since there are fewer electrostatic forces acting between the electrodes, a more significant inter-electrode gap delays the eventual generation of metal hydroxide flocs. Electrode spacing that is greater than what is considered optimal has a significant impact on the efficiency of the EC and results in an increase in the amount of power required to compensate for the slower passage of the released ions between the anode and the cathode. Therefore, it is essential to run EC at the ideal spacing between the electrodes. A minimal spacing of no less than 10 millimetres was employed in a number of research (Tahreen et al., 2020).

The elimination of contaminants may be affected by the distance that separates the electrodes. When the distance between the electrodes is relatively small, the efficiency of pollutant removal may be relatively low. This is because the generated metal hydroxides, which generally work to form flocs with the pollutants, will collide and self-aggregate with insufficient interaction with the pollutants. In these circumstances, the flow between the electrodes may be restricted because the distance between them is so small, and the pressure drop has become so great. When the inter-electrode spacing is just right, the system is able to remove the maximum amount of pollutants. Increases in both the transport process and the interaction between the coagulant and the pollutant may be expected to take place under these circumstances. An increase in the inter-electrode distance beyond the optimum leads to a decrease in the pollutant removal as the transport processes and interaction decrease, resulting in less formation of flocs for the coagulation of pollutants. This can be avoided by keeping the inter-electrode distance close to the optimum. In addition, if the distance between the electrodes grows, the amount of electrical energy that must be used will also grow, which will drive up the cost of the therapy (Mousazadeh et al., 2021).

2.3.4 Electrode Material

The most common types of electrode materials used in electrocoagulation are iron (Fe), aluminium (Al), carbon plate, low carbon steel, and stainless steel. This is due to the fact that electrocoagulation removes pollutants by sacrificing the electrolysis process of the anode in order to form metal ions with a high coagulation force (SS). In an EC setup where aluminium and iron are employed as electrodes, metal ions will be produced as a byproduct of the electrolytic dissolution of the anodes (Al^{3+}, Fe^{3+}, Fe^{2+}), as well as the formation of a large number of ionic monomer polymerised hydrolysates. These ions will reduce the minimum concentration of counter ions, which in turn will have an effect on the stability of colloid and suspended particles in the wastewater. The critical coagulation concentration is the concentration at which coagulation is induced (i.e., the tendency of particle aggregation) (Guo et al., 2022).

The kind of material used for the electrodes has a significant bearing on how well the EC reactor operates. The kind of cation that is brought into the solution is determined by the anode material. Numerous researchers have looked at the many materials that may be used to make electrodes, and they have come up with a wide range of hypotheses on which ones work best. Plates made of aluminium or iron were used most often as electrodes. In order to remove the colour from dye-containing solutions, Do and Chen evaluates the effectiveness of iron and aluminium electrodes and compare their results. Their investigation led them to the conclusion that the best EC conditions changed depending on whether iron or aluminium electrodes were used, which was found to be affected by the starting pollutant concentration, the pollutant type, and the stirring rate (Ghernaout et al., 2009).

To the best of knowledge, iron and aluminium electrodes are the ones that are used the most often due to the fact that they are relatively inexpensive, readily available, and have been shown to be effective. The materials that make up the anode and cathode may either be the same or different from one another. Aluminum is often more effective in removing contaminants than iron is, despite the fact that aluminium is more costly than iron. Research has also been done on the composition of iron and aluminium as electrodes. These metals are used in electrochemistry. It was reported that aluminium has a high performance for the removal of colour, phosphate, and fluoride, whereas iron has a high performance for the removal of COD. Because of this, a combination of these two electrodes resulted in a strong performance even when there was a mixture of various pollutants in the environment. It has been shown that electrochemical treatment of paper effluent with iron and aluminium electrodes achieves comparable levels of pollutant removal (Mousazadeh et al., 2021).

2.3.5 Other Factors

The speed at which the mixture in the reactor is stirred is a crucial aspect of EC since it helps maintain homogeneity in the mixture and boosts the rate at which pollutants are removed by imparting velocity via agitation. In most effluent control experiments, the stirring speed is maintained at a consistent rate, which is generally between 80 and 300 revolutions per minute (rpm). Nevertheless, a number of studies looked at how the speed of stirring affected the efficacy of the EC process when it came to removing pollutants. The mobility of ions and flocs created inside the EC reactor is improved when the mixing speed is increased, which results in an increase in the overall efficiency of the pollutant removal process. However, if the agitation is increased above the optimal range, it may have a detrimental effect on the efficacy of the EC by breaking apart the flocs that entrap the contaminants therein and perhaps restabilising the colloids (Tahreen et al., 2020).

2.4 Comparison Between Electrocoagulation Technique and Ultrasonic-Assisted Electrocoagulation Technique

2.4.1 Electrocoagulation process

In recent years, there has been a resurgence of interest in electrocoagulation (EC) technology, which may be attributed to the need for alternative wastewater treatment methods. The electrocoagulation method (EC) has certain similarities with the chemical coagulation technique, but it also has some significant distinctions (Al-Rubaiey et al., 2018). An aqueous medium is destabilised by the introduction of an electric current, which destabilises any pollutants that have been suspended, emulsified, or dissolved in the medium. It is possible to construct an electrocoagulation reactor from a single electrolytic cell with a single anode and cathode in its most basic form. The conductive metal plates, often known as ‘sacrificial electrodes’, may be formed of the same or different materials as the conductive metal plates (anode and cathode) (Emamjomeh and Sivakumar, 2009).

The oxidative termination of metals occurs in the anode, and metals may engage in a variety of chemical processes because of this process. This will produce speciation such as iron and aluminium during EC, which is very intricate. In the aftermath of this complex interaction, the reaction cell has a number of processes running at the same time in the same reactor as the parent reaction. If you compare the results of this sort of operation to the results of typical anticoagulation therapies, you will notice a significant difference. Because of this, other processes such as ultrasound may be added to the EC approach in order to improve water quality by improving the removal rates of certain pollutants from wastewater (Al-Rubaiey et al., 2018).

According to Li et al. (2011) studies using a Fe electrode, operating conditions included a current density of 4.96 mA/cm2, raw pH, Cl- concentration of 2319 mg/L, and an operating time of 90 minutes. The highest COD and NH3-N removal efficiencies were 49.8 % and 38.6 %, respectively, according to the researchers. When adopting an electrochemical technique using Fe electrodes as both cathodes and anodes, Kashani et al. (2012) found that the COD value and colour of the leachate could be effectively reduced by 81 % and 72 %, respectively. While waiting for more evidence, it seems that reaction time may be a crucial parameter in the effectiveness of the COD and colour removal from leachate.

2.4.2 Possible Mechanism during EC Process

The functioning of the electrocoagulation unit is affected by a variety of factors, including pH, the kind of pollutant, its concentration, bubble size and location, floc stability, and agglomeration size. The overall mechanism is a mixture of several processes that work together in a complementary fashion. During the course of the dynamic process, the dominant mechanism may undergo shifts as the response moves forward. The predominant mechanism will very definitely alter in response to variations in the operational conditions and the different kinds of pollutants. When a current is sent over an electrode made of metal (M^+), the metal is oxidised, becoming its corresponding cation (M^{n+})(Eq. 3.1). In the process, water is simultaneously broken down into hydrogen gas, and the hydroxyl ion (OH^-)(Eq. 3.2). EC does this by electrochemically introducing metal cations *in situ* via the use of sacrificial anodes (aluminum).

$$M \rightarrow M^{n+} + ne^- \quad (2.2)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (2.3)$$

The cations hydrolyse in water, forming a hydroxide with the dominant species determined by the solution pH. Eq. 3.3 – Eq. 3.6 illustrate this in the case of aluminum.

$$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+ \quad (2.4)$$

$$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad (2.5)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3^0 + H^+ \quad (2.6)$$

$$Al(OH)_3^0 + H_2O \rightarrow Al(OH)_4^- + H^+ \quad (2.7)$$

The production of polyvalent polyhydroxide complexes by highly charged cations is the mechanism by which colloidal particles of any kind are rendered unstable. These compounds have strong adsorption capabilities, allowing them to form aggregates with various contaminants. The release of hydrogen gas facilitates mixing, which in turn facilitates flocculation. After the floc has been produced, the electrolytic gas produces a flotation action which removes the contaminants to the floc-foam layer that is located at the surface of the liquid (Ghernaout et al., 2009).

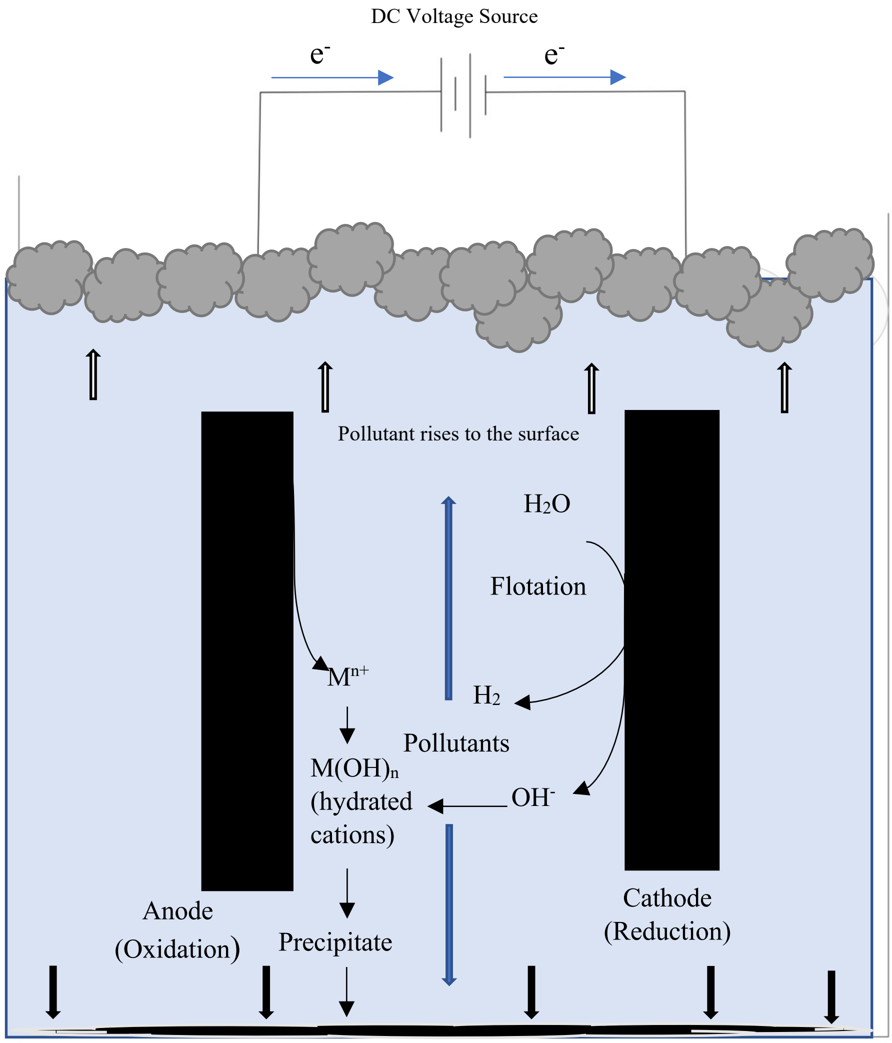

Figure 2.1: Schematic Diagram of a Bench-Scale Two-Electrode EC Cell

2.4.3 Ultrasonic-electrocoagulation process

Sonication is the technique of using sound energy to agitate particles in a sample, which may be used for a variety of applications. Ultrasound generates localised high-energy microenvironments in a medium that vary in intensity and frequency based on the insonation power. Sonication has been used in a variety of applications, including mixing, emulsification, homogenisation, and dispersion, to name a few (cavitation as well as acoustic cavitation). It has been combined with an electrochemical technique in order to improve the overall performance of the system. In contrast to traditional electrocoagulation, the process of sono-electrocoagulation was discovered to be different. Because sonication was delivered continually during the operation, floc development was prevented throughout the procedure. Anodic dissolution and mixing were more likely to be the cause. The amount of foam created at the surface as a result of the bubble formed at the cathode was reduced in this case. Sonication either fractured bubbles as soon as they formed into finer bubbles that could be seen more readily or merged the bubble with the solution, depending on the situation (Maha Lakshmi & Sivashanmugam, 2013).

Researchers have projected that managing wastewater in an electrochemical reactor using ultrasonic waves would significantly improve the kinetics and efficiency of electrode processes occurring in an electrolytic cell. This prediction has been supported by a number of studies. It contributes to the efficiency of the movement processes in the liquid by using ultrasonic waves to move the liquid. In previous research, it was discovered that the combined Ultrasonic-EC procedure increased the flocculation over an intense mixing process while also increasing the oxidation by generating species that contributed to an increase in the efficiency of the EC process through chemical refining of the flocs' surfaces and the reduction of dissolved contaminants in the bulk liquid. This conduct was utilised to explain the greater level of efficacy that had been attained. Furthermore, it was discovered that the performance of Fe-electrodes was much superior to that of Al-electrodes. Enhancing the diffusion performance of the contaminant into