THE POTENTIAL OF COPPER OXIDE NANOPARTICLES PHOTOCATALYST AND MICROALGAE FOR LEACHATE TREATMENT

By

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ABSTRACT

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The Municipal Solid Waste landfill has become a big challenge to the world nowadays. The percolating wastewater that comes out from this waste material, also known as leachate, is highly toxic and contaminated. Leachate contains high suspended solids, heavy metals and others hazardous substances such as xenobiotic compounds, ammonia, volatile organic compounds, hydrogen sulfide, methane and others. The objective of this research is to determine the effectiveness and efficiency of integrated methods using green synthesized nanoparticles and phyco-remediation using microalgae to treat leachate. In this study, the pre-treated leachate samples were treated with heterogenous photocatalytic degradation, under different concentrations of 100 mg, 150 mg and 200 mg of copper oxide nanoparticles (CuO NPs). The leachate samples were further polished using microalgae species known as *Chlorella vulgaris*. Microalgae were cultivated and grown in different percentages of 0%, 25%, 50%, 75% and 100% of photo-treated leachate samples for seven (7) days.

The water analysis for before and after treatment was carried out according to standard methods. Parameters such as pH, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5), Suspended Solids (SS), Ammoniacal Nitrogen (AN) were tested. Throughout this research, the mentioned integrated leachate treatment had achieved the total removal rate of 98% of COD, 99% of BOD_5, 93% of SS and 93% of AN. As a conclusion, the integrated system of nanoparticles and microalgae has shown the optimization of leachate treatment by achieving the most satisfactory reduction rate in the tested parameters.

Keywords: copper oxide nanoparticles, landfill leachate, durian husk extract, photodegradation, wastewater treatment

Subject Area: QD146-197 Inorganic Chemistry

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LIST OF ABBREVIATIONS

ADMI	American Dye Manufacturer's Institute
APHA	American Public Health Association
BBM	Bold's basal medium
BOD_5	Biochemical Oxygen Demand for 5 days
COD	Chemical Oxygen Demand
Cu	Copper
Cu^{2+}	Copper (II) ions
CuO NPs	Copper Oxide Nanoparticles
NH_4-N	Ammoniacal nitrogen
wt%	Weight percent
% (w/v)	Percent of weight of solution in the total volume of solution

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The management of municipal solid waste (MSW) is becoming more problematic because of rising populations and economies, making innovative solutions crucial. Creative solutions are extremely essential to address the growing problems associated with managing MSW, which are made worse through the population increase and economic expansion. Common disposal techniques such as landfilling have an adverse impact on water quality and cause leachate production, which is so hazardous for the ecosystem. This research work tackles this important problem and suggests a two-pronged strategy. The synthesis of copper oxide nanoparticles from durian husk waste is an eco-friendly method that converts agricultural waste into valuable resources. This process not only aids in waste management but also produces nanoparticles with unique properties for various applications, including catalysis and environmental remediation. By using durian husk, we promote sustainability and minimize environmental impact, making it a green alternative to traditional nanoparticle synthesis methods. Then, simultaneously *Chlorella vulgaris* culture in pre-treated leachate is thoroughly optimized.

These initiatives target to improvise green synthesis techniques and sustainable waste management strategies in order to mitigating the negative environmental effects of landfill leachate.

The management of MSW is becoming more difficult in response to the growing global garbage dilemma, which is being prompted by economic expansion along with the population growth.

As leachate is produced, landfilling, a common disposal technique in several developing countries, especially Asia, raises environmental obstacles. As the expanding of economic and human populations, the waste is continuously generated. The remediation of the leachate from MSW is also becoming challenging in the world. According to Twagirayezu et al., (2023), many poor nations have the option of using landfills as a waste disposal method. In Asia, landfills receive 70–90% of municipal solid waste according to El-Saadony et al., (2023). According to Mary et al., (2023), leachate is the liquid that flows out of a landfill and contains many kinds of contaminants, both organic and inorganic. When the leachate is generated, it will go through the underground water flow. If the leachate is not managed properly, it can cause watercourse pollution to the surface and underground water quality. Leachate is often tested to exceed standard for drinking water and surface water.

In Malaysia, any waste management need to get approval before dispose to landfill. Prior to disposal in a landfill, waste management in Malaysia must obtain approval. Solid waste increased from 0.5 kg per capita per day in 1980 to 1 kilogramme per capita per day in 2001, as reported by Yaashikaa et al., (2022). According to Ma et al., (2022), the amount of leachate that is produced is influenced by the disposal conditions and the initial water content of the municipal solid waste. There is around 75% of MSW is landfilled and only 5% is recycled. However, there are still many uncontrolled landfills whereby the rest of the MSW is illegally dumped. The most worrying part is the landfills are in bad condition and operated without proper protective measures such as lining systems, leachate treatment and gas venting by Yaashikaa et al., (2022).

According to the Environmental Quality Act 1974, all the leachate waste must be treated before discharged into the rivers. This is because the leachate waste is highly toxic and contains a high concentration of organic, inorganic, suspended solids which will severely affect aquatic life and the environment. There are many methods that can be used for leachate treatment such physical/chemicals, biological and combined methods. Type of leachate, concentration of leachate pollutants and its toxicity characteristics are some of the important factors that may be considered for the selection of the treatment method by Zaini et al., (2022). Due to the complexity, toxicity of landfill leachate composition and high in volume, the treatment process is complicated, expensive, and required various combination of treatment method.

The emerging worldwide waste conflict, which is being caused by increased population and economic expansion, it broadly highlights how urgently MSW management need to be addressed. Due to the production of leachate, landfilling is a prevalent disposal technique to develop nations, especially in Asia, that extensively raises environmental issues (Ma et al., 2022). The quality of surface as well as subsurface water is threatened by leachate, which is full of organic and inorganic pollutants. The hindrance is made worse in Malaysia through increasing output of solid waste and insufficient waste management techniques. Uncontrolled landfills that are not properly equipped with the necessary safeguards exacerbate environmental deterioration.

The research addresses this crucial problem and proposes algae treatment as an effective solution due to algae's ability to absorb nutrients and heavy metals, degrade organic pollutants, and provide a sustainable and eco-friendly method of water purification. The incorporation of the nutrient-rich environment of landfills, especially the valuable durian husk waste, the research targets to enhance *Chlorella vulgaris* culture through synthesizing copper oxide nanoparticles.

1.2 Problem Statement

Landfill disposal is one of the simplest disposal methods among others. Thus, it is detrimental to the surface and underground water when the leachate flows directly into the underground. This inappropriate leachate management will bring about long-term effects to human life and the whole ecosystem.

In the viewpoint, algae remediation can be used to resolve the problems caused by the landfill leachate. Landfill consists of high nutrients which have intrinsic value for algae cultivation. Some of the parameters such as ammonia, nitrate, total phosphate etc. will be reduced because the nutrients were absorbed by microalgae and used for growth. Landfilling is the most prevalent method of disposal, but it poses a significant threat to the environment since the leachate it produces can harm the quality of water on the surface and below. The inadequate management of leachate in several developing nations, such as Malaysia, has resulted in extensive environmental consequences.

Solid waste creation has been steadily increasing, going from 0.5 kg/capita/day in 1980 to 1 kg/capita/day in 2001 (Yaashikaa et al., 2022), highlighting the critical need to address this important issue immediately. According to Twagirayezu et al., (2023), just 5% of Malaysia's MSW is recycled, while the remaining 75% is disposed of in landfills.

Illegally dumped waste at unregulated landfills exacerbates the problem, particularly in those sites lacking safety measures including gas venting, leachate treatment, and liner systems.

The disregard for environmental standards, demonstrated by the existence of poorly managed landfills that extensively lack the required protections, is an urgent reason for concern. Leachate treatment is required prior to disposal into the rivers under the Environmental Quality Act of 1974, which strongly highlights the hazardous nature of leachate waste (El-Saadony et al., 2023). Sedimentation and the elevated levels of suspended particles and organic and inorganic pollutants are major hazards to aquatic life and the surrounding ecosystem. The volume, toxicity, as well as complexity of landfill leachate make the treatment process difficult, costly, and require a variety of techniques. The choice of the most appropriate treatment methodology is dependent on several parameters, such as the kind of leachate, the amounts of pollutants, and the toxicity characteristics of the material. These considerations can vary from physical/chemical treatments to the biological and combination methods (Mary et al., 2023). In this regard, the research work finds that leachate management calls for a long-term and practical solution.

The strategy that is being suggested makes use of the nutrient-rich environment found in landfills through employing algal remediation. One potential solution to reduce the environmental impact of landfill leachate is to employ durian husk waste in the green manufacture of copper oxide nanoparticles and *Chlorella vulgaris* culture. Preserving ecosystems and future human life depends on finding a solution to this problem, which is why doing so is of the utmost importance.

1.3 Research Objectives

The objectives of this research are:

1) To green synthesize copper oxide (CuO) nanoparticles using aqueous extract of durian husk waste and their characterizations using various analytical tools.

2) To study the optimum culture condition for microalgae species of *Chlorella vulgaris* grown in pre-treated leachate.

3) To study the effectiveness of the combined treatment methods on leachate by determining the pH, ammoniacal nitrogen. Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) of the treated leachate.

1.4 Novelty of Study

There remain several crucial consequences for the waste management procedures as well as environmental sustainability from this research. Innovative and long-lasting solutions are broadly required for addressing the growing problems with Municipal Solid Waste (MSW) disposal, particularly when it comes to landfilling.

The research of environmentally friendly copper oxide (CuO) nanoparticle synthesis employing waste from durian husks tackles the hindrances of waste valorization and nanoparticle manufacturing. This sustainable method of producing nanoparticles not only makes utilization of the natural nutritious content of durian husk waste, yet it also involved in promoting a circular economy through the incorporation of agricultural by-products (Zaini et al., 2022). The strong emphasis on enhancing *Chlorella vulgaris* cultivation conditions in pre-treated leachate is in accordance with the worldwide movement towards phytoremediation methods. The incorporation of microalgae to cure leachate not only provides a sustainable and economical solution, but it also lessens the environmental impact of landfill leachate. The overall quality of treated effluents can be improvised by significantly lowering dangerous contaminants such as ammonia, nitrate, along with total phosphate by the growth of *Chlorella vulgaris* in pre-treated leachate (Ghazali et al., 2022). The study's findings advance the knowledge of algae-based remediation techniques and simultaneously open the door to new developments in environmentally friendly waste management.

The incorporation of durian husk waste in the synthesis of nanoparticles broadens the scope of green synthesis techniques and promotes the creation of eco-friendly processes for producing nanomaterials.

The essentialism of this research lies in its ability to properly provide realistic as well as long-lasting solutions to the environmental problems landfill leachate presents, ultimately leading to a better and a cleaner ecology.

This research work broadly explores the crucial issues surrounding the management of MSW, especially the effects landfill leachate has on the ecosystem. Optimizing *Chlorella vulgaris* culture in pre-treated leachate along with producing copper oxide nanoparticles from durian husk waste are among the goals. These endeavors are in accordance with the global requirement for phytoremediation methods and sustainable waste solutions. The relevance is in providing environmentally friendly nanoparticle production, making use of agricultural residues, as well as the developing algae-based remediation for effective leachate removal. It demonstrates potential for improvising green synthesis techniques, environmental preservation, and sustainable waste management.

CHAPTER 2

LITERATURE REVIEW

2.1 Landfill Leachate Characteristics

The chapter on Literature Review thoroughly explores various approaches and developments while exploring the complex field of landfill leachate treatment. Every aspect of the process, from the synthesis of copper oxide nanoparticles to the complex arrangements of physical, chemical, and biological treatments, adds to the growing knowledge of long-term along with practical methods for dealing with the problems landfill leachate presents. Leachate from landfills is generally characterized as high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) wastewater and consists high value of organic and inorganic contaminants (Singh et al., 2021). The characteristics of leachate wastewater may vary depending on its degradation process, climate, age of a landfill and hydrological condition**.**

Landfill leachate can be classified into three types namely, young, intermediate, and mature leachate (Twagirayezu et al., 2023). Young leachate is characterized by low pH, high concentration of volatile acids, and simple degradable organic matter.

These are such examples, pH for mature leachate is slightly higher and consists of humic and fulvic fractions of organic matter are such example. The decomposition of organic matter such as humic acid turns the leachate from yellow to dark brown color. Table 2.1 shows the landfill leachate classification and its waste characteristics.

Table 2.1: Classification and characteristics of leachate (Baig, 1996; Aziz, 2018)

Leachate Category	Unit	Young Leachate	Intermediate Leachate	Mature Leachate

Age of landfill	Year	0 – 5	5 – 10	>10
pH	-	< 6.5	6.5 – 7.5	> 7.5
COD	mg/L	>10,000	5,000-10,000	<5,000
BOD5/COD Ratio	-	0.5 – 1.0	0.1-0.5	>0.1
Organic compound	%	70-90%	20-30%	Humic Acid and Fulvic Acids
Biodegradability	-	High	Medium	Low

The composition of the leachate is crucial to determine proper leachate treatment process, as leachate can be degraded both chemically and biologically (Yaashikaa et al., 2022).

Due to the complexity, toxicity of landfill leachate composition and high volume, the treatment process is complicated, expensive and required various combination of treatment methods. Treatment procedures are greatly influenced through the leachate composition, which is classified into three phases according to landfill age: young, middle, and mature. Young leachate (0–5 years) has 70–90% organic molecules, a low pH, and a high COD (>10,000 mg/L) (Amusa, Taib and Xian, 2023). A pH range of 6.5–7.5, considerable COD (5,000–10,000 mg/L), and simultaneously 20–30% organic molecules are observed in intermediate leachate (5–10 years). A mature leachate (>10 years) broadly contains fulvic and humic acids, has a pH >7.5, and a COD <5,000 mg/L (Gong et al., 2023). Due to the toxicity as well as large volume of leachate, proper treatment must take this complexity into account and provide specialized and efficient methods.

2.2 Leachate Treatment Methods

There are many methods that can be used for leachate treatment such physical/chemicals, biological and combined methods. Type of leachate, concentration of leachate pollutants and its toxicity characteristics are some of the important factors that may be considered for the selection of the treatment method (Ma et al., 2022). Combination treatment method of physical, chemical, and biological method has advantages over each single process and effectively treating the landfill leachate. Figure 2.1 shows the common landfill leachate treatment method.

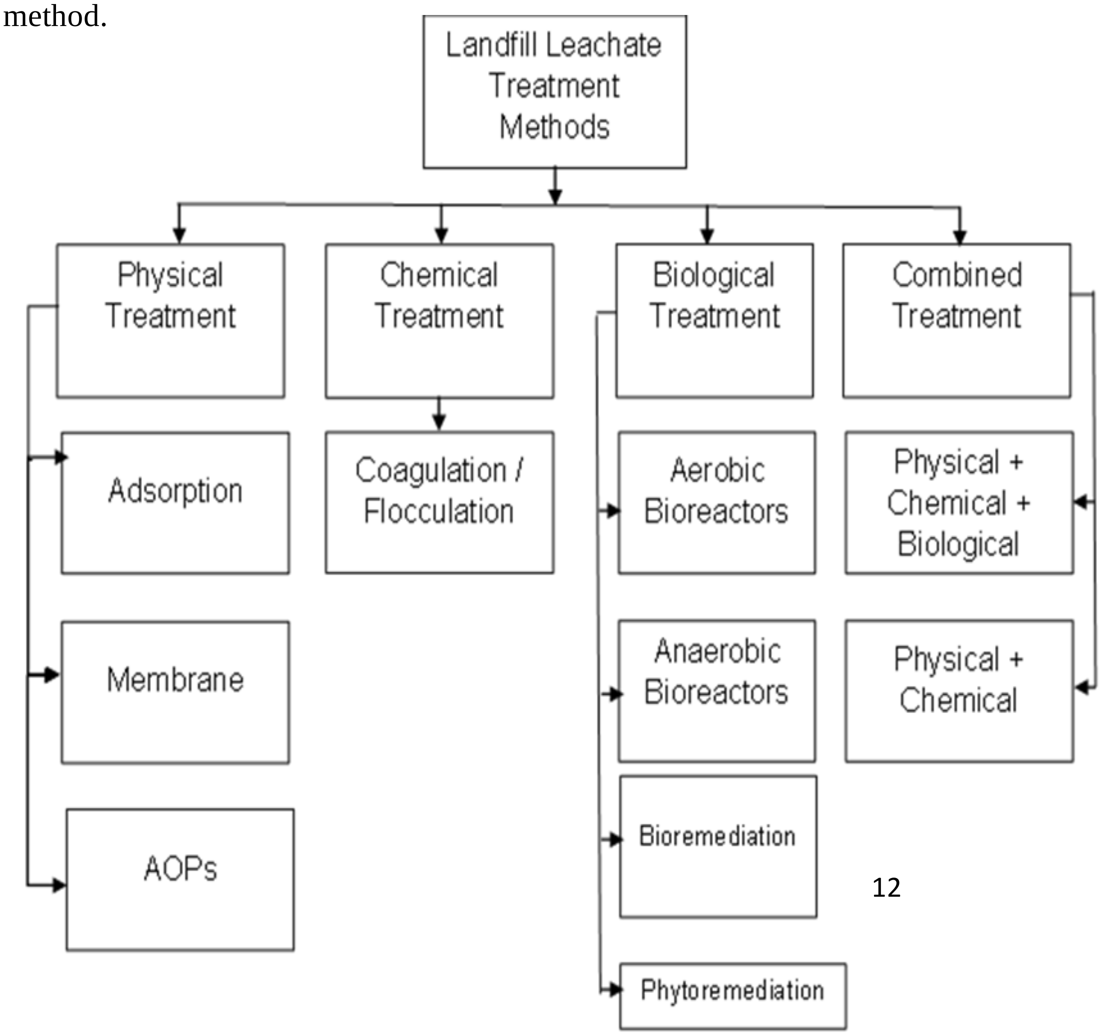


Figure 2.1: Common Landfill Leachate Treatment Method (Twagirayezu et al., 2023)

The above image depicting the "Common methods to treat the landfill leachate" shows the distinct physical (adsorption, membranes), chemical (coagulation/flocculation, "Advanced Oxidation Processes (AOPs)), and biological (aerobic/anaerobic bioreactors, bioremediation," phytoremediation) approaches.

These methods can be combined, e.g., physical-chemical or physical-chemical-biological methods, to allow an efficient leachate treatment focusing on given pollutants that will be removed, neutralized, or degraded to ensure environmental protection and compliance with regulations.

2.2.1 Physical Treatment

Physical treatment such as conventional filtration and advance filtration adsorption are common examples for leachate treatment. The conventional filtration method uses different layers combination of sand, gravel, stone, and anthracite in a multi-media filter (MMF) vessel. This conventional method can be acts as pre-treatment of leachate treatment by removing big particles and suspended solids presence in the leachate. It also as a polishing process to further polish “Chemical Oxygen Demand (COD)” and “Suspended Solids (SS)” before discharge (Zou, 2020). Advance filtration such as ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) and Reverse Osmosis (RO) are some examples of membrane types for leachate treatment. Table 2.2 shows the membrane types and function.

Table 2.2: Membrane types and functions (Zou, 2020)

Membrane Types	Function
MF	To eliminate colloids and SS
UF	To remove macromolecules
NF	To remove organic, inorganic, and microbial pollutants, capable of removing particles as small as 0.002 to 0.005 um in diameter
RO	Finest membrane filtration, capable of removing particles as small as 0.1nm

The RO membranes are protected by the efficient removal of bigger impurities and suspended particles by MF and UF. However, this membrane technology requires high energy demand, high operating cost and significant reject stream, which means that the RO reject volume can achieve up to 30% of the total volume treated.

Granular activated carbon (GAC), as the adsorbent media is used for pollutant removal in the leachate treatment. According to Twagirayezu et al., (2023), coconut shell GAC showed COD removal rate of 82% reduction for young leachate, where commercial GAC showed 19.1% of COD removal rate. Activated carbon has properties of high porosity, stability and surface area which are attributed to pollutants adsorption.

Once the surface area of GAC is fully occupied, regeneration and proper backwashing are needed before reusing it (El-Saadony et al., 2023). GAC is used to reduce the pollutants concentration and its leachate toxicity before going to further treatment. However, it is considered as expensive treatment if used solely, thus it must be combined with other treatment methods to achieve the desired water quality (Mary et al., 2023).

An “Advanced Oxidation Process (AOPs)” which applies a combination of oxidants and catalysts to produce hydroxyl radicals (OH) in solutions, such as Ultraviolet (UV), Fenton and Electrochemical Oxidation (EO) methods (Mahdi et al., 2021). However, this process involved high capital and operating costs.

The most well-established physical treatments for leachate include filtration and adsorption. MMFs or multi-media filters are employed for the removal of coarse particles and suspended solids by conventional filtration which is a commonly used step as pre-treatment or polishing for reduction of COD and SS (Abuhasel et al., 2021). The MF, UF, NF, and RO are advanced filtration methods that can remove specific pollutants, the use of these individual filtration methods is limited due to some major issues related to their high energy consumption, operational costs, and reject streams (30% or more). An increasing the adsorption capacity of pollutants, such as GAC, it can be used to adsorb contaminants, obtaining as high as 82% COD removal for young leachate, nevertheless, it appears to be expensive alone and operates with the necessity for regeneration. For maximum efficiency and cost-effectiveness, it needs to be integrated with other methods.

2.2.2 Chemical Treatment

The chemical treatment consists of three major processes which are pH adjustment, coagulation and flocculation process. Chemical treatment is the most common and widely used method in wastewater treatment plants and landfill treatment.

In the pH adjustment process, pH is required to adjust to desired pH value, range 6.5 – 8.5 using either acid or alkaline chemicals. In the coagulation process, coagulant neutralized the charge on the particle. Once charge is neutralized, tiny-suspended particles can stick together and the Micro-flocs are observed and formed in this process (Mary et al., 2023). Clearer water can be seen surrounding the formed micro-flocs. Rapid mixing is required to ensure the coagulant is properly dispersed to promote particle collision. Over mixing at this process does not affect the coagulation process. Contact time in this process is typically 1 to 3 minutes. Aluminum sulphate and ferric chloride are examples of inorganic coagulant, where polyamines are the examples of organic coagulant.

In the next process, flocculant is added to promote the clumping of micro-flocs, enable them to bind together and make the flocs bigger. Wide range of polymer selection such as anionic or cationic polymer will be used in water treatment. Selection of proper polymer required considerable jar test under simulated plant conditions. The flocculation process required gentle or slow mixing where the size of the particles is becoming bigger and visible. Once these flocs reached optimum size and strength, solid-liquid separation is achieved (Zaini, Hasan and Zolkepli, 2022). The design contact time for this process ranges from 15 to 20 minutes and requires constant mixing and velocity. According to Ghazali et al., (2022), chemical treatment showed COD removal rate up to 75% for mature leachate compared to young leachate which only achieved 25-38% COD removal rate. In short, the advantage of this chemical treatment is that this method is highly effective in removing organic matter and suspended solids. However, the cost of chemicals consumption and handling of generated sludge become drawback of this method.

Leachate chemical treatment schemes generally consist of pH adjustment, coagulation, and flocculation; pH adjustment acids or alkaline are used to ensure that the leachate pH is in the optimum range that is 6·5–8·5. The hydration with rapid mixing causes coagulants such as aluminum sulfate to neutralize the charge of particles and form micro-flocs (Asharuddin et al., 2023). It can create larger flocs, allowing solid-liquid separation by gently mixing for 15–20 minutes using polymers, this is called flocculation.

The method is efficient and has obtained up to 75% COD removal for landfill leachate which age range between 0 and 10 years. Chemical costs are considerable and effective sludge management is a major challenge. Chemical treatment, such as adjustment of pH, coagulation, and flocculation can remove organic materials and suspended sol1ids, and as much as 75% of COD can often be removed from mature leachate. The coagulants have been used, for example, aluminum sulfate, micro-flocs are produced, and polymers assist floc formation. This key method is efficient, but it is challenged with high chemical costs and sludge disposal necessities.

2.2.3 Biological Treatment

Biological treatment is a type of leachate treatment used to remove contaminants partially. However, the removal efficiency is relatively low to moderate because of several factors which emerging contaminants resistant to biodegradation (Zaini, Hasan and Zolkepli, 2022).

There are two categories of biological treatment which are aerobic and anaerobic treatment. This treatment method is used to reduce biodegradable organic matters such as nitrogen, BOD and COD. Examples of aerobic treatment such as aerated lagoons, aerobic bioreactors and activated sludge. The activated sludge method is most commonly and widely used, it is a suspended growth process that uses aerobic microorganisms to biodegrade the organic matters in the leachate (Mary et al., 2023).

During this process, microorganisms will biodegrade the organic material completely and transform into water and carbon dioxide. Sequencing Batch Reactor (SBR) is one of the activated sludge methods for landfill leachate treatment. In the presence of oxygen, it promotes the degradation of pollutants present in the leachate. However, this method required high concentrations of dissolved oxygen in bioreactor for denitrification process (Zaini, Hasan and Zolkepli, 2022). Example of anaerobic treatments are anaerobic lagoons and bioreactors. An Anaerobic treatment of leachate is a low-cost treatment. Anaerobic treatment involves the breakdown of inorganic and organic substances using microbes in the absence of oxygen, under anaerobic conditions. This method is environmental-friendly and generates less sludge and can generate biogas as energy resources. However, this treatment is very sensitive to pH which required to maintain pH at 6.5. – 7.8 and required long retention time (Mary et al., 2023).

For municipal wastewater which contained low concentration of COD and nutrients, aerobic process is the choice. Whereby, for higher COD concentration and higher biodegradable waste, anaerobic process is more economical. Anaerobic treatment required less energy and smaller reactor volume than aerobic treatment.

On top of that, the use of algae, microalgae, bacteria, and fungi are types of bioremediation treatment. According to the research of (Yaashikaa et al., 2022), bacteria such as *Firmicutes, Actinobacteria, Proteobacteria, Brevibacilluspanacihumi strain ZB1 and Pseudomonas putida* had been reported for the use in landfill leachate treatment. Phyto-remediation methods using plant soil systems to degrade have removed the potential toxic substances in leachate. Studies showed that aquatic plants such as *Colocasia esculenta, Pistia stratiotes, Eichhornia crassipes, Phragmites australis, Azolla filiculoides, Typha domingensis, Hydrilla verticillata, Azolla caroliniana, Salvinia Cucullata, Heliconia psittacorum, Azolla pinnata, L. minor, Lemna gibba, Lemna aequinoctialis, Gynerumsagittatum and Spirodelapolyrhiza* can be used for leachate treatment (El-Saadony et al., 2023). Up to removal rate of 70% to 47% in metals, COD and BOD were removed during contact time of 15 days using *Lemna minor* (Twagirayezu et al., 2023). Advantages of this method are low capital cost and energy consumption.

2.2.4 Phyco-Remediation Treatment

Phyco-remediation uses microalgae to remove or transform the pollutants including the nutrients from wastewater and CO_2 from waste air. This can be a promising green technology as it combines the concept of algae-waste water treatment. Microalgae plays a crucial role for the water cleanliness and suitable for consumption (Yaashikaa et al., 2022).

Microalgae are fast growing and easy to cultivate organisms and can reproduce themselves by utilizing sun energy to carry out photosynthesis to complete growth cycle itself (Ma et al., 2022). Microalgae have a higher growth rate and productivity. With enough nutrients and a favorable environment, microalgae can adapt to live well.

Microalgae cultivation could be potentially more cost effective than conventional farming (Alhalili, 2022). According to Bah et al., (2023) microalgae strains such as *Chlorella spp.* and *Scenedesmusspp.* It has shown their potential for water treatment application and tolerance for the significant reduction in ammoniacal nitrogen and heavy metals. Phyco-remediation is a promising leachate treatment which significantly shows reduction in COD, BOD, sludge and operation costs (Ghazali et al., 2022).

Zaini, Hasan and Zolkepli (2022) studies showed up to 90% of ammoniacal nitrogen and 60% of COD were removal using microalgae (*Chlorella sp.)* for leachate treatment. The leachate ratio is also important to promote the growth of *Chlorella sp*. in the leachate treatment and the result showed leachate ratio of 10% is a favorable media for microalga cell activity. This research showed that microalgae was effective for treating landfill leachate (Mary et al., 2023). Besides that, many studies have been conducted to prove the use of microalgae for leachate treatment and its degradation ability of organic compounds. Table 2.3 shows various microalgae species used.

The table illustrates the ability of different microalgae species for removing pollutants from the leachate by summarizing the work in this arena. Significant removal efficiency for total organic carbon (60%) and COD (68%), along with turbidity (98%) are clearly demonstrated by *Chlorella* sp. (Noor et al., 2023). According to Shareefdeen and Elkamel (2022), *Chlorella vulgaris* exhibits exceptional removal rates for both the COD (91%) and the NH4-N (99.9%) (Pratap et al., 2023). These factors extensively highlight the potential of microalgae in phyco-remediation, especially *Chlorella* species, which has the possibility to dramatically lower important contaminants in landfill leachate. Table 2.3 shows microalgae used for leachate treatment.

Table 2.3: Microalgae used for leachate treatment (Mary et al., 2023)

Microalgae	Pollutants Removal	Removal Efficiency (%)	Reference

Chlorella sp	Total Organic Carbon	60	(El-Saadony et al., 2023)
	COD	68	
	Turbidity	98	
Chlorella sp *Clamydomonassp*	NH4-N	83	(Twagirayezu et al., 2023)
	PO4 3-P	98	
	Nitrate	54	

Table 2.3: Continued

Microalgae	Pollutants Removal	Removal Efficiency (%)	Reference
Chlorella vulgaris	NH3-N	53.9	(Yaashikaa et al., 2022)
	BOD	52.7	
	COD	51.0	
Chlorella vulgaris	COD	91	(Ma et al., 2022)
	NH4-N	99.9	

2.2.5 Combined Treatment

There are several combinations of treatment methods of physical, chemical and biological have been identified to improve the efficiency of removal rate and reduce energy consumption. Table 2.4 shows the Combined Treatment process.

Table 2.4: Combined Treatment (Yan et al., 2023)

Combination	Methods	Result	Remark
Physical + Chemical	AOPs + membranes	94-96% removal of COD and 96-99% of color removal from leachate, through Fenton, NF and MF process.	(He et al., 2023)

Table 2.4: Continued

Combination	Methods	Result	Remark
Physical + Chemical	AOPs + Adsorption	Integrated H_2O_2 with granular activated carbon eliminate up to 97.3% of COD.	(Yan et al., 2023)
Physical + Chemical + Biological	AOPs + coagulation	70.3%, 58.3% and 58.3% removal rate in COD, Ammonia and Total Nitrogen respectively.	(Ahmad et al., 2022)
	Coagulation + Biological	72% of COD and 70% of total organic carbon were removed during coagulation and anaerobic bioreactor process.	(Esmaeeli et al., 2023)

Combination of physical, chemical, and biological are the most common landfill leachate treatment methods. This integrated treatment method is strongly recommended due to the high concentration of contaminants in leachate and its low biodegradability. Table 2.4 presents the several combinations of physical, chemical, and biological treatment processes that are incorporated in landfill leachate treatment to improvise removal efficiency and lower energy usage.

Prominent amalgamations encompass “Advanced Oxidation Procedures (AOPs)” in conjunction with the membranes, resulting in an astounding 94-96% removal of the COD and 96-99% elimination of color using procedures including Fenton, NF, and MF (Esmaeeli et al., 2023). Up to 97.3% COD removal is possible with integrated treatment, such as H2O2 combined with granular activated carbon (Noor et al., 2023). Significant removal rates of COD, ammonia, as well as treatment, which eliminates over 70% of ammonia, demonstrate the physical-chemical-biological synergy. A remarkable 72% COD along with 70% elimination of total organic carbon are obtained when coagulation is combined with biological treatment (Zamrisham et al., 2023). The efficacy of integrating several treatment techniques for managing the intricate characteristics of landfill leachate, characterized through elevated pollutant concentrations, and reduced biodegradability, is demonstrated by these integrated approaches. The results underscore the significance of utilizing all-encompassing approaches to augment the general efficacy of leachate treatment procedures.

2.2.6 Nanoparticle: Copper Oxide (CuO)

In recent years, development of green technology has brought a new potential to the world and gained interest of researchers that produce more valuable products and broader perspective of humanity world. Thus, green approach to synthesis nanoparticles has become an interesting and active research field due to its low-cost methods and eco-friendly advantages.

Nanoparticles can be used for various applications such as wastewater treatment, fuel cells, antibacterial activity applications and to state (Zamrisham et al., 2023). The use of metal oxide nanoparticles such as copper oxide, iron oxide and zinc oxide are rising in different industries like chemistry, material science, biopharmaceutical industries due to their unique optical, physical, and biological properties. Copper oxide NPs also can be applied as antibacterial agent with low cost and low toxicity in the superconductors, catalysis, solar energy conversion industry. The synthesis of CuO NPs has gained notable importance among all the metal oxide nanoparticles as researchers found its significant role in environmental remediation. COD removal under different concentrations of copper oxide at 0.1, 1, 10 and 50 mg/L were studied. Short-term exposure to CuO NPs at a concentration of 1 mg/L showed 77% COD removal rate. The COD removal was negligible at 0.1 mg/L of CuO NPs (Noor et al., 2023). The high concentration of CuO NPs at 10 mgL/L and 50 mg/L inhibited the growth of biological system.

Nanoparticles (NP) are revolutionary in treating wastewater because they have enormous surface area-to-volume ratios and tunability. CuO NPs, for example, show a 77% COD removal efficiency at a concentration of 1 mg/L but the concentration is inefficient (0.1 mg/L) and even the biological systems might be inhibited at high concentrations (10–50 mg/L). For example, iron oxide NPs are superior at adsorbing heavy metals (i.e., arsenic), and titanium dioxide NPs utilize photocatalysis to degrade recalcitrant organic pollutants.

However, these challenges remain, and targeting environmental toxicity, cost-effectiveness, and scalability should be further optimized for sustainable implementation on various wastewater systems.

The Green policy is new and reviewable and focused on nanoparticles (NPs) that are more in a hurry to wind up noticeably giving guarantee with eco-friendly generation stage from squandering h2o with lessened unfavorable environmental influences. These NPs are produced with natural reducing agents, such as plant extracts, microorganisms, or biowastes, and do not require a toxic chemical in the synthesis process to achieve the target desired properties of the NP (Aswathi et al., 2023). This strategy concurs with sustainability ambitions, leading to bio-inspired nanoarchitectures with remarkable features including biocompatibility and stability to meet the needs of environmental troubles.

The Metal oxide NPs including copper oxide (CuO), zinc oxide (ZnO), and iron oxide displayed a good record in wastewater treatment especially those that are synthesized using green methods. Moreover, CuO NPs have extraordinary antibacterial potential that helps eliminate morbid pathogens. One of their metabolic by-products, exopolysaccharides, is also involved in the reduction of chemical oxygen demand (COD) in that they help to degrade organic pollutants, with up to 77% removal efficiency when the correct concentration of EPS is available (vegetal), helping to reduce COD removal (vegetal). ZnO and TiO_2 NPs synthesized through green methods are predominantly applied in the photocatalytic degradation of dyes and other recalcitrant organic pollutants under solar light, which converts the pollutants into harmless end products (AlMohamadi et al., 2021). Likewise, the adsorption of heavy metals such as arsenic, lead, and chromium by green-synthesized iron oxide NPs is beneficial in the treatment of industrial effluents.

However, the applicability of green-synthesized NPs in wastewater treatment is hindered despite their potential. Limited studies exist on the scalability of green synthesis approaches and on the fate of NPs, especially over long-time horizons and hidden to the naked eye across aquatic compartments and habitats. There is also the challenge of delivering a high level of efficacy at the right price point. The ongoing research and technological developments might be pivotal to harnessing the potential of green-synthesized NPs on a commercial scale and sustainable applications in wastewater treatment up to date (Magalhães-Ghiotto et al., 2021).

Due to its enormous potential for an extensive range of applications, copper oxide (CuO) nanoparticle production has seen a surge in attention in recent years because of the development of green technology. Green synthesis techniques are becoming more and more popular due to their affordability and environmental benefits. CuO's unique optical, physical, and biological qualities have made it, along with other metal oxide nanoparticles such as iron oxide and zinc oxide, more useful in fields including chemistry, material science, and biopharmaceuticals (Esmaeeli et al., 2023). It is extremely important for environmental remediation as well, especially for wastewater treatment, where research on COD removal at different CuO concentrations (0.1 to 50 mg/L) demonstrates promising results.

An astounding 77% of COD is removed after a brief exposure of 1 mg/L, demonstrating CuO's effectiveness to eliminate environmental contaminants (Ighalo et al., 2021). Lower concentrations of 0.1 mg/L present very little reduction in COD, highlighting the essentialism for dose accuracy. On the other hand, larger quantities of 10 and 50 mg/L present inhibitory effects on biological systems, hence the incorporation of this substance needs to be avoided excessively (Las Heras et al., 2024). This intricate comprehension becomes essential for enhancing CuO usage in environmental contexts.

2.2.7 Nanoparticle: Green Synthesis of CuO NPs

There are few methodologies for CuO NPs synthesis include using physical and chemicals approaches such as sono chemical methods, sol-gel method, electrochemical reduction, chemical precipitation, and thermal decomposition. The drawback of this approach includes use of toxic chemicals as reducing agents, even if it is producing high yields of NPs.

On the contrary, green synthesis of CuO NPs using biological method is a more favorable approach as it is more stable, non-toxic, low cost and eco-friendly (Esmaeeli et al., 2023). Synthesis of CuO NPs from plant extracts have more advantages than others as the sources is more easily available and easy to manage.

As reported in the previous studies, CuO NPs were successfully green synthesized from plants extracts such as *Acalypha indica*, *Phyllanthus amarus*, *Terminalia arjuna* , *Calotropis gigantean*, *Malva sylvestris*, *Cassia alata* , *Gloriosa superba and Catha edulis* leaves (Bah et al., 2023). In addition, CuO NPs also had been reported synthesized from waste materials such as cauliflower waste (*Brassica oleracea*), peels extract (*Carica papaya*), orange peel extract (*Citrus reticulata*), potato waste extract (*Solanum tuberosum*) and pomegranate peels extract (*Punica granatum*) (Alhalili, 2022).

Researchers found that plant-mediated green synthesis of CuO NPs are safer to handle compared to chemical approach and had been successfully applied in biological and non-biological activities, such as antibacterial, photocatalytic and cytotoxicity.

Copper oxide nanoparticles (CuO NPs) have been synthesized incorporating a variety of physical and chemical procedures. Although these techniques have produced significant yields of nanoparticles, there is safety as well as environmental issues due to their use of hazardous compounds as reducing agents.

A more beneficial option has extensively emerged: the green production of CuO NPs by biological processes (Hasnine et al., 2022). More consistency, cost-effectiveness, along with environmental friendliness are provided by this specific method. The readily available and simultaneously easily manageable nature of plant sources makes the synthesis of CuO NPs from plant extracts beneficial. It has been effectively presented in previous investigations (Ahmad et al., 2022).

CuO NPs have been actively produced from potato waste (*Solanum tuberosum*), orange peels (*Citrus reticulata*), pomegranate peels (*Punica granatum*), cauliflower waste (*Brassica oleracea*), and peel extracts from *Carica papaya* (Yan et al., 2023). This broadly illustrates the adaptability of green synthesis techniques, which also generate CuO NPs from both easily accessible plant sources as well as agricultural waste. Compared to conventional chemical methods, plant-mediated green production of CuO NPs provides a safer option (He et al., 2023). Numerous biological and the non-biological applications have been effectively implemented incorporating the resultant nanoparticles. Among the noteworthy uses are antibacterial properties, where the green-synthesized CuO NPs demonstrate strong antibacterial properties.

CHAPTER 3

MATERIALS AND METHODS

3.1 Leachate Sample Collection

The leachate samples were collected from local landfill sites named "Tapak Pelupusan Sisa Pepejal, Wilayah Ulu Johan Papan" (Papan Sanitary landfill) which is located at Papan district, Perak. An amount of 25 L of leachate samples were collected in varied batches during the half-year duration in the Year 2019. Figure 3.1 shows the Papan Sanitary Landfill site location map.

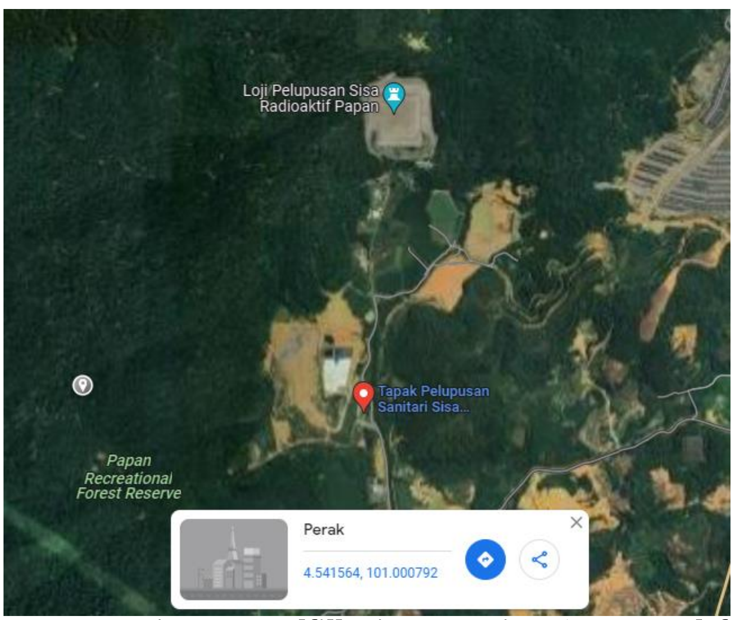


Figure 3.1: Papan Sanitary Landfill Site Location (Extracted from Google Maps, year 2023)

Samples were preserved as soon as possible after each collection and kept at temperature of 4^{o}C prior to analysis. The sample preservation technique was followed as per the Standard Operating Procedures (SOP) in Table 3.1. Parameters such as pH, COD, BOD_5, SS and AN were used in the sample preservation.

Table 3.1: Standard Operating Procedures of Sample Preservation

Parameters	Storage / Preservation technique
pH	On-site analysis using pH meter
Chemical Oxygen Demand (COD)	Add sulphuric acid (H_2SO_4) to pH > 2, refrigeration; 7 days
Biochemical Oxygen Demand (BOD_5)	Refrigeration, 48 hours
Suspended Solid (SS)	Refrigeration, can be stored for 7 days
Ammoniacal Nitrogen (AN)	Add sulphuric acid (H_2SO_4) to pH > 2, refrigeration; 7 days

APHA, AWWA, 2005. Standard Methods for the Examination of Water and Wastewater. 21st ed. Washington, D.C.: American Public Health Association, American Water Works Association.

3.2 Physical Filtration Treatment

A straightforward and cost-effective conventional filtration system was constructed using varying proportions of fine sand, coarse sand, and activated carbon in a 4.5 L plastic container. The setup involved layering the materials in the following ascending order: coarse sand, activated carbon, and fine sand, with a ratio of 1:1:3. About 2 L of leachate samples were used for this pre-treatment.

3.3 Synthesis of Copper Oxide Nanoparticles

3.3.1 Preparation of Durian Husk Extract

Durian husks were washed with deionized water to remove any impurities particles. Excess moisture was removed by drying at 80ºC for 8 hours. Dried durian husk then ground into fine powder. A total of 5 g of durian husk power were weighed and mixed with 150 mL of deionized water and controlled the temperature between 70ºC to 80ºC for 20 minutes. Durian husk extract was cooled down and filtered twice to increase the purity of extract.

3.2.2 Green Synthesis of Copper Oxide Nanoparticles

Copper oxide nanoparticles (CuO NPs) were green synthesized by using waste durian husk. 40 mL of durian husk extract was boiled at 80°C with constant stirring and adding 2 g of copper nitrate trihydrate acts as source of copper and continue with stirring. Then, this light green solution was observed turned into dark green color of paste. This paste was transferred to furnace using crucible for further heating at 500°C for 2.5 hours. The synthesis process of the CuO NPs shown in Figure 3.2.

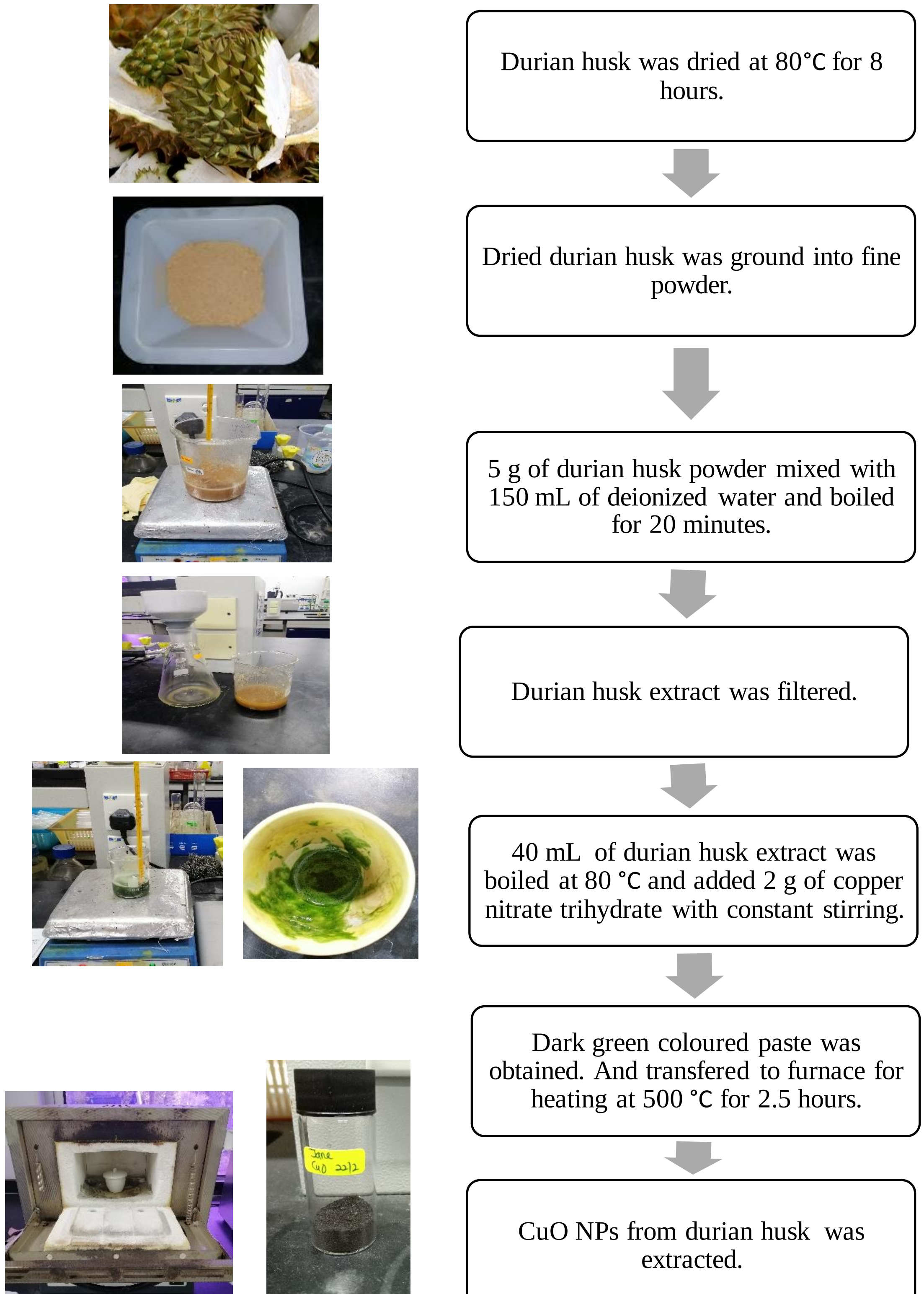


Figure 3.2: Schematic diagram of CuO NPs extraction from durian husks

3.4 Characterization of CuO NPs

3.4.1 Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX)

The CuO NPs were cleaned to remove any contaminants and dried to eliminate moisture. The dried sample was mounted on a stub using conductive adhesive to ensure proper electrical grounding. The CuO NPs samples were characterized by using Electron-dispersive X-ray spectroscopy (EDX) and Scanning Electron Microscopy (SEM) using Jeol Field Emission Scanning Electron Microscope (JSM-6710F). During the SEM imaging, Energy Dispersive X-ray (EDX) analysis was performed to determine the elemental composition of the samples.

3.4.2 X-Ray Diffraction (XRD) Analysis

The CuO NPs were finely ground to ensure uniform particle size, which improves the quality of the diffraction pattern. The ground sample was then placed on a sample holder by spreading evenly to create a thin, uniform layer on the holder. The prepared sample was then carefully placed into X-ray Diffractometer (XRD) for analysis. X-ray Diffractometer (XRD Shidmazu 6000) was used to identify the crystal phase of the extracted CuO NPs. The CuO NPs was analyzed from 10^{o} to 80^{o} in 2θ by X-Ray diffractometer with Cu Kα radiation (λ = 1.540600 Å, step size = 0.020 $^{o}s^{-1}$).

3.4.3 Photocatalytic Degradation of Filtered Leachate Sample

The photocatalytic degradation of pre-treated leachate sample using CuO NPs was carried out under illumination of a 18W UV lamp in a fully closed container. Different concentrations of 100 mg, 150 mg and 200 mg of CuO NPs were added into 300 mL of filtered leachate sample and put under UV irradiation exposure for 3 hours duration with constant stirring. About 2 mL sample used in water analysis before and after 3 hours. These photo-treated leachate samples were kept for further treatment using microalgae.

3.5 Cultivation of *Chlorella vulgaris*

A microalgae species named *Chlorella vulgaris* were grown in a 250 mL Erlenmeyer flask using Bold's Basal Modified Medium under sunlight exposure. Then after 1 week, about 250 mL culture was transferred and cultivated in 500 mL Erlenmeyer flask for continuation mass cultivation with aeration setup. Figure 3.3 shows the cultivation setup for *Chlorella vulgaris.*

Figure 3.3: Cultivation setup for *Chlorella vulgaris*

The composition of Bold's Basal Medium (BBM) as shown in the below Table 3.2.

Table 3.2: Preparation of 100% BBM

No	Chemical	Stock Solution	mL/L
1	KH_2PO_4	8.75 g / 500 mL	10
2	$CaCl_2.2H_2O$	1.25 g / 500 mL	10
3	$MgSO_4.7H_2O$	3.75 g / 500 mL	10
4	$MgSO_4.7H_2O$	12.5 g / 500 mL	10
5	K_2HPO_4	3.75 g / 500 mL	10
6	NaCl	1.25 g / 500 mL	10
7	$Na_2EDTA.2H_2O$ KOH	10 g/L 6.2 g/L	1
8	$FeSO_4.7H_2O$ H_2SO_4 (concentrated)	4.98 g/L 1 mL/L	1
9	*Trace metal solution	See below	1
10	H_3BO_3	5.75 g / 500 mL	0.7

Table 3.2 (continued): Preparation of 100% BBM

*Trace metal solution:

Substance	g/L
H_3BO_3	2.86
$MnCl_2.4\ H_2O$	1.81
$ZnSO_4.7\ H_2O$	0.222
$Na_2MoO_4.5H_2O$	0.390
$Co(NO_3)_2.6H_2O$	0.0494
$CuSO_4.5H_2O$	0.079

3.5.1 Cultivation of *Chlorella vulgaris* in the Pre-treated Leachate Samples

The photo-treated leachate was then transferred and further treated using microalgae *Chlorella vulgaris*. *Chlorella vulgaris* was grown under different concentrations of 0%, 25%, 50%, 75% and 100% of photo-treated leachate sample for 7 days. Treated water samples were further analyzed and conducted analysis. Figure 3.4 shows the cultivation of *Chlorella vulgaris* under different concentrations of pre-treated leachate samples.

Figure 3.4: Cultivation of *Chlorella vulgaris* under different concentration of pre-treated leachate samples

3.6 Water Analysis

Water analysis was carried out before and after every treatment of physical treatment, CuO NPs treatment and microalgae treatment. Testing parameters include pH, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5), Suspended Solid (SS) and Ammoniacal Nitrogen (AN). The analytical procedures of standard method for examination of water and wastewater according to the American Public Health Association (APHA) year 2005 and HACH standard methods were followed. Table 3.3 shows Standard Method for Examination of Water and Wastewater (APHA 2005).

Table 3.3: Standard Method for Examination of Water and Wastewater (APHA 2005)

Test Parameter	Test Methods
pH	APHA 4500
Chemical Oxygen Demand (COD)	USEPA Dichromate Method 8000
Biochemical Oxygen Demand (BOD_5)	Dilution Method 8043
Suspended Solid (SS)	Photometric Method 8006
Ammoniacal Nitrogen (AN)	Method 10031 Test N Tube Vials

3.6.1 pH

Mettler Toledo Benchtop pH meter was used to measure pH. Depending on the desired pH range, the samples were adjusted using either an acid or a base.

3.6.2 Chemical Oxygen Demand

Chemical Oxygen Demand (COD) was carried out using Colorimetric Procedure - Method 8000. The DRB 200 known as COD reactor was preheated to 150°C while preparing the testing sample. For blank sample preparation, 2 mL of deionized water was added into COD digestion vial using pipette.

2 mL of test sample was transferred into COD vial for analysis. All the COD vials were mixed gently before placing into the COD reactor. Then, the COD vials were heated at 250°C for 2 hours. After heating, the COD vials were taken out and cooled down to room temperature before measuring using Hach Colorimeter DR900. Figure 3.5 shows COD reactor (DRB200) and colorimeter (DR900).

Figure 3.5: COD Reactor (DRB 200) and Colorimeter (DR 900)

3.6.3 Biochemical Oxygen Demand (BOD_5)

The BOD_5 was carried out according to Method 8043 adapted from Standard Method for Testing Water and Wastewater (APHA 2005). The dilution water was prepared by adding a BOD nutrient buffer pillow, and each BOD bottle was then filled with this dilution water. Test samples was transferred to the BOD bottles and stopper was inserted carefully in each bottle to prevent trapped air bubbles. For blank sample preparation, the BOD bottle was filled with prepared dilution water.

The initial dissolved oxygen (D1) was tested on day 0 using YSI Dissolved Oxygen Meter (USA). All the prepared sample bottles were kept in an incubator 20°C for 5 days. After 5 days, measurement of dissolved oxygen (D2) was taken. The BOD reading was calculated by using the below formula:

$$BOD, \frac{mg}{L} = \frac{D1 - D2}{P}$$

(APHA, AWWA, 2005. Standard Methods for the Examination of Water and Wastewater. 21st ed. Washington, D.C.: American Public Health Association, American Water Works Association)

Where:

D1= DO of sample immediately after preparation, mg/L

D2 = DO of sample after 5-day incubation, mg/L

P= fraction of test sample volution to total combined volume

3.6.4 Suspended Solid (SS)

An amount of 500 mL of treated water sample were blended in a blender at high speed for 2 minutes.10 mL sample was poured into sample cell and ready for measurement. For blank sample preparation, 10 mL of deionized water was used. Measurement was taken using colorimeter (DR900) from United States (US).

3.6.5 Ammoniacal Nitrogen (AN)

The ammoniacal nitrogen test was carried out according to Method 10031 Test N Tube Vials – Salicylate Method adapted from Standard Method for Testing Water and Wastewater (APHA 2005). For sample preparation, 0.1 mL of tested sample was added to one AmVer Diluent Reagent Test N Tube. Meanwhile, blank samples were prepared by adding 0.1 mL of ammonia-free water to one AmVer Diluent Reagent Test N Tube. One packet of Ammonia Salicylate Reagent Powder Pillow and one packet of Ammonia Cyanurate Reagent Powder Pillow was added to each of the vials. The cap of the vials was closed and shook thoroughly and kept for 20 minutes for reaction. The measurements were taken after 20 minutes using colorimeter (DR900).

3.7 Statistical Analysis

The mean values of each treatment were compared using one way analysis of variance (ANOVA) with p-value of less than 0.005 was considered significant using Microsoft Excel. All the data obtained were presented as the average of the experiment ± standard deviation (SD).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Raw Leachate Characteristics

Raw leachate samples were collected from Papan Sanitary Landfill and various parameters analysis was conducted. The color of the raw leachate sample was dark brownish in color as shown in Figure 4.1, which often indicates a high level of organic material or certain contaminants. The leachate had a noticeable smell, which is identified as hydrogen sulfide. Hydrogen sulfide is a gas known for its characteristic "rotten egg" odor, often found in places with decomposing organic matter.

Figure 4.1: Raw leachate samples

Table 4.1 shows the tested result of raw leachate sample before conducted any treatment.

Table 4.1: Raw leachate analysis result (before treatment)

Parameters	Result
pH	8.38 ± 0.05
Chemical Oxygen Demand (COD)	1134.75 ± 66.3 mg/L
Biochemical Oxygen Demand (BOD_5)	237.50 ± 13.4 mg/L
Suspended Solid (SS)	321.15 ± 24.8 mg/L
Ammoniacal Nitrogen (AN)	59.25 ± 10.7 mg/L

Ratio of BOD_5/COD was used to indicate the biodegradability of the leachate and determine the age of the leachate. Eventually to identify the suitable treatment process and system for the leachate. From the above table, the BOD_5/COD ratio of the raw leachate sample was 0.15, considered as intermediate leachate. According to Zhang et al., (2012) research, a higher ratio suggests more biodegradable organic matter, which means it can be treated biologically, whereas a lower ratio means less biodegradable and requires chemical treatment. Young leachate has a higher BOD_5/COD ratio, whereas older leachate has a lower ratio due to the more resistant, non-biodegradable materials remaining after the easily degradable substances are broken down. There remain troubling signs in the raw leachate from the Papan Sanitary Landfill, pointing to significant levels of contamination.

The leachate sample collected tested 8.38 pH level broadly indicates alkalinity. At 2522.50 mg/L, the Chemical Oxygen Demand (COD) is high, which indicates a significant load of organic contaminants. This high COD value reveals that a substantial amount of oxidizable organic matter is present in the leachate, which can have adverse effects on aquatic environments if not treated properly. Moreover, the influence of organic matter on aquatic environments is demonstrated by the Biochemical Oxygen Demand (BOD_5), which is at 396.75 mg/L. Such a high BOD5 value indicates that the leachate has a considerable amount of biodegradable organic matter that can lead to oxygen depletion in water bodies, adversely affecting aquatic life. Effective leachate treatment is extensively required due to the elevated quantities of ammoniacal nitrogen (62.25 mg/L) and suspended solids (1605.75 mg/L), which further suggest possible environmental impact. These solids can carry various pollutants and cause turbidity in water, impeding light penetration and affecting aquatic plants and animals (Ahmad Jamrah, 2024).

4.2 Physical Filtration Treatment

The raw leachate was pre-treated using a conventional method. 2.0 L of leachate samples were used to go through the filtration setup. Figure 4.2 shows the color changes of the leachate after going through the conventional filtration, the color became light brownish.

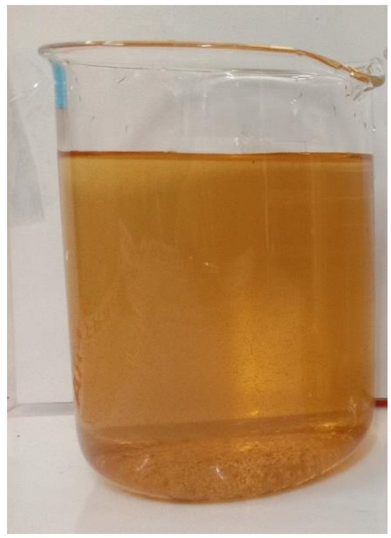


Figure 4.2: Pre-treated leachate sample (After conventional filtration)

Pre-treated leachate samples were collected and analyzed. The reduction rate of conventional filtration had achieved 55 % in COD, 40 % in BOD_5, 80 % in SS and 5 % AN. The adsorption using activated carbon media will help in the removal of organic substances like COD and BOD_5. According to the studies of John et al. (2002), filter vessels that consist of layers of different media will have more effective filtration and longer shell life. Table 4.2 shows the pre-treated leachate analysis result.

Table 4.2: Pre-treated leachate analysis result

Parameters	Result
pH	8.38 ± 0.1
Chemical Oxygen Demand (COD)	2522.50 ± 147.2 mg/L
Biochemical Oxygen Demand (BOD_5)	396.75 ± 22.4 mg/L
Suspended Solid (SS)	1605.75 ± 124.1 mg/L
Ammoniacal Nitrogen (AN)	62.25 ± 11.4 mg/L

The pH of raw leachate was 8.38 and remained after the physical filtrate treatment. This is due to the physical filtration only remove the insoluble solid substances in the leachate sample.

The conventional filtration system effectively reduced the Chemical Oxygen Demand (COD) from 2522.5 mg/L to 1134.7 mg/L, achieving a total reduction of 50%.

A substantial drop is thoroughly obtained with conventional filtration, indicating that the BOD_5 has been effectively reduced. It would be so much beneficial to thoroughly examine the precise changes and underlying mechanisms further to get useful knowledge for the enhancement of filtering techniques. The BOD_5 of raw leachate reduced the from 396.75 mg/L to 237.5 mg/L with total 40% removal rate.

The SS has been treated from 1605.75 mg/L to 321.15 mg/L with a total reduction of 80%. The conventional filtration shown drastically mitigates the parameter values, pointing to a potentially better or more focused filtering method.

The AN has been treated from 62.25 mg/L to 59.25 mg/L with a total reduction of 4% reduction. A minor decrease is obtained with the conventional filtration. Enhancing the general effectiveness of all of these physical treatment options can require more research into the particular alterations, treatment circumstances, or other techniques.

Conventional filtration exhibits better mitigation across all sets of pollutants than even modified filtration, presumably as it incorporates improvised procedures. According to the research, physical therapy outcomes can be properly optimized through the incorporation of conventional filtration procedures.

All things considered, these research findings highlight the significance of customizing physical treatment techniques, with conventional filtration to provide a viable path toward enhanced pollutant removal. The results strongly highlight the necessity for focused as well as creative physical treatment approaches to improve the methods incorporated to purify water or wastewater.

4.3 Instrumental Analysis of Copper Oxide Nanoparticles (CuO NPs)

4.3.1 Morphological Studies

Copper oxide nanoparticles (CuO NPs) were subjected to experimental investigation using Scanning Electron Microscopy (SEM). SEM is a high-resolution imaging method that broadly offers comprehensive surface morphology data.

The analysis disclosed CuO NPs' surface topography and structural properties. Comprehension of the size, shape, and aggregation of the nanoparticles are made easier through this microscopic study, which is extremely essential for the evaluation of their characteristics and their utilizations.

A thorough knowledge of CuO NPs is supported through the SEM data, which broadly provide crucial insights into the physical characteristics of the nanomaterial. The structure of CuO NPs was shown in Figure 4.3 Most of the CuO NPs were observed in uniform spherical in shape and agglomerated together.

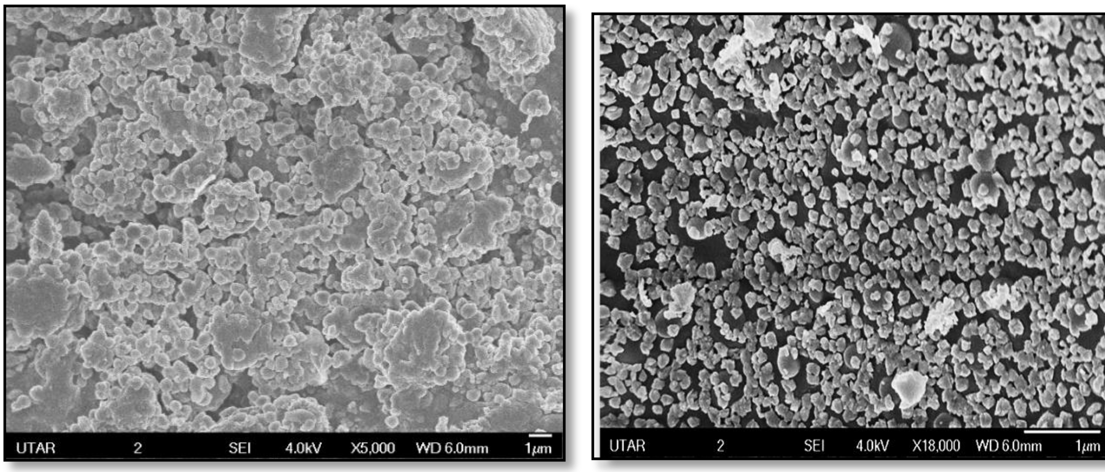


Figure 4.3: SEM Image of CuO NPs with magnification of X 5000 and X18000

4.3.2. X-Ray Diffraction Analysis (XRD)

CuO NPs were obtained using the green synthesized method. The CuO extraction from durian husk was analyzed using XRD and to study its crystal phase and crystallinity properties. Figure 4.4 shows the XRD Spectrum of CuO NPs.

The crystalline phases and crystallinity of CuO NPs were evaluated by XRD. The XRD spectrum of green-synthesized CuO NPs is shown in Figure 4.5, in which diffraction planes were observed at 2θ of 31.96°, 32.44°, 34.68°, 38.7°, 43.8°, 48.7°, 58.2°, 61.5°, 66.2°and 75.0°that assigned to (110), (-111), (111), (-112), (-202), (020), (202), (-113), (-311), (-311), (331), (-222) and (222) respectively.

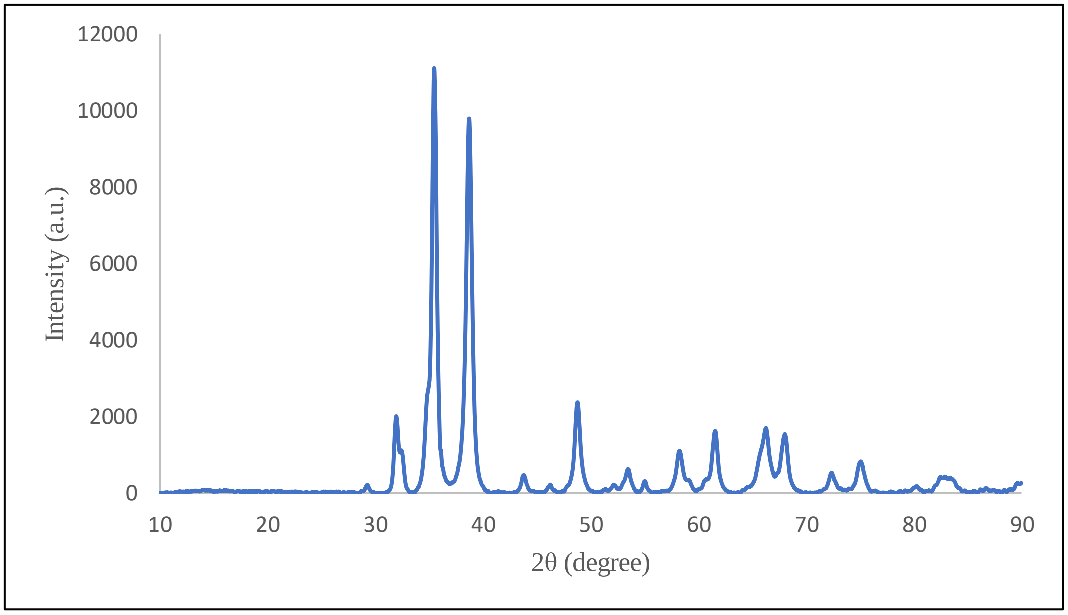


Figure 4.4: XRD spectrum of green-synthesized CuO NPs from durian husk extraction

4.3.3 Energy-Dispersive X-Ray Spectroscopy (EDX)

CuO NPs' chemical composition can be seen in the EDX spectrum, where copper (Cu) makes up 71.8% and oxygen (O) is at 28.2%.

The composition strongly emphasizes the significant presence of copper in the nanoparticles and its importance in their chemical structure. Figure 4.5 shows the EDX spectrum of green-synthesized CuO NPs.

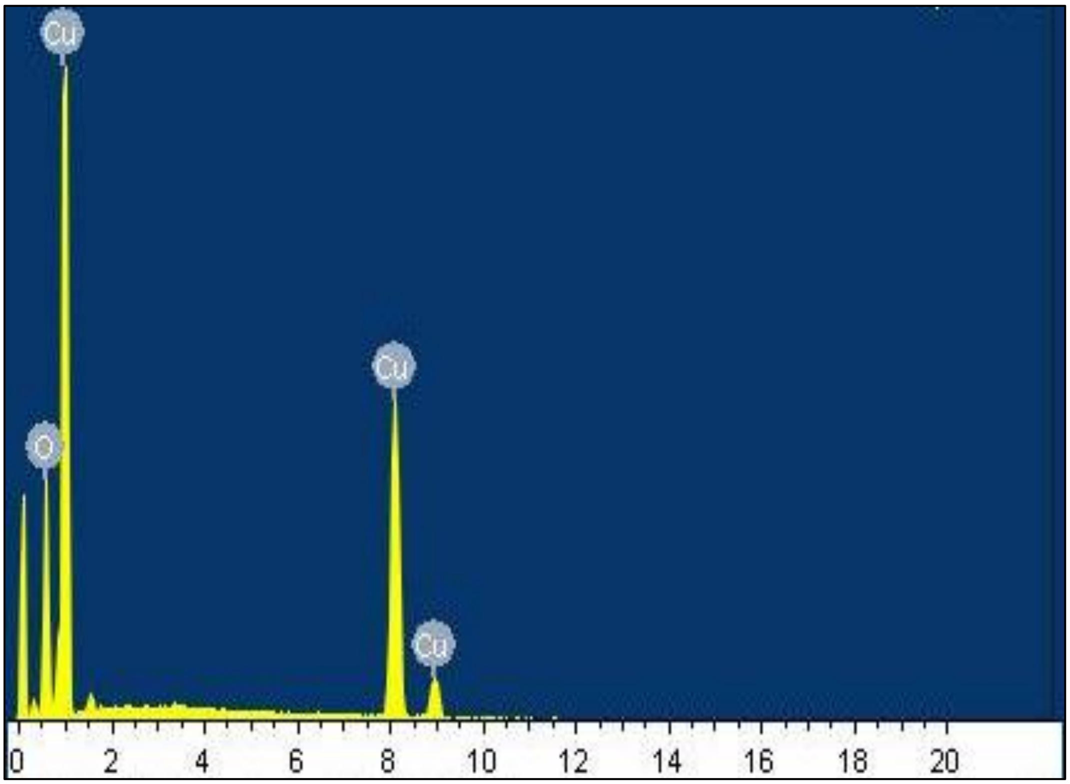


Figure 4.5: EDX spectrum of green-synthesized of CuO NPs

When compared to other studies using plant-based materials for nanoparticle synthesis, this method showcases the potential of utilizing agricultural waste effectively. Various plants have been used to synthesize nanoparticles, each yielding unique properties influenced by their source material and synthesis methods.

The fundamental benefits of these green synthesis processes include environmental sustainability and diverse applications ranging from environmental remediation to catalysis.

This comparison underscores the versatility and environmental benefits of using plant-based materials for synthesizing nanoparticles, providing a promising alternative to conventional chemical methods. For example, Jadoun et al., (2021) provide an extensive review of nanoparticle synthesis using plant extracts, highlighting their environmental and functional advantages. Similarly, Patil (2024) discusses the broad applications of plant-mediated nanoparticles in various fields. These references collectively illustrate the growing recognition and importance of plant-based nanoparticle synthesis in scientific research and practical applications.

4.4 Photocatalytic Degradation of Pre-treated Leachate sample

Different concentrations of 100 mg, 150 mg, and 200 mg of CuO NPs were added into 500 mL of pre-treated leachate sample and was placed under UV irradiation exposure for 3 hours with constant stirring. The primary goal was to observe the impact of varying CuO NP concentrations on the removal rates of Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD5) from the leachate.

COD is a measure of the total quantity of oxygen required to oxidize both organic and inorganic matter in the water, while BOD_5 measures the amount of oxygen needed by microorganisms to decompose organic matter over a five-day period. Both parameters are critical indicators of water quality, with high values suggesting significant contamination. Water samples were collected before and after the CuO NPs treatment.

As the concentration of the CuO increased, the removal rate of COD and BOD_5 decreased as well. This counterintuitive result suggests that higher concentrations of CuO NPs might have led to aggregation or other phenomena that reduced their efficacy. At 100 mg of CuO NPs, it showed the optimum removal rate in COD and BOD_5 which is 80% and 78% respectively. This indicates that at this concentration, the nanoparticles were most effective in breaking down or removing contaminants from the leachate. The optimal performance at 100 mg could be attributed to several factors, such as better dispersion and interaction with the contaminants in the leachate. In contrast, higher concentrations might have resulted in reduced surface area availability due to aggregation of nanoparticles, thereby decreasing their overall effectiveness in contaminant removal.

These findings highlight the importance of optimizing nanoparticle concentrations in treatment processes to achieve maximum efficiency. It also underscores the complexity of nanoparticle interactions in real-world applications, where factors such as aggregation, particle size, and surface chemistry play crucial roles in determining the outcome of the treatment process. Figure 4.6 shows the different parameters for the photocatalytic degradation of pre-treated leachate.

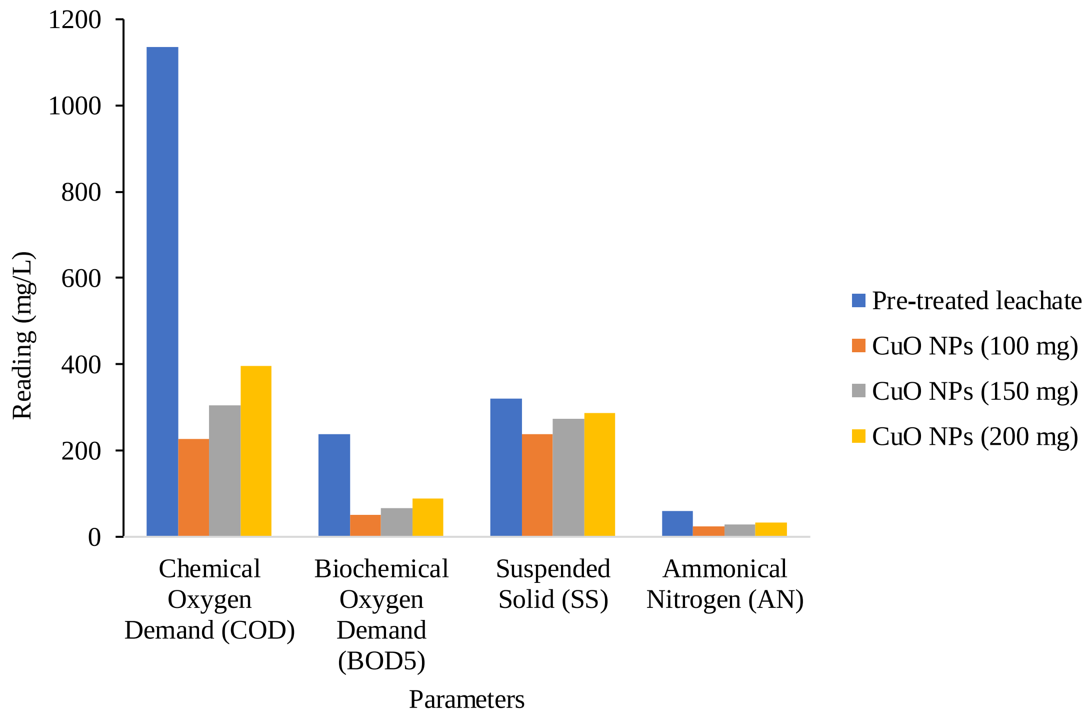


Figure 4.6: Graph of different parameters for the photocatalytic degradation of pre-treated leachate

According to Madeła (2020) studies, it was found that at higher concentrations, CuO NPs can lead to aggregation and sedimentation, which negatively affects their performance in removing contaminants like COD and

BOD_5. The study highlights that an optimal concentration of CuO NPs is crucial for achieving the best removal efficiency, aligning with the observation that 100mg of CuO NPs provided the highest removal rates of COD (80%) and BOD5 (78%).

4.5 Cultivation of Microalgae *Chlorella vulgaris*

The tiny structure of microalgae *Chlorella vulgaris was* clearly visible incorporating fluorescence micrographs, which also extensively shed light on the algae's possible function in the leachate's subsequent treatment. Figure 4.7 shows fluorescence micrographs image of *Chlorella vulgaris*.

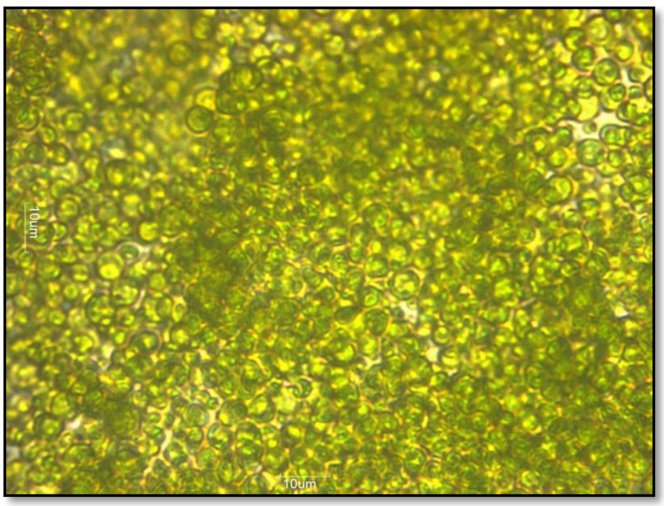


Figure 4.7: Fluorescence micrographs image of *Chlorella vulgaris under magnification of 100X*

4.5.1 Microalgae Treatment Using *Chlorella vulgaris*

The pre-treated leachate was subjected to further clean-up incorporating the microalgae species *Chlorella vulgaris* following photo-treatment. Microalgae were grown under different percentage of 0 % (Control Set), 25%, 50%, 75% and 100% of photo-treated leachate sample for 7 days. Treated water samples were collected and analyzed. Figure 4.8 shows result showed as below.

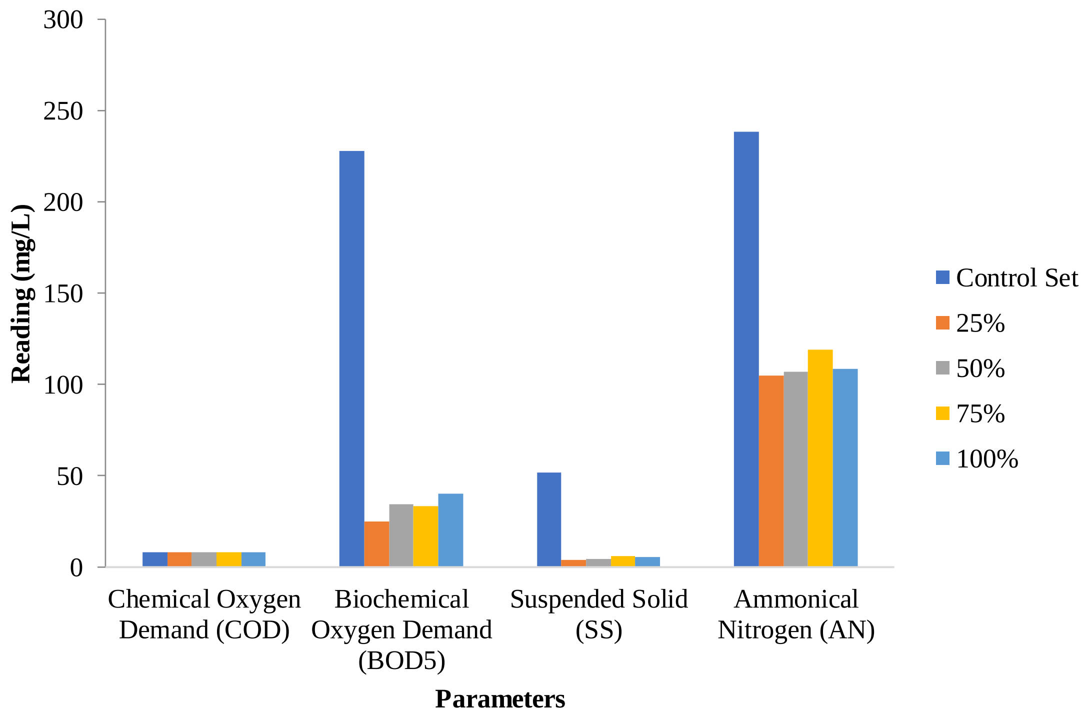


Figure 4.8: Graph of different parameters for the different concentration of pre-treated leachate

The water quality of the leachate treatment had been analyzed and compared between the treatments. The above result showed the result of pre-treated leachate and after microalgae treatment. The result had showed satisfactory removal efficiency in COD, BOD_5, SS and AN. The graph illustrates the notable enhancements in water quality that result from treating leachate with microalgae. Upon exposing the leachate to varying percentages of the photo-treatment for seven days, significant decreases in pivotal metrics are noted.

The treated water's stability is demonstrated by the pH level, which remains at a healthy 8.38. Figure 4.9 shows the microalgae cultivation in different concentrations of photo-treated leachate.

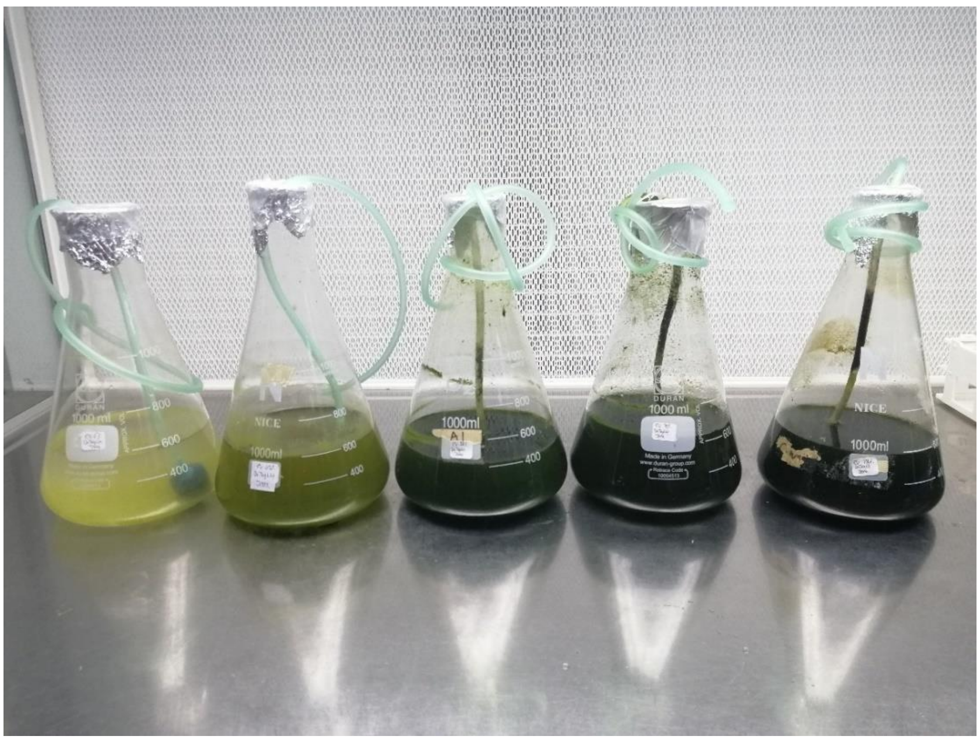


Figure 4.9: Microalgae cultivation in different concentrations of photo-treated leachate (After 7 days)

At 25% of photo-treated leachate, it showed the most optimum removal rate in COD and BOD_5 which is 89% and 92% respectively, which indicate effective removal of organic pollutants. At 50% of photo-treated leachate, the removal rate in COD and BOD_5 which is 85% and 91% respectively. Followed by at 75% of photo-treated leachate, the removal rate in COD and BOD_5 which is 85% and 88% respectively. The removal rate in COD and BOD_5 for 100% photo-treated leachate was 82% and 90% respectively.

In terms of industrial and economy perspective, the 100% photo-treated leachate is more economic and applicable used as biological treatment for microalgae cultivation. This will be an effective approach for microalgae cultivation under lower cost and high removal efficiency of nutrients from landfill leachate.

In summary, Table 4.3 illustrates the total removal rate of tested parameters.

Table 4.3: Leachate sample analysis result (before and after treatment)

Parameters	Unit	Raw	Treated	Removal

		Leachate (Before Treatment)	Leachate (After Treatment)	Rate (%)
pH	-	8.38 ± 0.1	8.38 +/- 0.1	NA
Chemical Oxygen Demand (COD)	mg / L	2522.50 ± 147.2	40.25 +/- 3.1	98
Biochemical Oxygen Demand (BOD_5)	mg / L	396.75 ± 22.4	5.33 +/- 0.4	99
Suspended Solid (SS)	mg / L	1605.75 ± 124.1	108.75 +/- 7.8	93
Ammoniacal Nitrogen (AN)	mg / L	62.25 ± 11.4	4.65 +/- 0.9	93

According to Strom (2010), the study reported that *Chlorella vulgaris* had achieved 86% and 78% efficiency of nutrient removal in terms of inorganic nitrogen and inorganic phosphorus. The removal of nutrients like inorganic nitrogen and phosphorus by *Chlorella vulgaris* is primarily due to its ability to uptake and assimilate these nutrients for growth.

Chlorella vulgaris is a microalga that thrives in nutrient-rich environments, and its metabolic processes enable it to efficiently remove nitrogen and phosphorus from the leachate. This nutrient removal is beneficial for treating wastewater as it helps in reducing the eutrophication potential of the discharged water (Ruan et al., 2024).

Comparing this study with others, CV has shown high nutrient removal efficiencies in various conditions. For instance, a study by Ruan et al., (2024) reported that CV achieved removal efficiencies of 87.69% for total nitrogen and 100% for total phosphorus in domestic wastewater1. Another study by Yousif et al., (2022) found that CV could remove up to 98.5% of total nitrogen and over 99% of total phosphorus in hydroponic wastewater under mixotrophic conditions.

In terms of effectiveness, CV appears to perform exceptionally well in nutrient removal across different studies, making it a promising candidate for leachate treatment. The high removal rates observed in these studies suggest that CV can be an effective and sustainable option for managing nutrient loads in wastewater. In this research, *Chlorella vulgaris* was able to grow in highly diluted or less diluted leachate samples.

4.6 Water Quality Analysis

4.6.1 pH

The pH of the raw leachate and after every treatment were measured and recorded. The pH of raw leachate was 8.38. The leachate was treated with CuO NPs photocatalysis under UV radiation primarily targets the degradation of organic pollutants and dyes, but it doesn't significantly change the pH of the leachate. This is consistent with your observation that the pH remained 8.38 after this treatment. After photodegradation, there were not many changes in the pH. After that, this photo-treated leachate was served as culture medium for microalgae *Chlorella vulgaris* and tested under different concentration. The pH level remained 8.38 and broadly indicates alkalinity. When using *Chlorella vulgaris* as a culture medium, the pH typically remains stable because the microalgae primarily consume nutrients and produce biomass without drastically altering the pH (Soukaina Bouaouda et al., 2023).

4.6.2 Chemical Oxygen Demand (COD)

Figure 4.10 demonstrates the fluctuations in copper oxide nanoparticles (CuO NPs) concentrations in four separate sets, each containing various levels of CuO (100 mg, 150 mg, and 200 mg). The COD values in Set 1, Set 2, Set 3, and Set 4 climb in tandem with the increase in CuO NPs concentration.

This strongly implies that the amount of CuO NPs and COD removal rate in each set are directly correlated. The most effective CuO NPs concentration was 100mg which the pre-treated leachate reduced the COD from 1134.75 mg/L to 227.75 mg/L with total 79% removal rate.

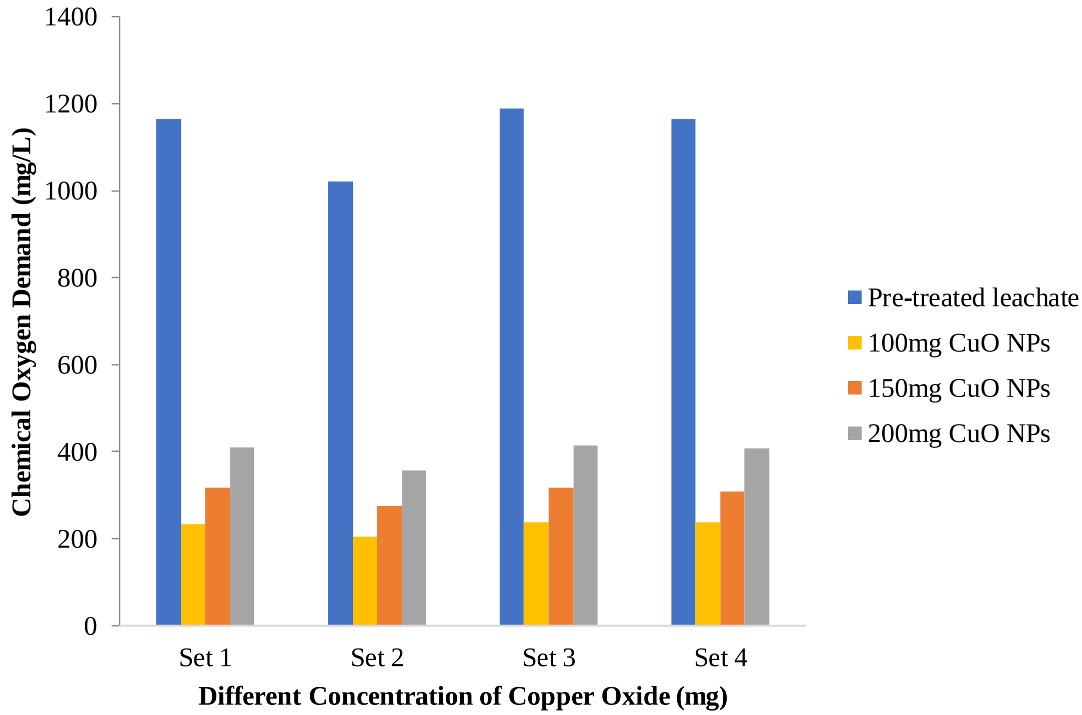


Figure 4.10: Graph of COD analysis for under different concentration of CuO NPs

The incremental trend demonstrates that the appropriate concentrations of CuO NPs are regularly added to the corresponding sets. This kind of information is extremely essential for the comprehension of comprehending the dosage-response relationship in experimental settings and helping to optimize CuO NPs concentrations for the uses, such as environmental remediation, nanotechnology, or catalysis, where exact control over CuO NPs concentrations is extremely essential to achieve desired results. According to the studies of Neena et al., (2018), the degradation efficiency was dropped when the amount of catalyst was above 150 mg. Figure 4.11 shows COD analysis under different concentrations of microalgae.

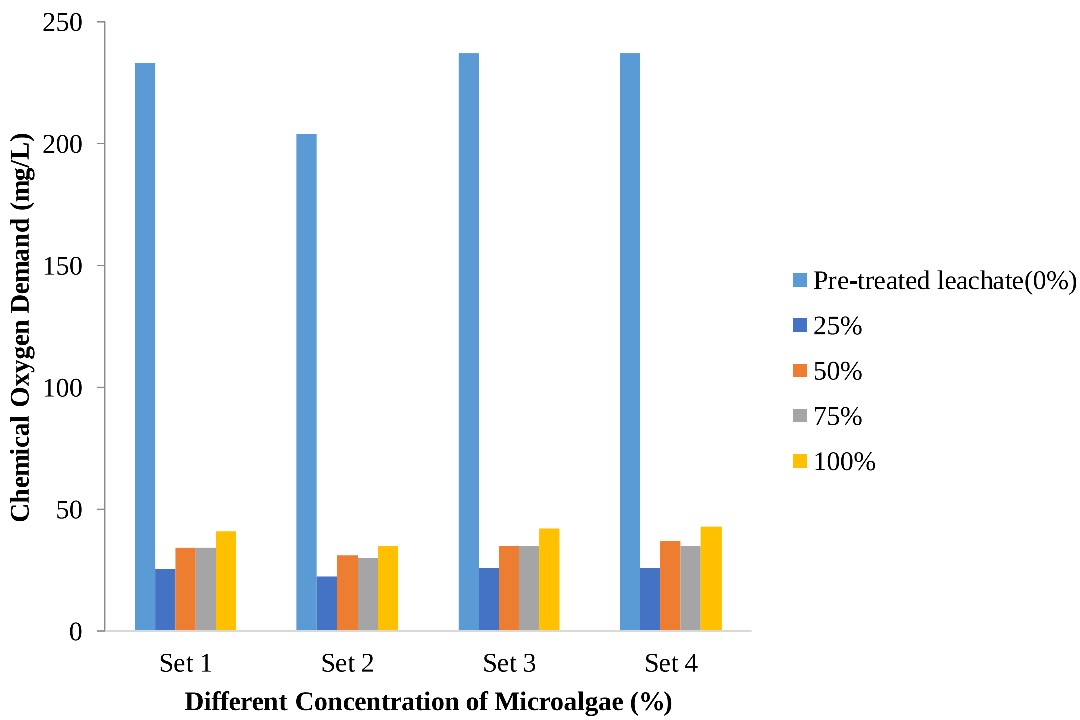


Figure 4.11: Graph of COD analysis under different concentration of microalgae

The concentrations of microalgae at the four sets of percentages, 25%, 50%, 75%, and 100% are broadly displayed on the graph. The concentrations for each group generally trend upward as the microalgae fraction emerges. This strongly implies that there remains a positive relationship between the concentrations of microalgae and the photo-treated leachate percentage.

Understanding the growth dynamics of microalgae under the various environments is significantly aided through these discoveries. About 82% reduction rate of COD has been achieved for the microalgae CV species grown in 100% photo-treated leachate. In other words, this means that the microalgae CV species are highly effective at breaking down and removing organic contaminants from the leachate. According to Liu et al., (2017), the study found that CV showed better growth and higher nutrient removal rates in the environments with higher levels of treated leachate.

The COD level also represents the organic matter present in the leachate sample. The COD test is the measurement of amount of oxygen required for the chemical oxidation of organic matters in the leachate sample to convert to water and carbon dioxide. Figure 4.12 shows the summary of COD reduction for leachate treatment.

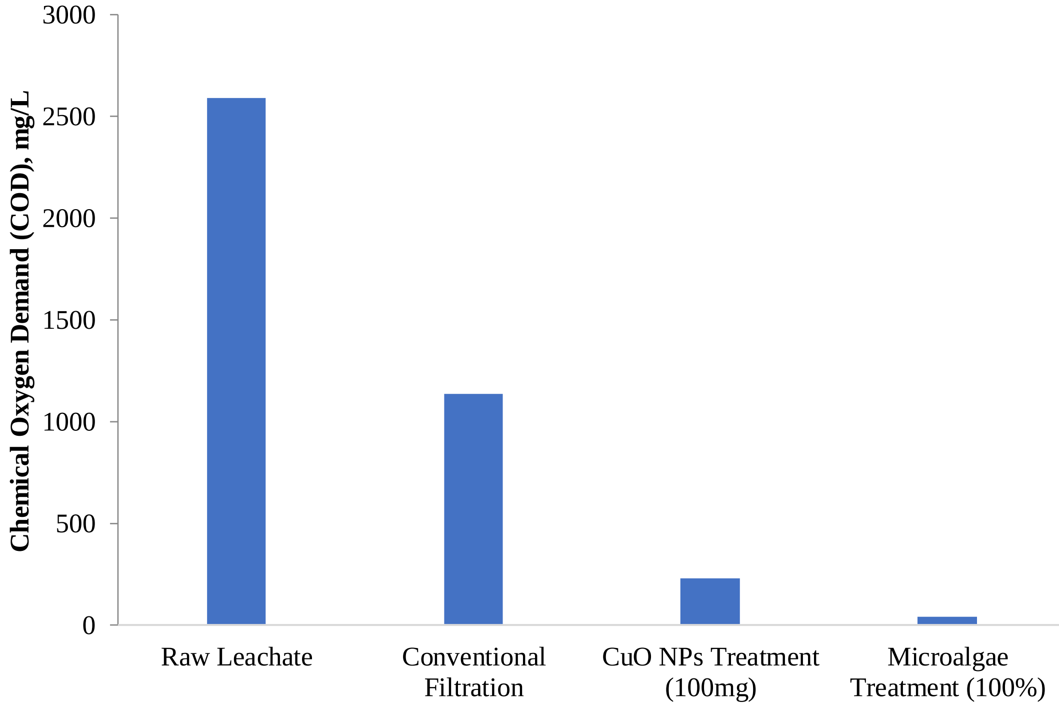


Figure 4.12: Summary of COD reduction for leachate treatment

According to Moreno et al., (2007), the oxidation process of COD as shown in the equation below:

$$\text{Organics} + Cr_2O_7^{2-} + H^+ \rightarrow CO_2 + H_2O + 2Cr^{3+}$$

The Chemical Oxygen Demand (COD) values following various of treatment are presented in the graph. COD levels dramatically drop during conventional filtration, demonstrating the efficient removal of organic contaminants.

The inclusion of the CuO nanoparticles results in a significant reduction in COD, indicating their effectiveness in further reducing organic content. The greatest decrease is seen following microalgae treatment, indicating its remarkable ability for removing COD. These findings indicate a step-by-step increase in the therapy effectiveness, with microalgae treatment having the notable effect. This broadly emphasizes the essentials of a diverse strategy in wastewater treatment through highlighting the possible synergy of integrating physical treatments. According to the findings, the combination of CuO nanoparticles with microalgae treatments might offer a thorough as well as practical approach for reducing COD in wastewater, which is essential for environmental concerns.

4.6.3 Biochemical Oxygen Demand (BOD_5)

The concentrations of copper oxide nanoparticles (CuO NPs) at the three different doses (100 mg, 150 mg, and 200 mg) are clearly presented in this table. Figure 4.13 shows the graph of BOD analysis for under different concentrations of CuO NPs.

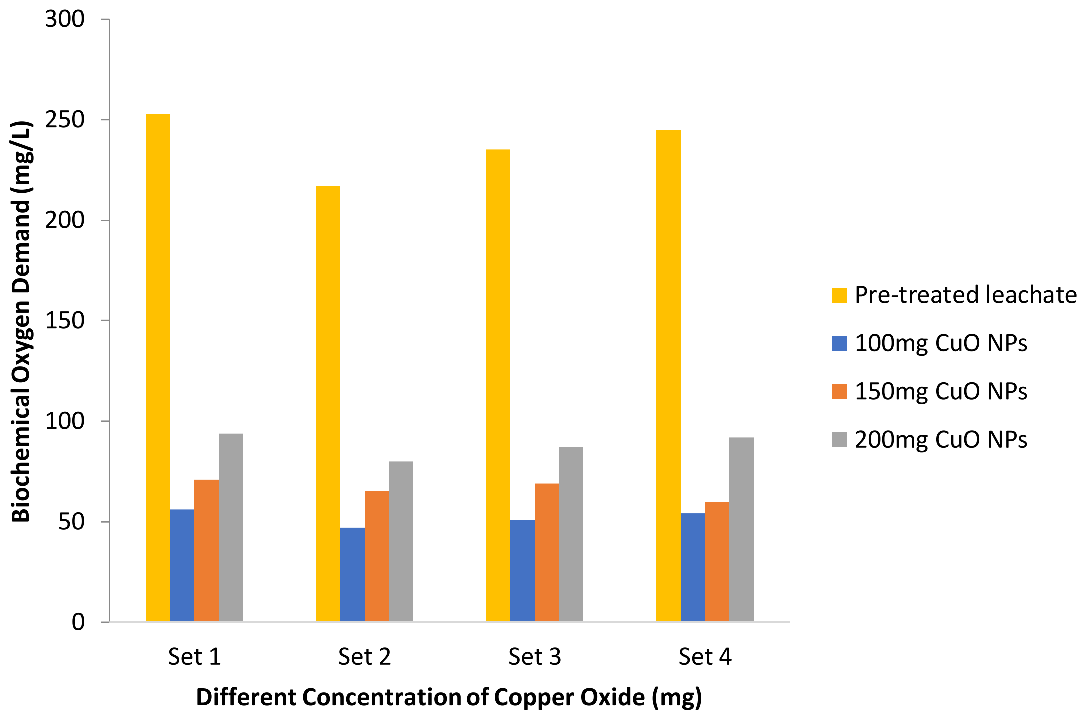


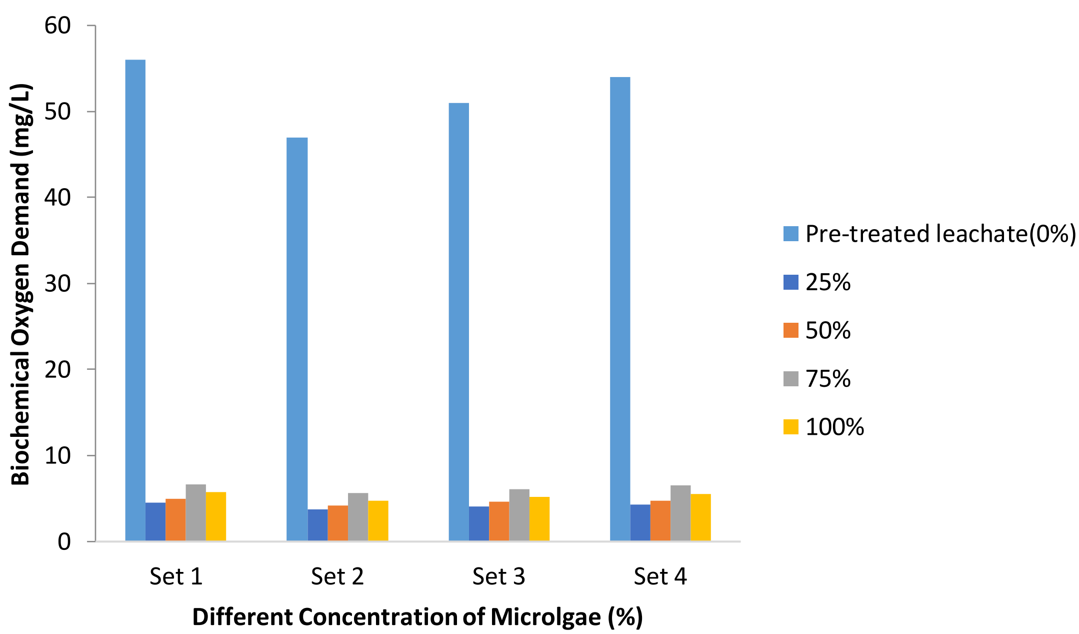
Figure 4.13: Graph of BOD analysis for under different concentration of CuO NPs

The concentrations in each of the groups show an ongoing rising trend as the CuO NPs dose rises, suggesting a proportionate link.

This also implies that the amount given affects the concentration of CuO NPs, which is important knowledge for the applications where exact control over CuO NPs concentrations is required.

These results broadly offer useful information for customizing CuO NPs incorporations in several fields, such as environmental remediation, nanotechnology, along with catalysis, where regulating CuO NPs concentrations is extremely essential to reach the certain goals. The most effective CuO NPs concentration was 100mg which the pre-treated leachate reduced the BOD_5 from 237.5 mg/L to 52.0 mg/L with total 78% removal rate.

Figure 4.14 shows strongly demonstrates the concentrations of microalgae in the four sets at four distinct percentage levels: 25%, 50%, 75%, and 100%. The



concentrations exhibit an intriguing non-linear trend as the percentages increase, implying intricate dynamics in the development of microalgae.

Figure 4.14: Graph of BOD analysis under different concentration of microalgae

The fluctuations broadly present that variables such as nutrient availability and ambient circumstances, which go beyond starting concentration percentages, deeply influence microalgae development.

It also highlights the need to consider multifactorial factors on microalgae development for efficient leachate waste management and the application optimization. About 89% reduction rate of BOD_5 has been achieved for the microalgae CV species grown in 100% photo-treated leachate. The BOD reduced from 52.0 mg/L to 5.33 mg/L. Figure 4.15 shows BOD reduction for leachate treatment.

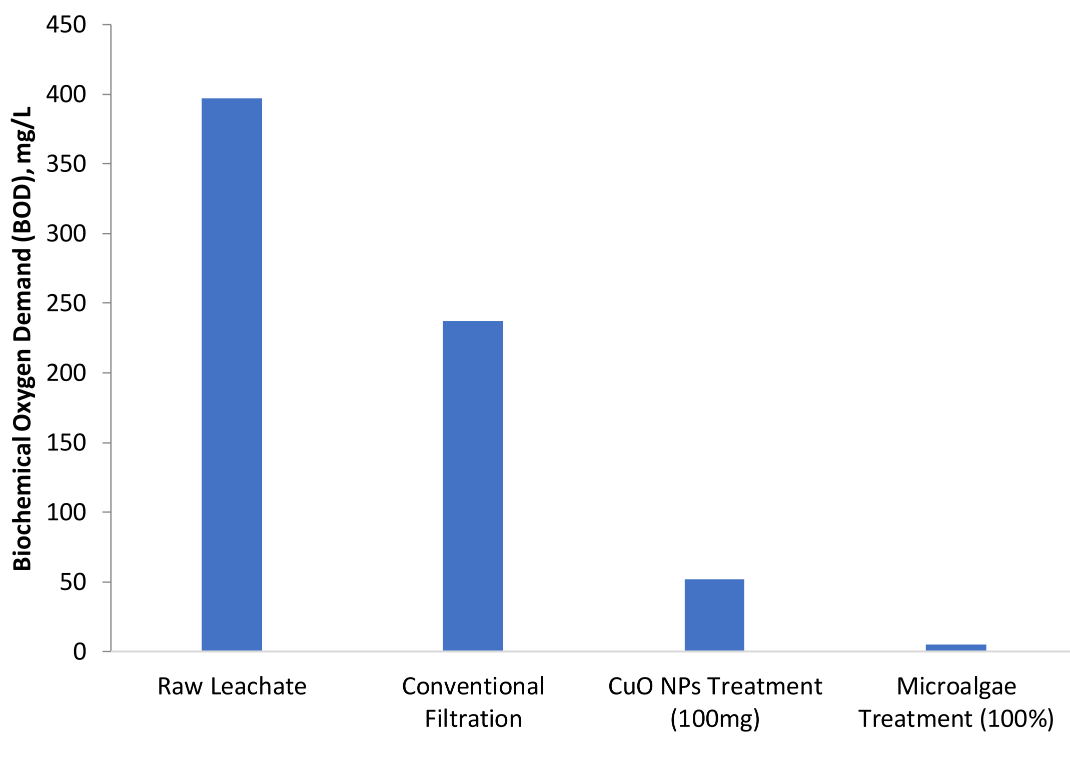


Figure 4.15: Summary of BOD reduction for leachate treatment

Figure 4.15 shows clearly displays the concentrations of biological oxygen demand, or BOD_5, following various treatment of physical treatment, CuO NPs and microalgae treatment. BOD_5 levels are significantly minimized by conventional filtration, demonstrating the efficient removal of organic contaminants. Treatment with the CuO NPs significantly mitigates BOD_5, indicating that they are effective in reducing organic content even more.

Microalgae treatment using *Chlorella vulgaris* showed a significant reduction in BOD_5, after pre-treatment by conventional filtration and photo-treatment using CuO NPs. This clearly demonstrates the remarkable capacity of microalgae to reduce organic contaminants, occasionally by means of adsorption as well as biofiltration. The findings represent how traditional and novel approaches, such as the deployment of microalgae, can work in concert to improvise BOD removal in water treatment procedures. This broadly highlights the potential of microalgae in the innovative wastewater treatment systems and has several crucial consequences for developing comprehensive and sustainable strategies for combating organic pollution, which is extremely essential for preserving ecosystem health and water quality.

4.6.4 Suspended Solid (SS)

The concentrations of copper oxide nanoparticles (CuO NPs) at the three distinct doses (100, 150, and 200 mg) are presented in the graph across four sets.

Figure 4.16 shows SS analysis for under different concentration of CuO NPs. A dose-response relationship is observed by the emerging concentrations in each set as the CuO dosage increases.

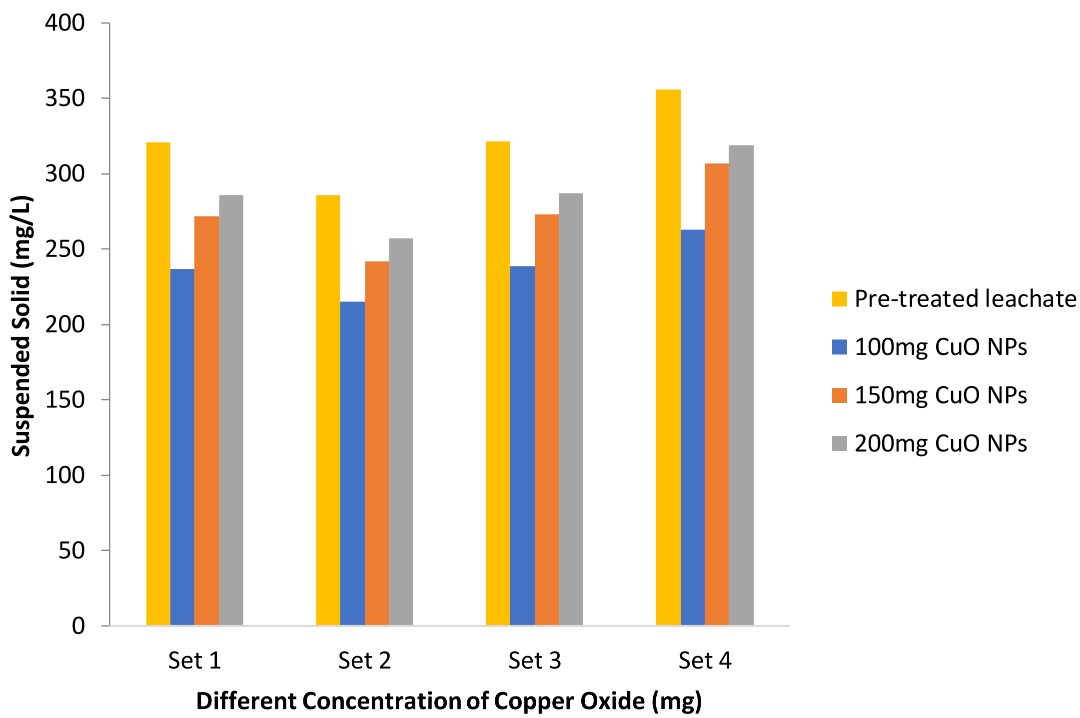


Figure 4.16: Graph of SS analysis for under different concentration of CuO NPs

At 100 mg of CuO NPs, the SS of pre-treated leachate reduced from 321.15 mg/L to 238.5 mg/L. This strongly implies that elevated concentrations are caused through significant concentrations of CuO, presumably as an outcome of the increased availability of copper ions.

The information is so vital for thoroughly understanding how different CuO NPs doses affect concentration levels, which is critical for uses in nanotechnology along with catalysis. Figure 4.17 shows SS analysis under different concentration of microalgae.

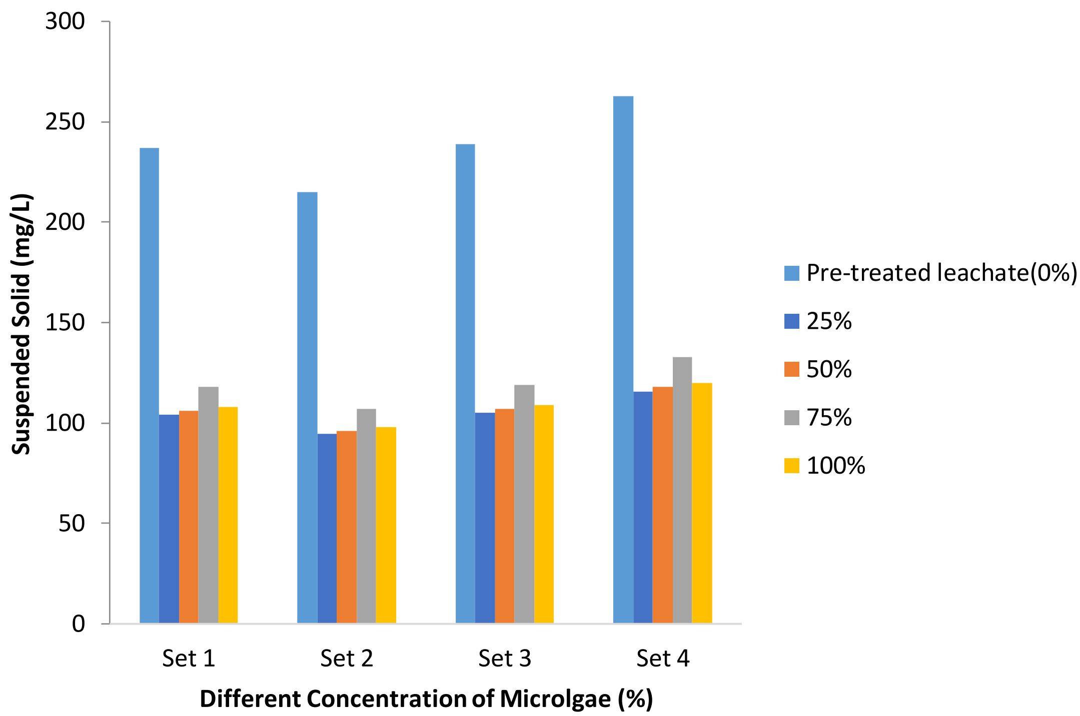


Figure 4.17: Graph of SS analysis under different concentration of microalgae

The concentrations of photo-treated leachate at the four sets experiments range from 25%, 50%, 75%, and 100% was demonstrated in the graph. At the significant percentage level of photo-treated leachate ratio, the SS concentrations demonstrated a descending trend.

Microalgae CV was tested not only able to grow under 100% of photo-treated leachate and working well in the SS reduction from 237.5 mg/L to 108.75 mg/L. Figure 4.18 shows summary of SS reduction for leachate treatment.

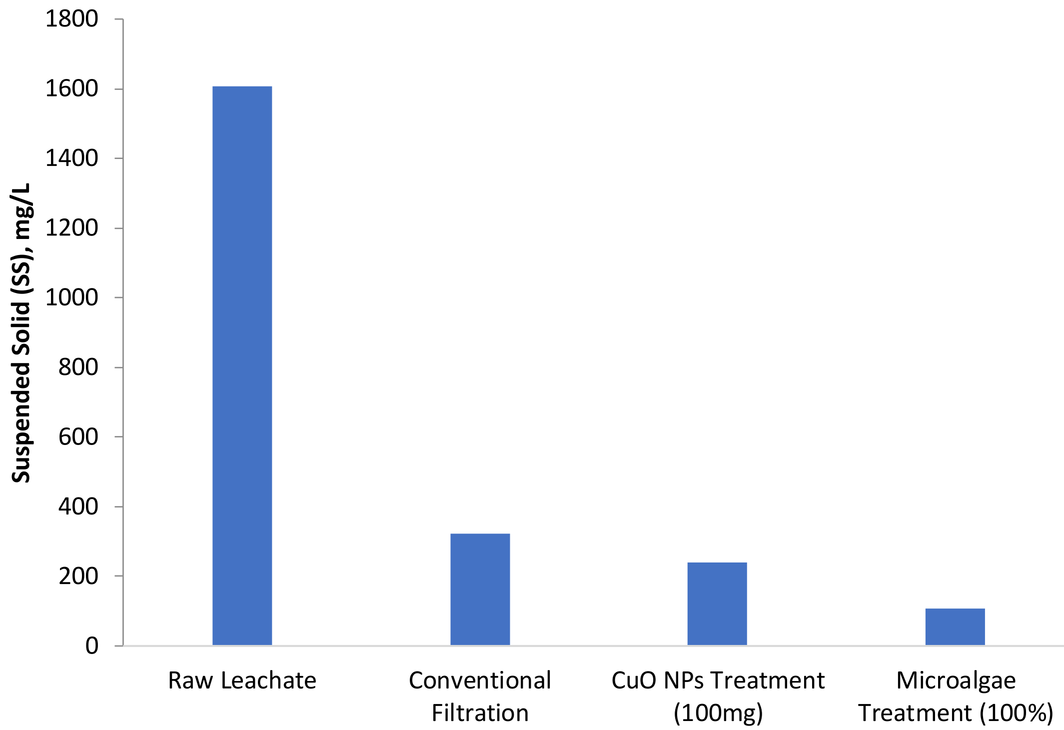


Figure 4.18: Summary of SS reduction for leachate treatment

Suspended Solid (SS) concentrations following various treatments was represented on the graph. Conventional filtration effectively and efficiently removes particulate matter as seen by the considerable reduction of SS levels. CuO NPs were added, and simultaneously this further mitigates the amounts of SS, highlighting their potential to improvise solid removal. Remarkably, microalgae *Chlorella vulgaris* treatment minimizes SS significantly.

This broadly demonstrates the amazing potential of microalgae to mitigate suspended particles, by adsorption as well as biofiltration. According to the findings, SS removal of suspended water treatment procedures can and sustainable strategies for dealing with the suspended solids, which are essential for preserving the health of ecosystems and water quality.

4.6.5 Ammoniacal Nitrogen (AN)

Figure 4.19 broadly demonstrates the concentrations of four sets of copper oxide nanoparticles (CuO NPs) at the different doses (100, 150, and 200 mg).

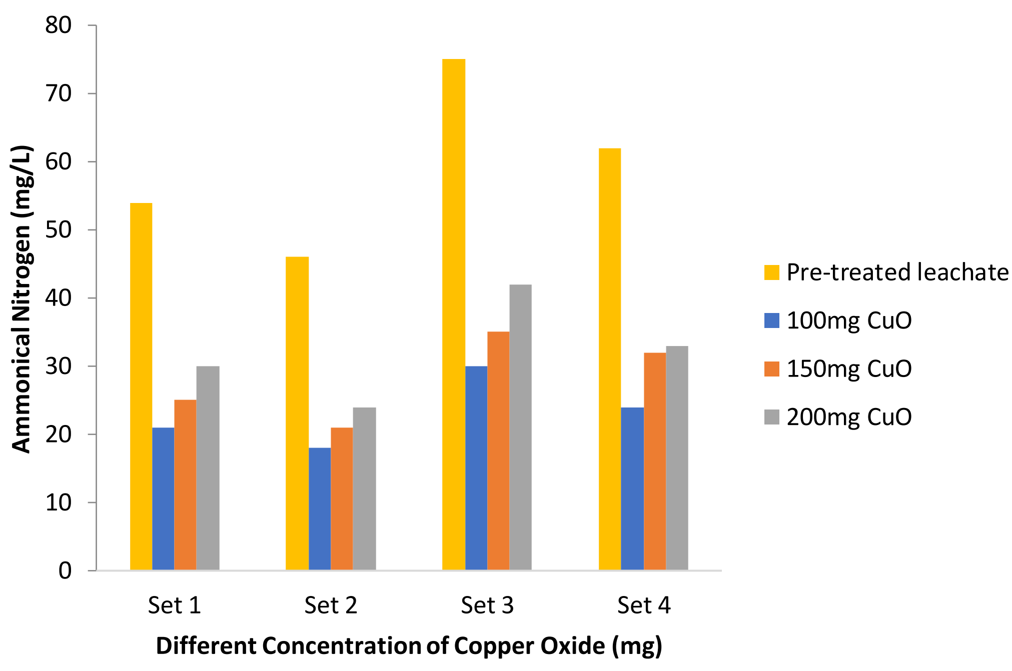


Figure 4.19: Graph of AN analysis for under different concentration of CuO NPs

CuO NPs dose and AN removal rate are positively correlated, according to the pattern that has been found, with the significant dosages resulting in lower removal of AN from the pre-treated leachate.

The tested AN of 100 mg CuO NPs and 150 mg CuO NPs was 23.25 mg/L and 28.25 mg/L respectively. Higher dose of CuO NPs was lowering the degradation of AN. Understanding the inter-connections between the CuO NPs dose and the reduction of AN is extremely essential for attaining desired results and simultaneously maximizing the efficiency of various processes, whether in catalytic reactions, material synthesis, along with environmental cleanup.

Figure 4.20 presents the concentrations of microalgae in four sets at varying percentage levels: 25%, 50%, 75%, and 100%.

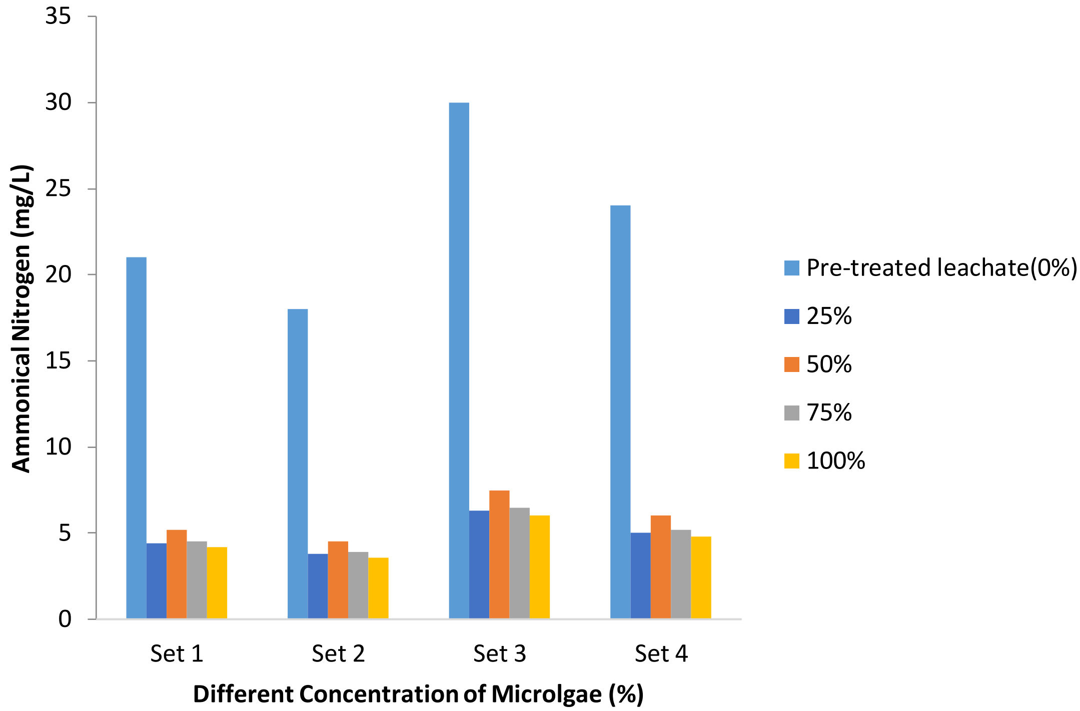


Figure 4.20: Graph of AN analysis under different concentration of microalgae

To effectively and efficiently control biomass and simultaneously optimize application in a variety of industrial and environmental contexts, it extensively highlights the essentialism of considering multifactorial influences on microalgae growth.

About 80% reduction rate of AN has been achieved for the microalgae CV species grown in 100% photo-treated leachate. The AN reduced from 23.25 mg/L to 4.65 mg/L. Figure 4.21 shows AN reduction for leachate treatment.

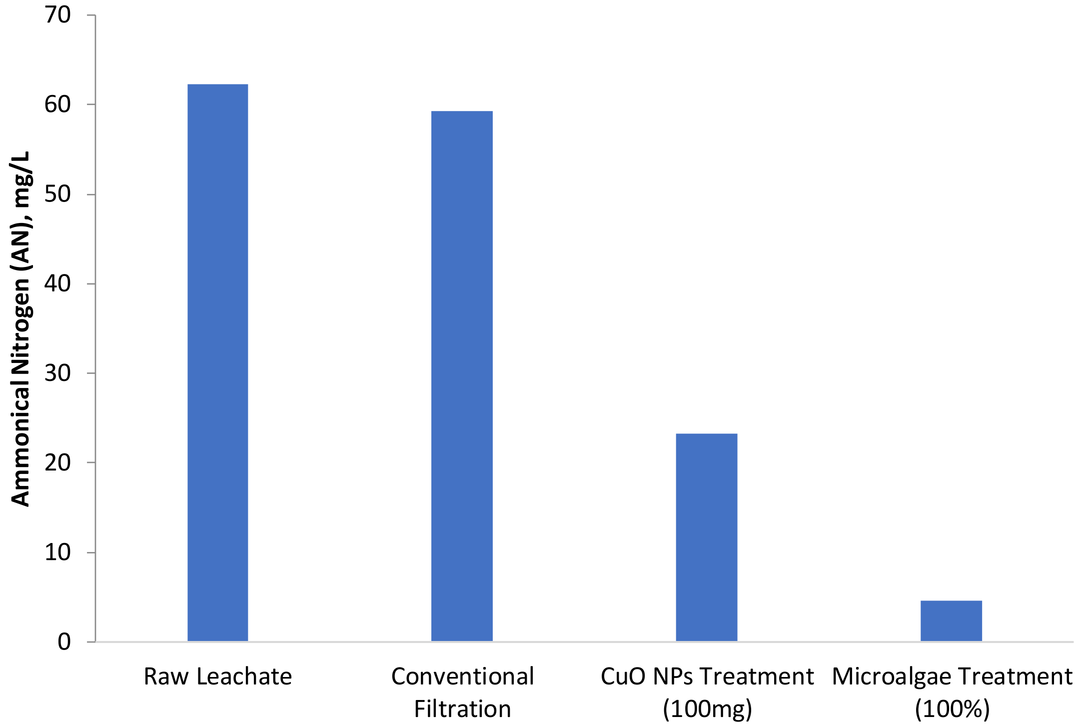


Figure 4.21: Summary of AN reduction for leachate treatment

Figure 4.21 presents the concentrations of ammoniacal nitrogen (AN) following four sets of distinct physical therapies. Conventional filtration effectively removes nitrogenous compounds as seen by the reduction of AN levels. Treatment with the CuO NPs and microalgae *Chlorella vulgaris* significantly further mitigates the AN concentration, demonstrating their effectiveness in further lowering nitrogen content.

The findings broadly imply that AN removal in the water treatment procedures can be improvised in a synergistic pathway through combining traditional and novel treatments, including using microalgae.

This has significant consequences for the development of the comprehensive along with sustainable strategies for addressing nitrogen pollution, which is extremely essential for preserving ecosystem health, water quality, and simultaneously avoiding the harmful effects of excess nitrogen on the environment. Figure 4.22 shows raw leachate and treated leachate, before and after treatment.

Raw leachate	Pre-treated leachate	Treated leachate (After microalgae treatment)

Figure 4.22: Raw leachate and treated leachate (before and after treatment)

Figure 4.22 demonstrates the significant color changes of the raw leachate pre-treated, and after microalgae treatment. The changes from dark brownish in color turned to very lightly brownish clear treated water.

The final treated sample was analyzed. The COD, BOD_5, SS and AN was tested and result was 40.25 mg/L, 5.33 mg/L, 108.75 mg/L and 4.65 mg/L respectively. Figure 4.23 shows the summary of tested parameters for optimum integrated leachate treatment.

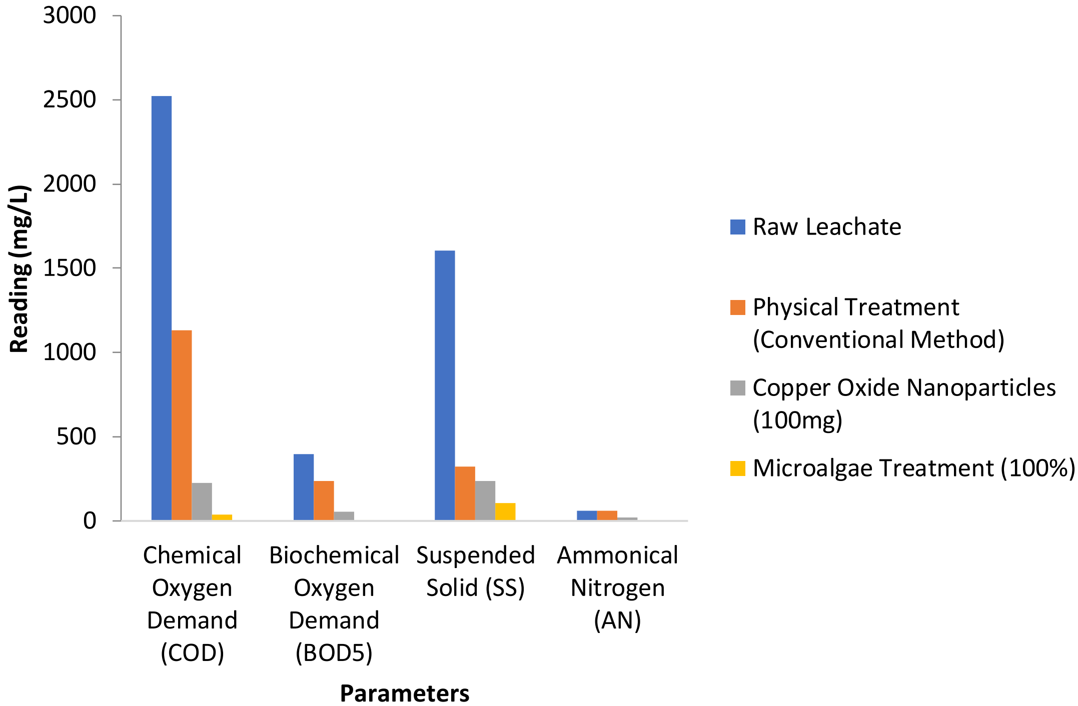


Figure 4.23: Summary of tested parameters for optimum integrated leachate treatment

As a conclusion, Figure 4.23 illustrates the most performing combined treatment for the landfill leachate, which is using 100 mg CuO NPs photocatalytic degradation, and undergoes microalgae treatment. The overall parameters such as COD, BOD_5, SS and AN showed significantly total removal rate of 98%, 99%, 93% and 93% respectively.

CHAPTER 5

CONCLUSIONS

5.1 Conclusions

Green synthesis of CuO NPs from durian husk was achieved and used as photocatalyst in the removal of contaminants in the leachate sample. Pre-treated leachate samples were subsequently treated with 100 mg of CuO NPs treatment and then microalgae treatment using species of *Chlorella vulgaris.* The integrated leachate treatment had achieved the removal rate of 98% of COD, 99% of BOD_5, 93% of SS and 93% of AN.

The integrated system of nanoparticles and microalgae has shown the optimization of leachate treatment by achieving the most satisfactory reduction rate in the tested parameters. Combination treatment of chemical, and biological methods has advantages over each single process and effectively treating the landfill leachate.

5.2 Limitations of Study

Throughout the research, there was limited access to the landfill for the sample collection during the pandemic of Covid-19 and changed over of new management of the landfill site. Part of the research progress was affected due to the announcement made by the government for the Movement Control Order (MCO). For the on-site sample collection, we need to send an application notice to the new management for approval before we can enter the site. However, the research was completed and conducted smoothly.

The cost-effectiveness of using CuO NPs and microalgae for large-scale leachate treatment needs to be evaluated. The production, maintenance, and operational costs associated with these methods might be high compared to traditional treatment methods. Economic analyses are essential to determine whether the benefits of improved leachate treatment outweigh the costs.

5.3 Recommendations for Future Studies

The exploration of the anthracite as effective filtration media to substitute the activated carbon in the research can be further studies. This is due to its ideal characteristics such as being able to run longer service life, higher flow rate with minimal backwash rate and better contamination tolerance properties.

Use of other microalgae species and harvesting of microalgae for lipid extraction can be further studies. There are potential microalgae species that are effective in removal of organic contaminant such as BOD_5, COD and can be used to produce biodiesel.

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Appendix A

Table A.1 Single factor ANOVA analysis of COD against every treatment stage

SUMMARY

Groups	Count	Sum	Average	Variance
Raw Leachate	4	10090	2522.5	28892
Pre-Treated Leachate	4	4539	1134.75	5868
Photo-Treated Leachate	4	911	227.75	254
Chlorella vulgaris Treated	4	161	40.25	13

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	15409028	3	5136343	586.5567144	2.82346E-13	3.490295
Within Groups	105081.3	12	8756.771			
Total	15514109	15				

Appendix B

Table B.1 Single factor ANOVA analysis of BOD_5 against every treatment stage

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Raw Leachate	4	1587	396.75	666.9167
Pre-Treated Leachate	4	950	237.5	241
Photo-Treated Leachate	4	208	52	15.33333
Chlorella vulgaris Treated	4	21.3	5.325	0.1825

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	387920.7	3	129306.9	560.1141	3.71612E-13	3.490295
Within Groups	2770.298	12	230.8581			
Total	390691	15				

Appendix C

Table C.1 Single factor ANOVA analysis of SS against every treatment stage

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Raw Leachate	4	6423	1605.75	20538.25
Pre-Treated Leachate	4	1284.6	321.15	821.53
Photo-Treated Leachate	4	954	238.5	385
Chlorella vulgaris Treated	4	435	108.75	80.91667

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5829359	3	1943120	356.1159	5.48131E-12	3.490295
Within Groups	65477.09	12	5456.424			
Total	5894836	15				

Appendix D

Table D.1 Single factor ANOVA analysis of AN against every treatment stage

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Raw Leachate	4	249	62.25	172.9167
Pre-Treated Leachate	4	237	59.25	152.9167
Photo-Treated Leachate	4	93	23.25	26.25
Chlorella vulgaris Treated	4	18.6	4.65	1.05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9470.88	3	3156.96	35.75941	2.90659E-06	3.490295
Within Groups	1059.4	12	88.28333			
Total	10530.28	15				