QATAR UNIVERSITY

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BIOTREATMENT OF GTL PROCESS WATER AND PESTICIDES CONTAMINATED WATER USING *PSEUDOMONAS AERUGINOSA*: A COMPARATIVE STUDY

BY

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ABSTRACT

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Title: Biotreatment of GTL Process Water and Pesticides Contaminated Water Using *Pseudomonas Aeruginosa* : A Comparative Study

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Over 40% of the world's population suffers from water scarcity, a problem that is expected to get worse because of global warming and desertification. Therefore, the mean of treatment and reuse of wastewater has become more critical. Very limited studies have investigated the biodegradation of organic contaminants in GTL process water and propamocarb HCl fungicide-contaminated water. Therefore, the objective and novelty of this work are to perform a comparative study on the biodegradation of organic contaminants in GTL process water and propamocarb hydrochloride-contaminated wastewater using *pseudomonas aeruginosa*. Response Surface Methodology (RSM) was used to optimize the biodegradation of the contaminated wastewater using *Pseudomonas aeruginosa* immobilized in PVA matrices in a specially designed Spouted Bed Bioreactor System (SBBS). The initial COD of GTL process water and fungicide-contaminated water ranged from 1000 to 3000 mg/l and 500 to 1000, respectively. The parameters investigated include the PVA volume fraction, COD concentration, and pH. Maximum COD reduction efficiency of GTL process water and propamocarb contaminated water was found to be 89% and 42% at an initial COD of 2595 mg/l, PVA v% of 27, and pH of 7.3, and at initial COD of 1000 mg/l, PVA v% of 30, and pH of 8, respectively. The results revealed that propamocarb fungicide is very toxic and difficult to biodegrade, as

it consists of compounds containing aliphatic aldehyde and amines. Thus, the rest of the study focused on the biodegradation of organic contaminants in GTL PW. The findings from continuous experiments showed that the biodegradation rate of GTL process water increased with increasing the air flow rate, and decreasing the liquid flow rate. The rate of biodegradation is predicted to be significantly affected by mass transfer limiations.

***Keywords*:** GTL process water; Pesticides; Biodegradation; Spouted Bed Bioreactor; *Pseudomonas aeruginosa*; Response Surface Methodology.

DEDICATION

In appreciation of their unconditional support and faith in my abilities, I dedicate this work to my parents, sisters, brothers, and friends..

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Chapter 1: Introduction

1.1 Research Overview

As scarcity and need for freshwater are increasing globally, the meaning of wastewater treatment and reuse options are becoming more significant[1]. Industrial activities such as coal conversion, oil refining, pharmaceutical, and petrochemical sectors discharge large amounts of wastewater into the environment. Different organic and inorganic contaminants, as well as dissolved and suspended particles, are commonly found in these effluents. Discharging such wastewater into bodies of water can have devastating consequences for human health and well-being. Wastewater must therefore be properly treated to comply with the reported discharge limit. To lower the concentrations of Total Organic Compounds (TOC), phenols, Chemical Oxygen Demand (COD), and toxic heavy metals in wastewater, several physical and chemical approaches have been developed. However, the high expenses of chemicals, manufacturing chemical sludge, and equipment make these methods typically impractical. Biological approaches, on the other hand, are popular in the wastewater treatment field because of their ease of use, environmental friendliness, and low cost [2].

Biological approaches involve using organisms like bacteria, fungi, and algae to neutralize or break down contaminants into less dangerous compounds. The use of bacteria is beneficial since these bacteria are flexible representatives and contain a variety of Actinomycetes species[3]. Furthermore, these bacteria can produce spores, resist a variety of contaminants, and survive in a variety of environments. Brown et al, [4] mentioned that biological treatment is generally considered an efficient, cost-effective, and long-term method for degrading various pollutants in a variety of situations. The

biodegradation of chemical compounds in the presence of a wide range of microbial communities is measured using standard biodegradation tests, which were first investigated and developed in the 1980s and 1990s (inoculation from river water, seawater, activated sludge, and soil). These tests included biodegradation screening tests, which assess the susceptibility of a chemical to biodegradability under extreme conditions, and higher-level simulation tests, which assess kinetics and transformation products for biodegradation in a variety of scenarios under more environmentally relevant conditions [4]. Over 28 days, simple indicators such as oxygen consumption, carbon dioxide production, and dissolved organic carbon consumption are measured to determine degradation. Chemicals that meet the biodegradation criteria (biodegradation levels of 60% or 70%, depending on the test) are seen to degrade rapidly in the environment under normal conditions [5]. These "rapidly biodegradable" compounds are not believed to be permanent [4].

Hybrid growth systems, attached growth systems, and suspended growth systems are the three types of biological treatment systems reported by Sonune et al. [6]. In suspended growth systems, the microorganisms are kept suspended in the solution in batch reactors under aerobic and/or anaerobic conditions. The attached growth system, on the other hand, is generated by the attachment of biomass as biofilms or granulation of activated sludge. This method uses a granular sludge reactors, fluidized bed bioreactor (FBB), spouted bed bioreactors (SBBR), rotating biological contactors (RBC), packed bed reactors (PBR), and biological active filters to increase biomass concentration within the biological system [7]–[9].

The need for environmentally friendly fuels and for energy has been steadily increasing recently. Gas-to-liquid (GTL) is a technological breakthrough that uses the Fischer-

Tropsch (FT) process to transform natural gas (NG) into high-performance, ultra-clean liquid fuels. This innovative and rising technology is likely to contribute to a higher proportion of global gas processing in the future. The development of GTL technology has advanced technologically over the past ten years, and many commercial-scale plants have been constructed across the world [10]. GTL has confirmed to be a compelling and complementary option to liquefied natural gas, with significant economic, social, and environmental benefits [10], [11]. Evans and Smith, [12] reported that natural gas is used as a feedstock to produce synthetic hydrocarbons, or other GTL products, through the Fischer-Tropsch process. With longer hydrocarbon chains, the process mostly produces linear alkanes with increasing levels of branching.

The use of pesticides is considerably increasing for the enhancement of food production, especially in equatorial developing nations [13]. Pesticide refers to a wide range of materials that include insecticides, fungicides, herbicides, bactericides, rodenticides, nematicides, and others [14]. The definition of pesticides diverges from country to country and from time to time, however, there is a consensus that pesticides are very effective mixed materials and poisonous to target organisms, conversely, they are harmless to non-target organisms [15]. These compounds are very useful in controlling pests in agriculture, thus, enhancing crop yields, decreasing food expenses, as well as providing an effective food production process [16], [17]. On the other hand, the extensive use of pesticides leads to the contamination of soil, plants, and water which are considered to be very toxic and harmful to the ecosystem, drinking water sources, microbial imbalance, and human health [18]. Bonner and Alavanja, [19] reported that pesticides adversely affect natural systems and disturb biodiversity and ecological stability. Moreover, it accumulates in the plants and human bodies, therefore, increasing

disease susceptibility (e.g. Neurotoxic, cancer risks) [19]. Due to these drawbacks, the need for developing processes that guarantee the removal of pesticides in a safe, economical, and efficient way is essential. Table A1 in the appendix shows the main characteristics, composition, examples, and use of pesticides.

Several types of bacteria have been used over the years for the biodegradation of organic contaminants. *Pseudomonas* was first identified as a gram-negative, polar-flagellated, and rod-shaped bacteria by Migula in 1894, during the 19th century [20]. It is one of the prokaryote genera that has undergone the most research (bacteria). The description of *Pseudomonas* has expanded since its initial detection, and new techniques have been created to improve the thorough investigation of its appearance and physiology. It is important to note that the morphological characteristics of these bacteria are shared by multiple bacteria genera and are not very helpful in confirming the genus's identity (*Pseudomonas*). Advanced nucleic acid-based techniques can distinguish these bacteria from other genera that are similar to them with ease, exposing the taxonomic relationships between different bacterial species, including the genus *Pseudomonas* [20] as shown in Figure 1. *Pseudomonas aeruginosa* is a Gram-negative bacterium that can be found in almost any environment. Their metabolic capacity is vast, as evidenced by their ability to synthesize a wide range of secondary metabolites and polymers, as well as their ability to employ a wide range of carbon sources and electron acceptors [21].

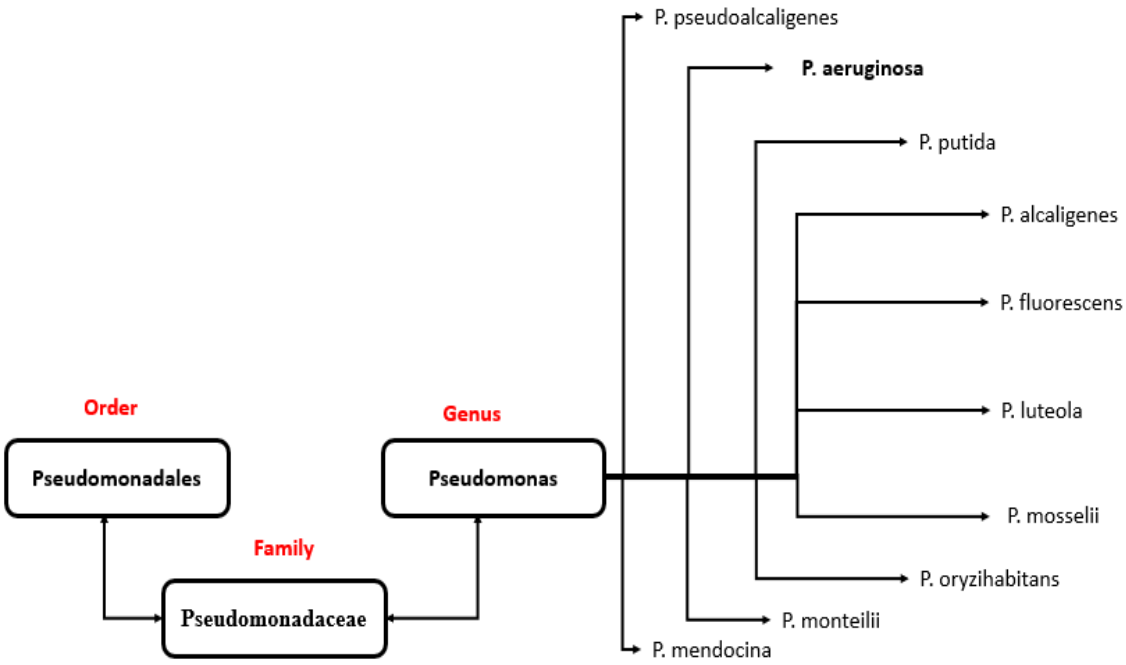


Figure 1: Various types of *Pseudomonas* [20].

1.2 Research Objectives

The overall aim of this thesis is to assess the biotreatment of GTL process water and propamocarb hydrochloride fungicide-contaminated wastewater using *Pseudomonas aeruginosa* strain in PVA gel. The following major objectives make up this goal:

1. Compare how effective this type of bacteria extracted from soil in Qatar for the biodegradation of organic contaminants in GTL process water and propamocarb hydrochloride fungicide-contaminated wastewater.
2. Investigate the impact of many variables on batch biotreatment of GTL process water and propamocarb hydrochloride fungicide-contaminated wastewater including initial COD concentration, operating temperature, pH, and PVA volume fraction.
3. Use response surface methodology (RSM) to determine the optimum operating conditions under which the biodegradation performance is maximized.
4. Investigate the impact of liquid flow rate and air flow rate on the biotreatment of GTL process water.
5. Perform a comparative study between GTL process water and propamocarb hydrochloride contaminated water in terms of biodegradation efficiency, structure, and mechanism.

1.3 Research contribution

Many researchers have studied *Pseudomonas aeruginosa* ability to degrade various chemicals in batch and continuous bioreactors under various conditions. These include degradation of 0.02 % naphthalene [22], biodegradation of volatile organic compounds [23], biodegradation of petroleum compounds [24], degradation of octamethylcyclotetrasiloxane (D4) [25], and bioremediation of heavy metal [26]. However, the application of *Pseudomonas aeruginosa* for the biotreatment of GTL process water and propamocarb hydrochloride fungicide-contaminated wastewater has never been investigated before. Hence, the aim of this work is to compare how this bacterium is effective in the biotreatment of GTL process water and propamocarb HCl-contaminated wastewater. The study gives an overview of degradation pathways, and various treatment technologies. In addition, it underlines the significant experimental factors in the biodegradation processes including initial COD concentration, operating temperature, pH, and PVA volume fraction. Additionally, it helps to determine the optimum experimental conditions under which the wastewater treatment performance is enhanced utilizing (RSM). Moreover, very limited studies investigated the degradation methods of GTL process water such as advanced oxidation, thermal evaporation, membrane filtration, and bioreactors. Therefore, this study is important to direct future researchers and help them to compare and decide on the suitable system for GTL process water degradation.

1.4 Thesis structure

This thesis includes five chapters. Chapter 1 gives a general introduction to the research work, highlights the main objectives and contribution, and underlines the outcomes generated from this work. The second chapter offers an overview of GTL process water and pesticide wastewater including current treatment technologies, classifications, and environmental impacts. The chapter also includes the biodegradation mechanisms of both GTL process water and pesticide-contaminated wastewater, the common microorganism used for biodegradation, and the factors that affect the biodegradation process. Additionally, the chapter presents the application of *Pseudomonas aeruginosa* in the biodegradation of various compounds, the application of biomass immobilization, and the application of treated water. Moving on to the third chapter, which provides the materials and reactor system required to conduct the experimental study. Furthermore, it provides a detailed explanation of the methodology used to accomplish the objectives outlined in Section 1.2. The fourth hapter illustrates the outcomes of the experimental work executed on the lab scale. Lastly, Chapter 5 provides a comprehensive summary of all the approached findings of this research study. In addition, it suggests future recommendations for enhancing the process performance and reveals the future research prospects of interest for the biodegradation process.

1.5 Thesis outcomes

- Optimization of biotreatment of GTL Process Water Using Pseudomonas Aeruginosa Immobilized in PVA hydrogel. Submitted to Processes.
- Removal of pesticides from wastewater: An overview of the different treatment processes. (in preparation)
- Application of Pseudomonas *Aeruginosa Bacteria* in Biodegradation of Wastewater: A Mini Review (in preparation)

Chapter 2: Literature Review

2.1 Overview of the GTL process

Gas-to-liquids (GTL) is a new way to invest in the country's natural gas resources by converting them into premium liquid fuels and products. These products include motor lubricants, vehicle fuels, and components for everyday goods such as plastics, detergents, and cosmetics. It provides a mechanism to access the huge international market for petroleum products. Small-scale GTL facilities are containerized units that include a reformer for producing synthesis gas, a Fischer Tropsch reactor for producing Syncrude, and, in some circumstances, an upgrade package for further refining FT products into the needed transportable fuel [35]. On-site building expenses are greatly reduced because these containerized units have approximately 70% of their construction completed before arriving at the plant site. Added units can be simply supplied via truck or ship and linked in tandem with the existing process in circumstances when capacity needs to be expanded. Capacity can vary from 100 to 15,000 barrels per day (BPD) based on the technology. Figure 2 shows the large-scale GTL plants that are currently operational including Pearl GTL, Oryx GTL (Qatar), Escravos GTL (Nigeria), Bintulu GTL (Malaysia), and Mossel Bay GTL (South Africa). The combined capacity of these five plants is roughly 259 Mbpd. Shell's Pearl GTL complex, with a capacity of 140 Mbpd, accounts for more than half of the world's entire commercial-scale GTL volume [27].

Figure 2: GTL plants in operation worldwilde (commercial-scale)[28].

2.1.1 GTL process phases

Fischer-Tropsch is a chemical process that converts bitumen from biomass into liquids (BTL), oil sands into liquids (OTL), coal into liquids (CTL), and gas into liquids (GTL). There are three primary phases in the GTL process. Synthesis gas, also known as syngas, is produced in the first stage when natural gas is partially oxidized to produce a mixture of hydrogen and carbon monoxide. Impurities are subsequently taken out of syngas. Using a catalyst, the second stage transforms the synthesis gas into liquid hydrocarbons. In this phase, a liquid that feels and looks like wax at room temperature is created. Cracking and isomerization, the last step, "cuts" the molecular chains into shorter lengths. High-quality liquids like diesel, kerosene, and lubricating oil are produced as a result. GTL products have very low concentrations of contaminants like sulfur, aromatics, and nitrogen that are present in crude but are colorless and odorless. Figure 3 shows GTL

process phases and products. The three distinct technological portions in each of the four processes are:

- **Syngas production**

Initial separation of the carbon and hydrogen from the CH_4 molecule is followed by reconfiguration through steam reforming and/or partial oxidation. Carbon monoxide and hydrogen make up the majority of the syngas produced.

- **Catalytic (F-T) synthesis**

Depending on the technology, a variety of Fischer-Tropsch (F-T) reactors process the syngas to produce a variety of paraffinic hydrocarbon products (synthetic crude), especially those with long-chain molecules (e.g., those molecules that include up to 100 carbon atoms). The reaction of Fischer-Tropsch is represented in the following equation:

$$CO + 2n\ H_2 \xrightarrow{\textbf{Catalyst}} -c(CH_2-)_n- + H_2O \ \text{(very exothermic)} \qquad 1$$

- **Cracking**

Diesel, naphtha, and lubricating oils are made from Syncrude using traditional refinery cracking techniques for commercial markets. The cracking processes can be somewhat modified by beginning with very long chain molecules to create more of the goods that the market is now looking for. Lubricants offer high-margin products for markets with lower volumes, whereas the highest-value bulk products are frequently middle distillate diesel and jet fuels. The F-T GTL unit designs and operations are routinely modified in modern plants to achieve a variety of product slates and the desired product distribution.

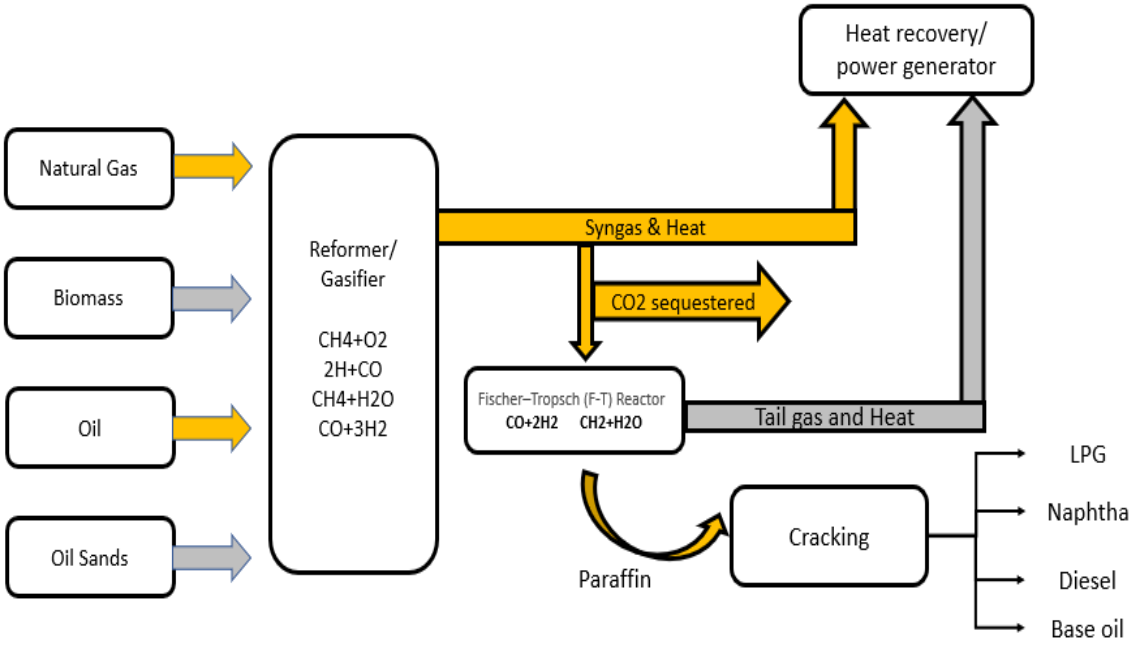


Figure 3:GTL process phases and products.

2.1.2 GTL products environmental aspects and benefits

GTL products are less hazardous to the environment compared to typical petroleum alternatives due to their compositional characteristics. They are projected to degrade more easily than petroleum-derived products due to their composition (linear and branched alkanes), which tend to have substantially more cyclic and a higher degree of branching [12], [29]. GTL technologies are a great way to decrease gas flaring while increasing returns because they can convert effluent gas streams that would otherwise be flared into valuable liquid transportation fuels and chemicals, like high-quality gasoline or methanol, or into a separate stream of hydrogen-rich vent gas. Additionally, by using CO_2 streams as co-feed and converting them into gasoline or methanol, GTL systems can reduce greenhouse gas emissions even more. This is a useful application for what is normally thought of as a low-value or even negative-value gas stream. GTL Fuel is

characterized by improving aquatic and soil biodegradability as well as decreasing aquatic and soil ecotoxicity. The performance of fuels created via the FT method is noticeably higher than that of petroleum-based alternatives. Because FT-derived diesel burns cleaner than petroleum-derived fuels and lacks aromatics and sulfur, it emits less NOx, SOx, and PMs. Experiments on exhaust emissions on GTL products showed a considerable overall decrease in CO (22%–25%), hydrocarbons (30%–40%), and NOx (6%–8%). The opportunity exists for the sale of GTL diesel as a premium blendstock. These properties demonstrate that GTL Fuel is less likely to harm the environment than clean conventional fuels. In addition, to meet commercial diesel environmental requirements, FT diesel can be blended with lower-cetane, lower-quality diesel[30]. However, according to Höök et al. [31] the GTL process has some environmental effects in common, including GHG emissions, particle emissions, and water usage. Other risks are specific to unconventional extraction, such as the possibility of contaminating aquifers, wastewater disposal, and seismic activity, or to conventional extraction, such as gas flaring.

2.1.3 GTL process water treatment technologies

GTL PW is a by-product of the Fischer-Tropsch (F-T) reaction that is produced in significant quantities ~25% more than other hydrocarbon products, on a weight basis. Process water produced by GTL industries must be treated to meet regulatory agency standards for both safe releases into the sea or other bodies of water and effective reuse[32]. Since the gulf countries are located in one of the driest parts of the planet, wastewater treatment and management for reuse and disposal is crucial. Depending on the stream's characterization, various technologies have been used to remediate GTL-produced wastewater. The removal effectiveness of harmful chemicals from GTL process wastewater varies depending on the technique used, such as advanced oxidation, thermal evaporation, membrane filtration, and bioreactors [33]. GTL process wastewater is primarily treated by anaerobic biological digesters decause of the low concentrations of sulfur and nitrogen in GTL process wastewater, which are widely dispersed in other wastewater streams. The standard GTL process wastewater treatment facility starts with coarse screening to get rid of large debris, then it goes through a biological process with the addition of a coagulant to remove soluble material. The waste is then separated via coagulation and collected in colloidal form. To reduce (BOD) levels, wastewater is treated after coagulation by adding disinfecting and oxidizing chemicals [34].

Mild oxygenates, such as C1-C3 alcohols and carbonyl compounds, which have lower boiling points than water, are typically extracted using distillation or stripping columns and are graded as saturated feedstocks based on the properties of the F-T treatment water in particular. The remaining product from the distilled wastewater is sent to the biological treatment unit [35], which still has a significant number of residual alcohols and organic acids, resulting in a high COD content (30 g COD/l) and low pH value (pH = 3.0). Table

1 and Figure 4 below show the main components and compositions of the synthetic Fischer–Tropsch wastewater including the Hydrocarbons, the volatile fatty acids, the short-chain alcohols, and the long-chain alcohols, and their COD concentration.

Table 1: Composition of the synthetic Fischer–Tropsch wastewater [35].

Compounds	Examples	Total COD (mg/l)	Contribution
Hydrocarbons (HCH)	Pentane, Hexane, Heptane, Acetone	1255	4%
Volatile Fatty Acids (VFA)	Acetic, Propanoic, Butanoic, Pentanoic, Hexanoic	3002	11%
Short-chain Alcohols (SCA)	Methanol, Ethanol, Propanol, Butanol, Pentanol	21,531	77%
Long-chain Alcohols (LCA)	Hexanol, Heptanol, Octanol, Nonanol, Decanol	2296	8%

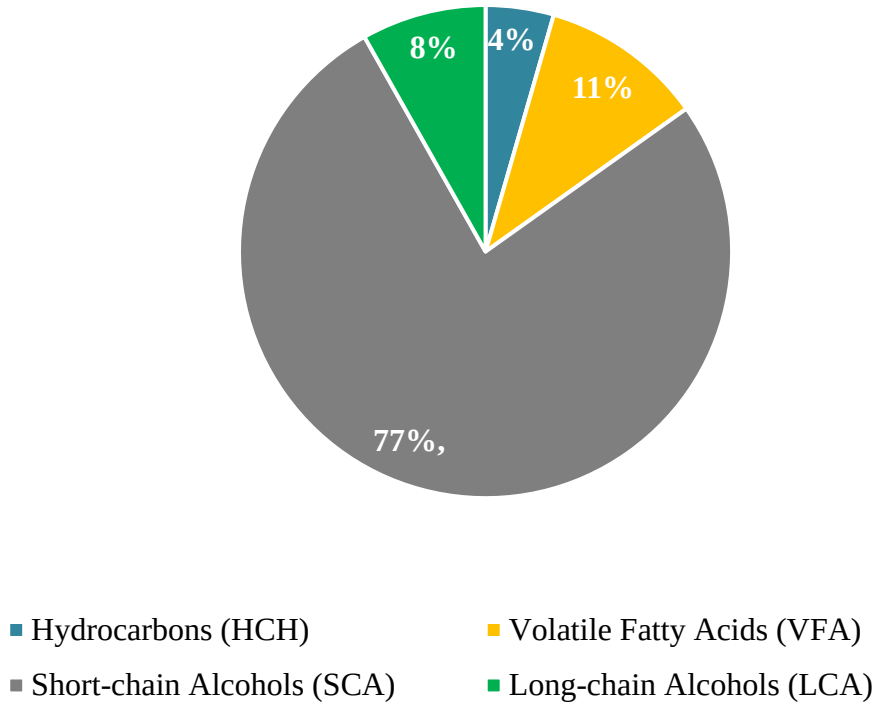


Figure 4: Composition of Fischer–Tropsch wastewater.

2.1.4 GTL process water Biotreatment

The majority of COD in the total GTL PW water stream comes from alcohols, which can be effectively treated biologically in anaerobic environments. The course of treatment may also combine anaerobic and aerobic conditions. Anaerobic biological treatment is more desirable since it can generate energy as a byproduct by creating methane in addition to eliminating organic pollutants from GTL effluent [36]. Several studies on GTL wastewater, namely F-T wastewater, were undertaken, ranging from the size of laboratory benches to the experimental scale using industrial and actual wastewater, biological treatment has been studied under anaerobic conditions [37].

Three steps of GTL PW treatment, including chemical, biological, and physical treatment

approaches, were described by Pon Saravanan and Van Vuuren [11]. The three integrated step GTL treatment plant used chemical treatment in the first stage to remove free oil and suspended hydrocarbons, followed by biotreatment in aeration tank to eliminate carbonic and nitrogenous compounds, and lastly physical treatment, such as sand filtration, in the third stage to eliminate suspended solids, oil , chemical oxygen demand and related biological oxygen demand. Oil-water separation, reaction water treatment, cooling of water effluent, and neutralization are all components of primary treatment. The primary reaction water treatment unit removes non-acidic substances from the reaction water, including alcohols, aldehydes, ketones and other non-acidic compounds. Ammonia is removed by combining nitrification and denitrification in an activated sludge process, which aims to remove both COD and ammonia. High-quality treated water is produced by the tertiary treatment, which uses direct air flotation with an integrated sand filter to remove suspended solids, oil, and related BOD and COD from wastewater. With BOD and COD concentrations less than 50 mg/l and less than 100 mg/l, respectively, the tertiary treated water has suspended solids and total dissolved solids in the range of 0-20 mg/l and 1000-1500 mg/l [11], [32]. Municipal and industrial wastewater is treated using the well-known biological process known as conventional activated sludge (CAS) treatment. This method of treatment is based on biomass, which is held by a settler, aerobically degrading organic contaminants. The CAS effluent can undergo post-treatment ultrafiltration (UF) to remove unsettled particles and further lower the COD in the effluent, allowing for the reuse of the treated water. This combined process is referred to as a conventional activated sludge system followed by ultrafiltration (CAS-UF) [38]. To treat Fischer-Tropsch (FT) reaction water from gas-to-liquids (GTL) industries, the potential of a membrane bioreactor (MBR) system was assessed and compared to the current treatment system, which consists of a conventional activated sludge system

followed by an ultrafiltration (CAS-UF) unit [38]. Majone et al, [39] investigated the anaerobic biodegradation of synthetic F-T wastewater with a high concentration of COD (~28 g/l) generated by long-chain alcohols utilizing a continuous flow packed bed biofilm reactor (FPBBR) on a laboratory scale. They steadily increased the COD content in tests to evaluate the inhibitory effect of long-chain alcohol concentrations. About 96% of COD was removed and converted to methane. Aerobic degradation of F-T wastewater was studied by Chain et al, [40] to decrease the high COD specifically from short-chain alcohols, and volatile fatty acids as they represented around 87% of the given wastewater. The FT wastewater was synthesized from SCA's, and VFA's in a mineral salt solution and a COD of 67.9 g/l. Using *Bacillus sp.*, up to 90% of COD was reduced within 3 days. Table 2 below summarizes the common reactors used for the biotreatment of GTL process water.

Table 2: Common reactors used for the biotreatment of GTL process water.

Reactor	COD (mg/l)	Time (days)	Removal%	Ref
Membrane bioreactor (MBR), and ultrafiltration (CAS-UF)	1000	645	~98	[38]
Continuous-flow packed-bed biofilm	28,000	1.4	96	[39]
Up-flow anaerobic fixed bed (UAFB)	32,855.3–38,461.4	125	Averagely 11.2	[41]
Up-flow anaerobic sludge blanket (UASB) coupled with bio electrochemical system (BES)	28,910.6–31,230.8	160	86.8	[42]
Up-flow anaerobic sludge blanket system (UASB) coupled with micro-electrolysis cell (MEC)	11,417.9±744.9	335	93.5	[43]
A thermo reactor	67.9 g/L	3	90%	[40]

2.2 Agricultural wastewater (pesticides) overview

Pesticides are essential toxic organic compounds of several agricultural management systems. Their use is significantly increasing especially in the equatorial regions for preventing and controlling pests, diseases, rodents, and weeds, therefore, increasing food production[13], [19]. Worldwide, a huge number of pesticides are applied year after year, reaching up to 3 million tons equivalent to a market value of USD 40 billion. The World Health Organization (WHO) defined pesticides as a chemical complex that is utilized to kill pests such as insects, rodents, fungi, and weeds. Moreover, the Food Agriculture Organization (FAO) defined pesticides as any substances proposed for preventing, killing, or controlling pests including unwanted plants or animals causing harm and vectors of human or animal diseases [44]. Based on scientific studies demonstrating their safe use without posing unreasonably high hazards to people or the environment, EPA registration is required for all pesticides that are marketed or distributed in the United States[45].

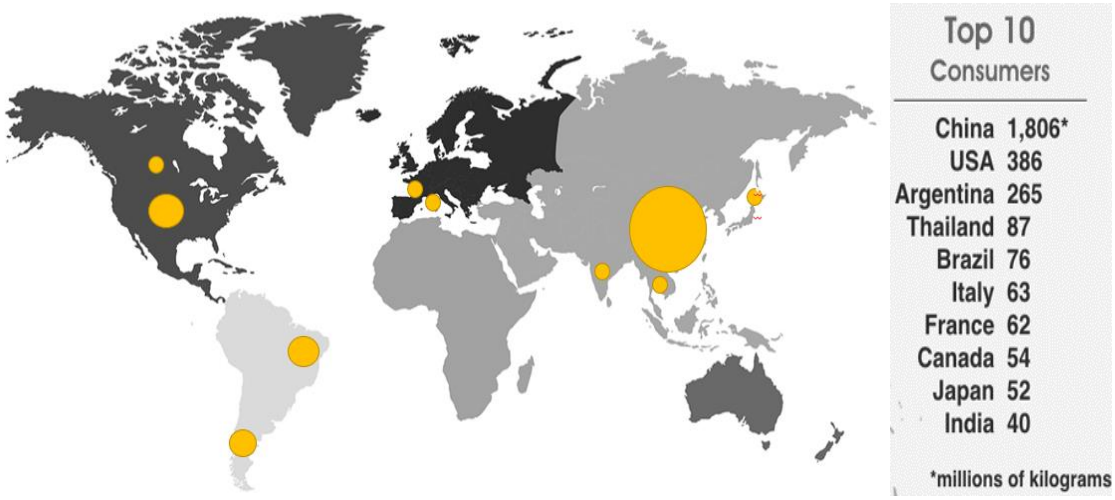


Figure 5: Main pesticides consumers [46].

2.2.1 Classification of pesticides

Pesticides are mainly classified by target group into herbicides, insecticides, and fungicides; however, the most common and useful classification of pesticides is based on their chemical composition and the nature of their active ingredients [47]. Pesticides are classified- based on their chemical composition- into main groups including organochlorines, organophosphorus, carbamates and pyrethrin, and pyrethroids. This classification provides useful information for identifying chemical properties, applications, and precautions of pesticides. Another classification of pesticides is performed by WHO where pesticides are classified according to their potential hazard into extremely hazardous (< 5 mg/kg oral, and < 50 mg/kg dermal), highly hazardous (5–50 mg/kg oral, and 50–200 mg/kg dermal), moderately hazardous (50–2000 mg/kg oral, and 200–2000 mg/kg dermal), slightly hazardous (over 2000 mg/kg oral, and over 2000 mg/kg dermal), and unlikely to present acute hazard 5000 mg/kg or higher [48]. Table 3 below shows the common classification of pesticides.

Table 3: The common classification of pesticides.

Common classification of pesticides		
By target group	Based on their chemical composition	According to their potential hazard
• Herbicides • Insecticides • Fungicides	• Organochlorines • Organophosphorus • Carbamates • Pyrethrin	• Extremely hazardous • Highly hazardous • Moderately hazardous • Slightly hazardous • Unlikely to present acute hazard

2.2.2 Environmental impacts and discharge limits

Ideally, the use of pesticides should only affect the target organisms and no other organisms in the environment. Still, many pesticide applications can affect non-target organisms and move beyond the application site. Pesticide deposits get into the environment due to their many applications such as in agricultural systems and may be found in the air, water, and soil. They can enter the environment in many ways, such as through storm drain, rainfall, volatilization, leaching, and others[49]. Many factors increase the probability of pesticides polluting the environment, such as the nature of the pesticide, type of formulation, its ability to break down in a given substrate, the frequency and rate of its application, and the environmental conditions. Pesticide exposure can cause damage to the immune system and can cause various diseases including allergies, cancer (leukemia, brain cancer, lymphoma, breast cancer, ..etc), asthma, hypersensitivity, and hormone disruption [50]. Several studies investigated the effects of pesticides on human health and discuss potential diseases associated with pesticide exposure [50]–[58]. Regarding the regulatory limits of pesticides, the Environmental Protection Agency (EPA) has issued an NPDES Pesticide General Permit (PGP) that includes pesticide applications in a few states and territories. These regulations are legally enforceable primary standards and treatment methods applicable to public water systems. Basic standards and treatment methods protect public health by reducing levels of pollutants in drinking water.

2.2.3 Current methods for pesticides removal

The need for promising and suitable technologies for pesticide removal is very essential due to its adverse effect on humans, plants, animals, and the ecological system. Pesticides have various chemical and physical properties; thus, their environmental fates are

different and various approaches are required for their removal process. Various treatment methods exist to remove pesticides from contaminated water; However, current treatment methods that include a combination of physical, chemical and biological methods have been used to investigate and detect the problem of pesticide removal from contaminated water. Many techniques have been used for the removal of pesticides including adsorption, biodegradation, electrocoagulation, photodegradation, ultrafiltration, and advanced oxidation processes. They have been thoroughly discussed by several researchers[18], [59], [68], [60]–[67]. Each treatment method has its advantages and disadvantages based on several criteria such as capital and operational costs, efficiency, environmental impacts, reliability, pre-treatment requirements, and sludge production. For example, the biodegradation technique has high efficiency and fewer environmental impacts; however, it requires high cost and sensitive environmental conditions (temperature, pH, etc), and it cannot be always applied on a large scale [69]. Only common treatment methods including adsorption, electrocoagulation, photodegradation, and biodegradation were discussed in this section as shown in Figure 6.

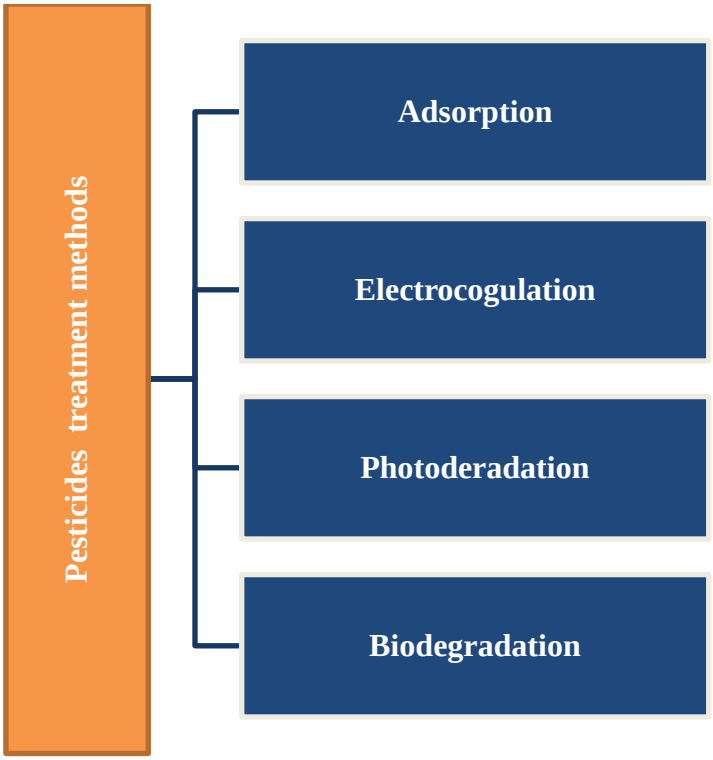


Figure 6: Common methods for the removal of pesticides.

2.2.3.1 Adsorption

The adsorption process of pesticides has been widely used and proved to be very efficient for pesticide treatment. Adsorption works by attracting various types of contaminants to attach to the surface of the adsorbent. There are three mechanisms for the adsorption process to take place which include the attraction force between the pollutant and the surface of the adsorbent particle. Thereafter, the pollutants keep traveling via the surface pores deeper inside the adsorbent, where in this case the attractive forces are the greatest, and more pollutants are attracted till full capacity is achieved. Once this happens, the adsorbent will demand to be substituted with a new one or regenerated [69], [70].

The degradation processes using nanoparticles are at the forefront of the rapidly emerging field of nanotechnology [71]. Their unique size-dependent properties make these

materials superior and indispensable in many areas of human activity [72]. Nanoparticles such as TiO_2 and Fe are determined to be great adsorbents and effective photocatalysts for OCs and their toxic metabolites degradation as shown in Figure 7. According to M. Rani et al, [73] these techniques are very effective, fast, eco-friendly, as well as economical [74].

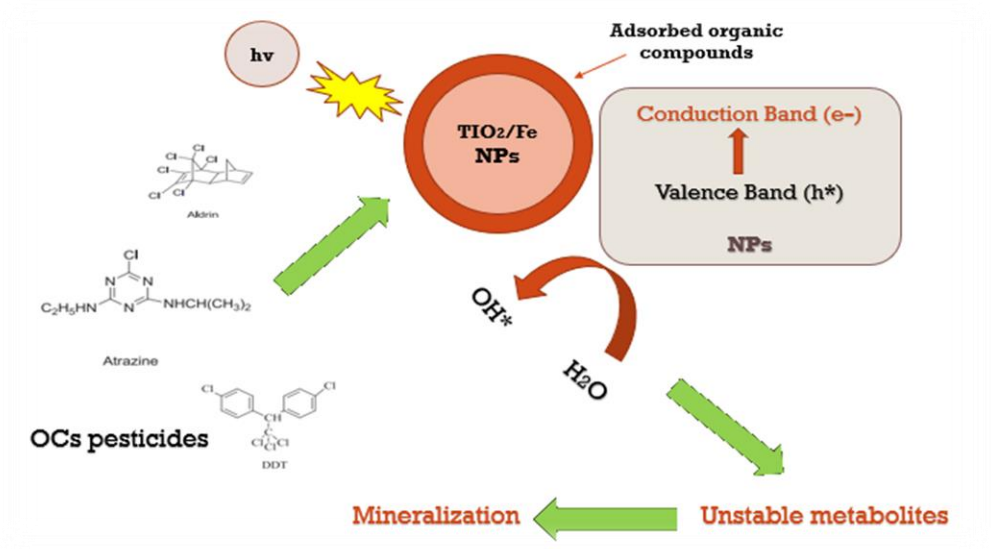


Figure 7: Photocatalysts for OC_S using TIO2/Fe adsorbent [72].

Wang et al, [64] performed batch adsorption experiments using microplastic materials to find out the adsorption process, and mechanisms of pesticides. Different five types of pesticides were investigated and the results illustrated that polyethylene microplastics (PE MPs) can be a great carrier of pesticides in the agricultural field. Cederlund et al, [75] discussed the adsorption of pesticides with various chemical properties using mixing biochar which was shown to be very effective, and viable for the adsorption optimization of all model composites. Furthermore, Gilliom et al. and Memon et al. [66], [76], [77] investigated the use of modified polymer adsorbents for the removal of pesticides from

water. Cyclodextrin-based polymers (CDPs) were used as an adsorbent, which was found to be very effective, with the advantages of specific affinity, simple design, and low price[66]. Pedro et al. indicated that activated carbon (AC) has been frequently used for the removal of organic compounds such as pesticides from wastewater[78]. It displayed high adsorption capacities for various spectrums of contaminates with initial concentrations between 15 and 80 mg/l. The results obtained showed that AC has many advantages such as high porosity, high adsorption capacity, and large surface area[79]. On the other hand, AC is limited to being applied on a large scale due to its high cost. Moving on, Salman et al, [60] stated that the adsorption capacity of insecticide (carbofuran) removed by AC reached 164 mg/g. Furthermore, the regeneration effectiveness of AC using ethanol ranged from 90% to 96%. Another study made by Cazetta et al, [80] discussed the use of activated carbon as an adsorbent where a magnetic, and graphitic carbon nanostructure was utilized for pesticide (2,4-dichlorophenoxyacetic acid) removal. This nanostructure was formulated using biomass materials such as filter paper and cotton with adsorption capacities of 77 and 33 mg/g, respectively. Cao and Li [81] reported that Graphene can be considered one of the promising adsorbents of contaminants due to many advantages including its high thermal conductivity, large surface area, high-speed electron mobility, high electrocatalytic activity, and excellent optical properties. Madej et al.,[82] reported that the adsorption of pesticides on graphene occurs due to its hydrophobic behavior over noncovalent interactions, mainly the pep stacking interaction with the aromatic rings of the considered compounds, and due to its large surface area. Zhang et al. and Yamaguchi et al.[83], [84] achieved more than 95% and 89% removal efficiency of triazine pesticides and glyphosate (herbicide) by utilizing cellulose/graphene composite and ferrite manganese/graphene respectively. Biochar has been also stated as a good adsorbent material due to the existence of organic groups on

its surface which attracts the negative charge, therefore, its cation exchange capacity (CEC) might be enhanced [85]. Other characteristics such as the high porosity, large surface area, and availability make biochar one of the promising adsorbents. The adsorption mechanism of pesticides using biochar and other adsorbents (eg. clay-based adsorbents, zeolite-based adsorbents, etc..), was extensively studied by many researchers [86], [87]. Many factors affect the adsorption capacity such as the types of pollutants being adsorbed, the composition of the wastewater, pH, temperature, and contact time [69]. Researchers demonstrated that the application of different adsorbents such as, activated carbon, modified biochar, nano-adsorbents (such as carbon nanotubes and graphene), composite adsorbents, and others are being used for pesticides removal from water and wastewater [62]. Table 4 summerize the recent studies of pesticides removal using adsorption process.

Table 4: Recent studies on pesticides removal using the adsorption method.

Type of pesticide	Type of water	Type of adsorbent	Method	Removal %	Ref
Insecticide (Diazinon)	Synthetic water	Iron and nanotitania-modified activated carbons	Batch adsorption	Up to 95%	[88]
Chlorpyrifos	Synthetic water	Bagasse based biochar	Batch adsorption	89 %	[89]
Atrazine and imidacloprid	Synthetic water	Biochar	Batch adsorption	95%	[90]
Fenuron	Synthetic water	CNTs	Batch adsorption	90%	[91]
Pentachlorophenol	Synthetic water	Modified chitosan	Batch adsorption	High removal %	[92]
Organophosphorus (profenofos)	Synthetic water	Bioadsorbents based on date pits	Batch adsorption	High removal % up to 100%	[93]
Carbendazim, dipterex, diflubenzuron, malathion, difenoconazole	Synthetic water	Polyethylene (PE) agricultural soil films microplastics	Batch adsorption	Up to 18% (CAR), 70%(DIP), 86% (DIF), 60 (MAL), 85% (DIFE)	[64]
Atrazine, Pymetrozine, Acetamiprid, Diuron, Thiacloprid, Imazalil, Pyraclostrobin, Azoxystrobin, Difenoconazole, Trifloxystrobin, Chlorantraniliprole	Synthetic water	Mesoporous activated carbon	Vortex mixer	> %80	[94]

2.2.3.2 Electrocoagulation

Electrocoagulation (EC) technology is one of the promising electrochemical processes for the removal of suspended solids, metals, radionuclides, colloidal substances as well as pesticides, and various harmful organisms. In the EC process, a direct current is applied to the water and electrode plates are dissolved into the solution, which leads to a rise in the metal concentration in the solution that eventually precipitates in the form of oxide precipitates [95]. The design of the EC process is constantly improving; thus, it has been widely approved and gained attention recently. The EC process allows the treatment of a large volume of pollutants at a low cost and it effectively removes pesticides from water such as methyl parathion, atrazine, and triazophos[96]. Ghalwa et al, [97] investigated three potential mechanisms in the EC process including electrocoagulation, electro-flotation, and electro-oxidation. In the electrocoagulation process, when a direct current flows through the electrodes, the coagulant is produced on-site due to the electrolytic oxidation of the anode matter. Then, $Fe(OH)_2$ and $Al(OH)_3$ are formed and released to the anode by utilizing an iron-aluminum anode [97].

Once the metal hydroxides (iron hydroxides and aluminum hydroxides) are generated, the concentration of negatively charged colloids is getting increases in the area near the anode. Thereafter, monomeric hydroxide ions and polymeric hydroxide complexes will be formed because of the hydrolysis of ferrous ions generated, and both complexes depend on the pH of the solution. Moreover, the flocks will be formed when the highly charged polymeric hydroxide cations destabilize the negatively charged colloids. When the solubility of the metal hydroxides (Fe (OH)n and Al (OH)n) is overcome by the amount of iron in the solution, the amorphous metal hydroxide precipitates are produced, which generated sweep flock coagulation. Behloul et al,[98] performed a laboratory-scale

electrocoagulation experiment using a Plexiglas reactor. The aluminum cathode and anode were connected to a direct electric power supply that ranges between 0 to 5 A current or 0 to 30 V voltages and inserted into an 800 ml volume of wastewater containing malathion pesticides. Periodic samples of 10 mL were taken from the EC cell and then filtered to exclude sludge formed during electrolysis, to determine the malathion pesticide concentration in the water solution using a spectrophotometer. The results show that after 60 min of electrolysis, the removal efficiency of malathion concentrations of 15, 40, 50, 75, and 100 mg/l were reached 91.3%, 85%, 88.5%, 89.3%, and 90.7% respectively. Abdel-Gawad et al, [67] examined the degradation of pesticides from the simulated wastewater by the EC process using ion electrodes. Moreover, he investigated the optimization of the EC process by studying the effects of different operational parameters such as pH, current density (CD), initial pesticide concentration, and the amount of NaCl on the pesticide's removal performance. A very high removal % was obtained that reached up to ~ 98-99%. A 100% removal was achieved when the initial parameters were pH of 6-7, CD of 1mA/cm^2, 10 min of electrolysis time, NaCl concentration of 1g/L, and initial pesticide concentration of 0.5%. Additionally, an agreement between a pseudo-second-order equation model solution, and the experimental results was obtained [67]. The recent studies on pesticide removal using the EC process are summarized in Table 5.

Table 5: Recent studies on pesticides removal using the EC method.

Type of pesticide	Type of water	Electrode used	Method	Removal%	Ref
Malathion	Clay and groundwater	Aluminium and iron electrodes	electrolytic reactor	85%	[99]
Chlorpyrifos, Fenitrothion, and Acetamiprid	Synthesized water	monopolar iron electrodes	bipolar electrochemical cell	87%	[100]
Malathion	Synthesized water	Aluminium electrodes	Reactor	over 90%	[100]
Oxyfluorfen	Synthetic wastewater	Iron and stainless steel	bench-scale plant with a single compartment electrochemical flow cell	Higher than 90 %.	[101]
Acetamiprid	Simulated wastewater	Aluminium electrodes	Batch reactor	Up to 83%	[102]
Imidacloprid	Synthesized water	Iron and aluminium electrodes	electrochemical reactor	95% Fe and 80.8% Al	[103]
Abamectin	Synthesized water	Stainless Steel and Iron	electrochemical reactor	94% SS and 64.5% Fe	[104]
Malathion, imidacloprid and chlorpyrifos	Simulated Wastewater	Iron Electrodes	electrolytic cell	98-99%	[67]

2.2.3.3 Photodegradation

Photodegradation is considered one of the promising technologies for abiotic transformations and the removal of pesticides in wastewater. Unlike hydrolysis and microbial degradation, photodegradation involves characteristic reactions such as bond scission, rearrangement, and cyclization occurring by the high energy of sunlight. Both direct and indirect photolysis are considered in the photodegradation of pesticides which

generally generate less toxic compounds in aquatic organisms than pesticides. In the direct photolysis process, pesticides get excited to determine their basic photochemistry by absorbing natural or artificial sunlight. However, indirect photolysis includes sensitization by dissolved organic substances or oxidation by reactive oxygen species [105]. Burrows et al, [105] explained that most pesticides display UV–Vis absorption bands at quietly short UV wavelengths. Generally, the direct photodegradation of pesticides using sunlight is predicted to be of only restricted meaning. Many researchers studied it, however, with a steady-state and/or laser-pulsed UV radiation. The pesticides get promoted to their excited single states once exposed to direct irradiation which may then intersect the system to generate triple states. Thereafter, these excited states might undergo other processes such as homolysis, heterolysis, or photoionization, as shown in Figure 8.

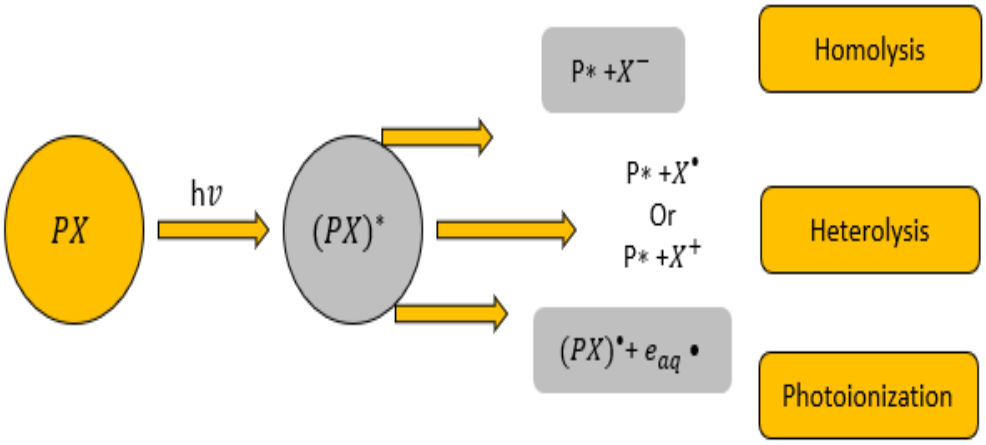


Figure 8: Direct photolysis chemical cases [105].

The photodegradation process is not a method that is appropriate for all types of organic contaminants. Furthermore, it is required to conduct the lab analysis thoroughly before

implementing any approach on a large scale. Goodwin et al, [69] discussed the photodegradation of pollutants in wastewater using ultraviolet (UV) light. It can be divided into four groups according to its wavelengths, such as UV-A (315–400 nm), UV-B (280–315 nm), UV-C (180–280 nm), and vacuum UV light (10–180 nm). The effect of UV light increases when the wavelength is lower. Different types of UV lamps have been widely used in wastewater treatment plants for the photodegradation of pollutants. Yet, it is not enough to use only UV light for the degradation process and there is a need to combine UV light with other photochemical degradation processes. Kumar,[106] mentioned that the photodegradation process has many advantages over other water purification methods such as low cost, complete degradation, and that it is an eco-friendly process. Many researchers studied the photodegradation of the pesticides process and elaborate on the reaction pathways and mechanism in detail [61], [73], [105], [107]–[111]. The recent studies on pesticide removal using the photodegradation process are summarized in Table 6.

Table 6: Recent studies on pesticides removal using the photodegradation method.

Type of pesticide	Type of water	Nanoparticles	Method	Removal%	Ref
Chlorpyrifos, atrazine	Synthesized water	GNPs/ZrV_2O_7 &ZrV_2O	Batch experiments	89–91%	[112]
Atrazine (ATR), malathion (MAL) and glyphosate (GLY)	Groundwater	-	Direct UV-C pilot	70-80%	[113]
Chlorpyrifos	Synthesized water	$CoFe_2O_4$@TiO_2	Batch system	High Removal%	[114]
Chlorpyrifos and Endosulfa	Synthesized water	TiO_2	Annular slurry photo reactor under UVilluminati on	80–99%	[115]
Dichlorvos	natural water compartment	-	Sunlight and UVC-254 irradiation	Up to 97%	[116]
Chlorpyrifos and dimethoate	Synthesized water	-	BL-GHX-V photochemic al reaction and simulated sunlight	75.12% and 94.31%, respectively	[117]
Diuron, alachlor, isoproturon and atrazine	Natural and ultrapure water matrices	Bare TiO2 and graphene oxide TiO2	Semicontinuo us slurry photoreactor and enclosed by 10 fluorescent lamps	Up to 100%	[118]
Fluazaindolizin e	Synthesized water	-	XPA-I photochemic al reactor coupled with a special glass filter and simulated sunlight	Lower than 4.2% of fluazaindoli zine degraded in 5 days by hydrolysis	[119]

2.2.3.4 Pesticides biodegradation pathway and mechanisms

Naturally, pesticides might eventually degrade completely due to the transformation and degradation by different types of microorganisms and microbial consortiums [120]. However, persistent types of pesticides may undergo biomagnification, which is the process when toxic chemicals build up in the environment and accumulate within plants, soil, and the food chain. The degradation of pesticides by microorganisms and conversion into nontoxic compounds are called biodegradation of pesticides [120]. The detoxification process occurs through a wide range of enzymes through fortuitous metabolism. However, fungi and bacteria are the most common microorganisms to metabolize pesticides. Verma et al, [121] mentioned that pesticides and other chemicals are counted as carbon sources and electron donors for specific types of microorganisms.

Microorganisms can interrelate with the compounds physically and chemically, which eventually leads to a change in the structure of the molecule, thus, complete degradation will occur. As previously mentioned, fungi and bacteria are considered the main microorganisms for pesticide treatment. In general, fungi degrade pesticides by changing the molecule's structure, thus transforming it into nontoxic material. The biodegradation of pesticides involved a wide spectrum of catalytic mechanisms and degrading enzymes due to the variety of chemistries used in pesticides [122] [123]. According to Laura et al, there are three main enzyme systems included in the degradation of pesticides such as hydrolases, mixed-function oxidases (MFO), and esterase in the initial metabolism phase, while the glutathione S-transferases (GST) system, in the second stage [124]. Many metabolic reactions catalyzed by enzymes occur in the degradation process, such as oxidation, hydrolyses, dehalogenation, reduction, sulfur replacement, oxygen addition, metabolism of side chains, and others.

Lushchak et al, [125] reported a three-phase process in the metabolism of pesticides. In the first phase, the primary properties of the active substance are converted to less toxic and more water-soluble materials compared to the original compound. Moreover, the water solubility increases and the toxicity decreases by conjugation of pesticide metabolite to amino acid or sugar compounds which occurs in the second phase. While in the third phase, the metabolites produced in the second phase are converted into secondary conjugates that are also non-toxic compounds. These processes include the production of intracellular or extracellular enzymes (e.g. oxygenases, hydrolases, peroxidases, etc) by Fungi, and bacteria [126], [127].

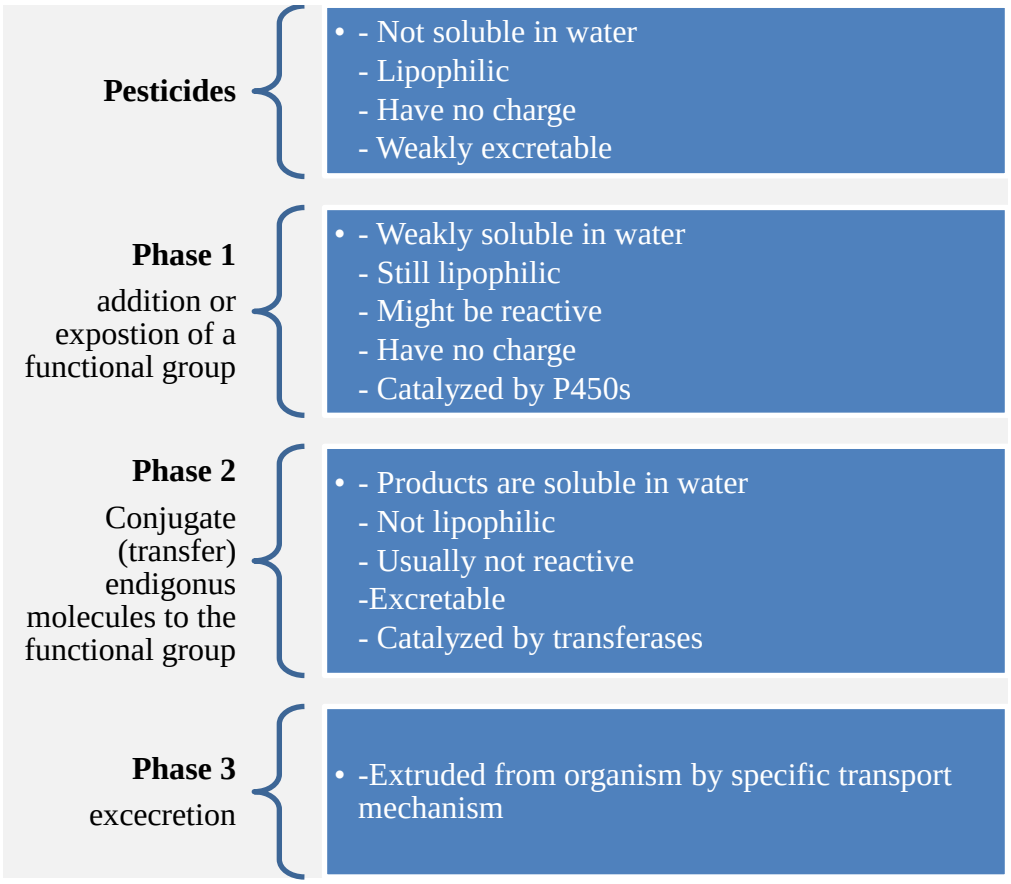


Figure 9: Biotransformation of pesticides [125].

Hou et al, [128] reported that organophosphorus pesticides can be indirectly degraded through some of the microorganisms' activities that change the chemical or physical environment. These activities include mineralization, co-metabolism, and intergeneric synergistic metabolism. Mineralization refers to the process when the metabolic activity of microbes is directed to the organic pesticide, thus, it decomposes or oxidizes into inorganic and other easily available forms. Moreover, co-metabolism can be defined as the biotransformation of an organic matter that is not utilized as an energy source, or as a constituent component of the organism [129]. The last possible mechanism is the interspecific synergistic metabolism which refers to the same surrounding conditions in some microbial metabolites of specific pesticides [128].

Many factors help in choosing the most appropriate treatment method to achieve optimum pesticide removals such as cost, sludge produced, environmental condition, large-scale implementation, and efficiency. It has been concluded that all the techniques have advantages and limitations, however, to achieve optimum performance, the usage of combined is recommended. Additionally, further experimental evaluation of the processes is essential to assert process design, costs, or efficiencies. The advantages and disadvantages of pesticides treatment methods are shown in Table 7.

Table 7: Advantages and disadvantages of pesticides treatment methods.

The treatment method	Advantages	Disadvantages	Ref
Biodegradation	• Environmentally friendly • Site-specific • Produces non-toxic intermediates and products • High efficiency	• Relatively slow process • Highly dependent on pH, temperature, oxygen (presence/absence)	[130]
Adsorption	• Simplicity • The design is flexible, and the operation is easy. • High insensitivity to toxic pollutants.	• Slow kinetics. • Depend on the mobility and polarity of pesticides sites. • High sorbent costs • High processing temperatures.	[64], [78], [86]
Photodegradation	• Low cost • Eco-friendly process	• Low efficiency of light adsorption • The source of the light • Low rate of charge transfer • High combination probability of the photogenerated electron-hole pairs	[106], [109], [110], [131]
Electrocoagulation	• Simple equipment requirement, easy operation, no chemical use requirement, rapid sedimentation, sludge stability, low sludge production, and environmental compatibility. • Ability to treat large volume and for its low cost.	• Electrodes are impermanent. • Intensive • Many factors can affect the results of the process such as the material and design of the electrode the polarity of electrodes the current density, pH and conductivity of the wastewater, the particles size, and others.	[61], [95], [97]

2.2.4 Common microorganisms

Microorganisms and different biological systems have been used incessantly to bio-transform pesticides. Several studies have investigated the capability of microorganisms in degrading pesticides either by using them directly as a source of carbon and nitrogen [132]–[134] or co-metabolically [128], [135], [136]. For example, Zhao et al, [132] reported that *Bacillus cereus GW-01* - isolated from a sheep's rumen chyme- degraded *β-cypermethrin*. HPLC analyses showed that strain GW-01 degraded approximately 60 % of 100 mg/l β-CY within 7 days. Moreover, Bose. et al, [137] reviewed the microbial degradation of chlorpyrifos by various types of microorganisms such as *Pseudomonas, Klebsiella sp., Enterobacter sp., Arthrobacter sp., Serratia marcescens, Sphingomonas sp., Stenotrophomonas sp., Fla-vobacterium sp., and fungal species like Verticillium sp., Trichoderma harzianum, Phanerochaete chrysosporium, Aulosira fertilissima, Aspergillus terreus, Fusarium, valderianum, Verticillium sp. DSP, Synechocystis sp., Phormidium,* etc. The study showed that *Pseudomonas sp*. degraded the pesticide and its primary metabolite both in the absence and presence of external nutritional supplements effectively. However, as the biodegradation process is time-consuming, it can speed up when combined with other effective methods like adsorption and photocatalytic degradation.

A pilot-scale tubular photobioreactor for the removal of selected pesticides (acetamiprid and propanil) from the water was investigated by García-Vara. et al, [138]. The photobioreactor batch experiment was operated for 8 days using algal-mediated microorganisms and the removal % of acetamiprid and propanil were found to be 71 and 99 respectively [138]. Table 8 below shows the common degrading microorganisms for pesticide removal.

Table 8: Common degrading microorganisms for pesticides removal.

Microorganism	pesticide	Degradation mechanism	Removal efficiency%	Ref
Arthrobacter, Bacillus, Burkholderia sp, Cupriavidus sp, Pseudomonas	Aldrin	Deoxygenation	-	[133]
Algal	Acetamiprid and propanil	Photobioreactor	71 and 99	[138]
C. Vulgaris	Atrazine	Biosorption	89.2	[139]
Bacillus cereus GW-01	β-cypermethrin	Batch exp	60 %	[132]
Microalgae	Propanil and acetamiprid	Tubular photobioreactor	99% and 71%	[134]
Fungal strains	Chlorpyrifos	Batch exp	98.4 %	[140]
Microbial consortium and bacteria-pure strains isolated from a bio-mixture	Atrazine, carbofuran, and glyphosat	Batch experiment	> 90%	[141]
Kosakonia oryzae strain-VITPSCQ	, Profenofos (PF) and Quinalphos (QP)	Vertical flow Packed Bed Biofilm Bioreactor	up to 82% and 92%	[142]
Heterotrophic (e.g., *Flavobacterium and Acinetobacter johnsonii*)	Chlorpyrifos (CHL) and Malathion (MAL)	Moving bed biofilm reactor (MBBR)	70% (CHL) and 55% (MAL)	[143]
Microalgae (i.e., *N. muscorum*, *A. oryzae*, and *S. platensis*)	N. muscorum 91%, A.oryzae 65%, and S.platensis 54%,	Batch experiment	N. muscorum 91%, A.oryzae 65%, and S.platensis 54%,	[144]

2.2.5 Biotreatment of Propamocarb hydrochloride fungicide

Propamocarb hydrochloride ([propyl 3-(dimethyl-amino) propyl carbamate hydrochloride, a systemic carbamate fungicide that is commonly used in Qatar to control Pythium spp., Phytophthora spp., Downy Mildew, on outdoor woody, turf, and

herbaceous ornamentals[145], [146]. The fungicide is designed as a soluble liquid that is dispersed and absorbed by the tissue of the plant. Propamocarb hydrochloride fungicide ($C_9H_{21}ClN_2O_2$) is colorless, faintly aromatic, has an average molecular mass of 224.728 g/mol, a melting point of 64.2 °C, and its structure contains a nitrogen atom and amine group as shown in Figure 10 [147]. The main usage of propamocarb hydrochloride in the US is focused on golf fields with about 100,000 to 200,000 pounds of active ingredient used per year[148].

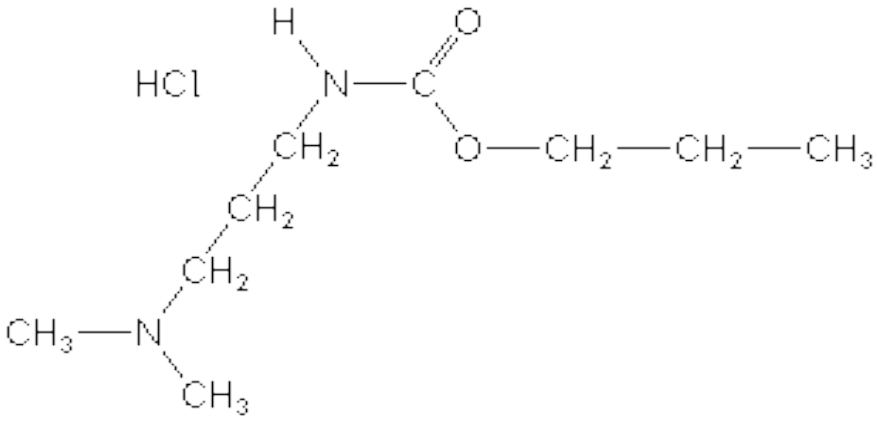


Figure 10: Propamocarb HCL fungicide chemical structure [147].

There are only a few studies that discussed the biotreatment of propamocarb hydrochloride [149]–[151]. A previous study conducted by Knowles et al, [149] in 1981 investigated the microbial degradation of four carbamate pesticides, namely, phenmedipham, desmedipham, promecarb, and propamocarb. The study described the activity of several soil microorganisms including *Aerobacter aerogenes, Bacillus megaterium, Proteus Vulgaris, Penicillium cyclopean, Aeromonas liquefaciens, Bacillus subtilis, Pseudomonas putida, Bacillus cereus, Flavobacter sp., Torula Rosea, and Aspergillus Versicolor* on pesticides. The study reveals that the fungicide propamocarb was the least degraded by any of the microorganisms studied. Moreover, the

biodegradation of pesticides by selected strains of plant growth-promoting rhizobacteria (PGPR) was investigated by MyresiotiS et al, [150]. The results revealed that around 19, and 36% of propamocarb hydrochloride were degraded using strain *B. amyloliquefaciens* IN937a and B. *pumilusSE34* respectively. Ardal et al, [151] investigated the phycoremediation of fungicides contaminated wastewater including propamocarb, cyprodinil, mandipropamid, and metalaxyl using microalgae *Chlorella vulgaris.* The study was divided into two primary experiments: a short-term experiment (60 min) to investigate the biosorption of fungicides using dead and living biomass cells, and a long-term experiment (4 days) to evaluate the biodegradation of fungicides using Chlorella vulgaris. In the short-term and long-term experiments, the propamocarb concentration was shown to have decreased by 30% and 50%, respectively.

2.3 Application of Pseudomonas aeruginosa bacterium strains

2.3.1 Biotreatment of Petroleum Compound Using Pseudomonas aeruginosa

Polycyclic Aromatic Hydrocarbons (PAHS) are significant pollutants that enter the environment in a variety of ways, including anthropogenic sources, combustion, unintentional discharge of oil tankers, and spills near refineries and gas plant facilities [152]. These substances are carcinogenic, toxic, and mutagenic, making them a major threat to human health and the environment. Although there are numerous pathways for PAH degradation depending on the number of fused rings, the process typically begins with hydroxylation to activate the ring, followed by ring-cleaving and several transformations that result in the formation of two important intermediates, phthalate or salicylate, which are then further degraded into metabolites of the tricarboxylic acid cycle (TCA) [153]. Darsa et al, [24] studied the biotreatment of Petroleum Compound Using *Pseudomonas aeruginosa.* Soil samples were collected from petrol bunks around

Madurai in sterile containers and taken to the laboratory to isolate the bacterial strain. The soil samples were diluted and placed in separated plates on Bushnell Hass mineral salt medium ($MgSO_4$ 0.2 g, CaCl2 0.02 g, KH_2PO_4 1 g, K_2HPO_4 1 g, NH_4NO 1 g, and $FeCl_3$ 0.05 g in 1L) containing 2.5% of petrol. These Petri plates were incubated for 24 hours at 37 ° C. Among the developed colonies, only the *Pseudomonas aeruginosa* bacterial colony was chosen for further studies. The isolated strain was able to grow in minimum broth (Dextrose ($C_6H_{12}O_6$) 1 g, $(NH_4)_2SO_4$ 1 g, K_2HPO_4 0.7 g, KH_2PO_4 2 g, Sodium citrate ($Na_3C_6H_5O_{7)}$ 0.5 g, and $MgSO_4$ 0.1 g) with concentrations of petrol of 2.5 percent, 5 percent, 7.5 percent, and 10%, indicating that the organism was capable of decomposing petrol and using it as a source of growth. The efficiency of the isolated strain was assessed by examining the pH, optical density, and CO2 produced during petrol breakdown. The degradation of petrol by *Pseudomonas aeruginosa* was also validated using High-Performance Liquid Chromatography (HPLC) [24], [154]. Moreover, Medić et al, [153] described the biotreatment of petroleum alkanes(n-hexadecane, and nonadecane), and PAHs (fluorene, phenanthrene, and pyrene) by *Pseudomonas aeruginosa.* During seven days and at initial concentrations of 20 ppm, *Pseudomonas aeruginosa* demonstrated a high capability for biotreatment of diverse hydrocarbon mixtures and aromatic fractions from crude oil. Experiments were conducted on aliphatic and aromatic fractions recovered from non-biodegraded, paraffinic crude oil to explore the degradation capability of *Pseudomonas aeruginosa* in complex hydrocarbon mixtures. The results revealed that the n-hexadecane, nonadecane, fluorene, phenanthrene, and pyrene biodegradation efficiencies were 80%, 98%, 96%, 50%, and 41% respectively.

2.3.2 Biotreatment of low-density polyethylene using Pseudomonas aeruginosa

For several years, people have been aware of the manufacturing of plastic packaging and its impact on society. Plastic bags, water and milk bottles, food packaging, and toys are all produced from them. In natural conditions, the degradation of LDPE takes time and is affected by a combination of variables such as environmental (temperature, air humidity, moisture content, pH, and solar radiation), polymer characteristics, and the physiological and biochemical nature of microorganisms [155]. As a result, the removal of these dangerous substances from the environment is a pressing need. Gupta et al, [155] discussed the biotreatment of low-density polyethylene by the *Pseudomonas aeruginosa* strain. The polyethylene-degrading bacteria *Pseudomonas aeruginosa* strain was isolated and maintained on nutrient agar at 4ºC for biodegradation tests in the laboratory. PE films (0.1g) were introduced aseptically to 100mL of solution Bushnell Hass broth (BHM) and Minimal Salt medium (MSM) and inoculated with 5 mL of *Pseudomonas aeruginosa* active culture for 60 days at a temperature of 37ºC. Surface modification and formation of fissures on polyethylene surfaces, as well as variations in the intensity of functional groups and an increase in the carbonyl index, were used to confirm microbial degradation using field emission scanning electron microscopy (Fe-SEM) and Fourier transform infrared spectrophotometry (FTIR). These findings suggest that *Pseudomonas aeruginosa* strain ISJ14 could be a good choice for LDPE waste treatment without endangering human health or the environment.

2.3.3 Degradation of 0.02 % naphthalene

Naphthalene is a combustible, solid chemical compound made up of two fused benzene rings. Because of its bicyclic aromatic structure, naphthalene is classified as a polycyclic

aromatic hydrocarbon (PAH). Because of the interaction with these particles, naphthalene frequently passes through the soil layer and into groundwater, contaminating the water and being hazardous, mutagenic, and carcinogenic. Retmana et al, [22] studied the biodegradation of 0.02 % naphthalene using *Pseudomonas aeruginosa* bacteria. The bacteria was isolated within volcanic mud at Renokenongo Village, Sidoarjo Regency, East Java. Sjamsuridzal and Oetar's methods for bacterial culture preparation and genomic DNA separation were followed. For bacterial growth and CFU determination, Nutrient Broth [Merck], Nutrient Agar [Merck], and Cetrimide Agar [HiMedia] were utilized. The naphthalene degradation was studied using a Bushnell-Haas medium supplemented with 0.02 % naphthalene. *Pseudomonas aeruginosa* was cultured for 96 h in a shaker incubator at 60 rpm and 30 °C using 30 mL Bushnell Haas broth medium with 0.02% (w/v) naphthalene. Ethyl acetate from each flask was added to the separating funnel in a ratio of 50% (v/v). After 15 minutes of shaking the funnel to separate the organic and non-organic layers, 1 ml of the organic layer was collected into the 2 mL vial container. High-Performance Liquid Chromatography (HPLC) was used to test the extract. The results reveal that the total cell number increased from 3.96 x 10^9 CFU/mL to 3.08 x 10^{10} CFU/mL after 96 hours of incubation, while naphthalene biodegradation reached 70.87%.

2.3.4 Degradation of dyes

Dye pollution poses the greatest challenge to the aquatic ecosystem because it alters light penetration into deep water and interferes with photosynthesis in addition to being hazardous. There are several classes of these pollutants that have been produced, and new items are still being produced frequently [156]. There are several methods utilized for water reclamation, however, due to their harmony with nature, biological approaches are

preferred [157]. The biotreatment of brown 706 dye by the *Pseudomonas aeruginosa* bacterial strain which showed a high decolorization activity; was studied by Khan et al, [157]. After three days of measurements, pH 7, 20 ppm concentration, 37 °C temperature, 0.5 g of added glucose, and 0.1 g of NaCl salt content, were found to be the ideal conditions for evaluating the impact of physicochemical parameters on the efficiency of biodegradation process. The chosen dye was degraded by 73.91% after all these ideal conditions were combined in a single experiment. GC-MS and FTIR spectroscopy were used to extract and analyze the metabolites produced in the previous experiment. The metabolites were then separated using a silica gel column, and only P-Xylene was validated using GC-MS and NMR analysis out of the spectroscopic data collected. Azole reductase has broken down the color, and as a result, deamination and methylation have produced xylene [157]. The textile industry uses a lot of water and generates a lot of wastewater. Shah et al, [156] studied the bio remedial application of *Pseudomonas aeruginosa* in wastewater treatment. By enriching cultures with the azo dye, bacteria isolated from industrial effluent were tested for their capability to degrade the dye. The most effective isolates for the degradation of azo dye were those that could grow on liquid media with a higher concentration of dye (100 %). The majority of the bacterial isolates screened for this investigation were white and appeared bluish in hue when exposed to direct light. They also tested positive for the catalase test but negative for gram staining. Catalase is produced by most aerobic organisms. These isolates were classified as gram-negative and aerobic based on their physical and biochemical characteristics which were found to be *Pseudomonas aeruginosa* traits. The microbial populations in wastewater were screened by DNA-based approaches to detect this bioremediation organism in contaminated sites from various climatic zones and various types of wastewater. To use species-specific primers in PCR amplification, genomic DNA was first extracted. The

initial procedures for extracting DNA from bacterial culture produced a good yield of DNA that could be used in PCR amplification. Direct lysis for DNA extraction was found to be far more effective at obtaining significant amounts of DNA from ambient samples than DNA extraction without optimization. With primers designed specifically for Pseudomonas aeruginosa, all extraction products acquired using various procedures could be amplified. The lambda ladder's region between 564 bp and 125 bp showed an amplified band, indicating the existence of the anticipated PCR product. The reliability of the PCR reaction was explained by the lack of a band in the negative control [156].

2.3.5 Bioremediation of Chlorpyrifos

EPA defines chlorpyrifos as an organophosphate insecticide that is mainly used to control foliage and soil-borne insect pests. The accumulation of these compounds results in concerns regarding environmental impact and public health. Fulekar et al, [158] studied the bioremediation of chlorpyrifos by *pseudomonas aeruginosa* using a scale-up technique. The isolated microorganism was adapted by being exposed to various chlorpyrifos concentrations, including 10, 20, 50, 75, and 100 mg/l in an incubator shaker at 37 °C and 150 rpm. According to GC-MS analysis of the chlorpyrifos biodegradation, chlorpyrifos at 10, 25, and 50 mg/l were completely degraded over periods of 1, 5, and 7 days, respectively. Moreover, Kharabsheh et al. [159] investigated how *Pseudomonas aeruginosa* degraded CPF in freshwater environments to reduce toxicants. Based on HPLC analysis, the results showed that after 5 days *Pseudomonas aeruginosa* entirely decomposed CPF to its primary metabolites, CPF oxon and 3,5,6-trichloro-2-pyridinol (TCP). The efficiency of *Pseudomonas aeruginosa* in bioremediation of chlorpyrifos toxicity was described by Hussain Al-Janabi and Hashim [160]. In Iraq-Al Diwaniyah, where chlorpyrifos pesticide is widely used, the soil samples used for the isolation of

pesticide-degrading bacteria were gathered from agricultural areas, residential buildings, and garden yards. HPLC was used to determine the removal% of chlorpyrifos achieved by bacteria. The HPLC analysis results demonstrated that *Pseudomonas aeruginosa* is very effective at degrading chlorpyrifos and 99% removal was achieved. A summary of various studies of *Pseudomonas aeruginosa* application for biotreatment of different pollutants in wastewater is shown in Table 9.

Table 9: A summary of various studies of *Pseudomonas aeruginosa* application for biotreatment of different pollutants in wastewater.

Compound	Extraction source	Analysis used	Efficiency	Ref
Petroleum Compounds	Soil samples from petrol bunks and automobiles around Madurai	HPLC	-	[24]
Brown 706 dye	-	GC-MS and NMR	73.91%	[157]
Low-density polyethylene (LDPE)	Waste dump sites	Weight loss of PE film, Fe-SEM, and FTIR	BHM (8.70%) as compared to MSM (6.5%)	[155]
0.02% naphthalene	Isolated from volcanic mud in Renokenongo Village, Sidoarjo Regency, East Java	High-Performance Liquid Chromatography (HPLC)	70.87%	[22]
N-hexane	Oil-polluted soils	Gas chromatograph	Up to 46.6%	[25]
Chlorpyrifos	The National Collection of Industrial Microorganisms (NCIM), Pune, India.	GC-MS	100%	[158]
Chlorpyrifos	Carolina Biological Supply Company (Burlington, NC)	HPLC	100%	[156]
Chlorpyrifos	Agricultural fields, residential buildings, and Garden yards from the Iraq-Al Diwaniyah	HPLC	99%	[160]

Table 9: A summary of various studies of *Pseudomonas aeruginosa* application for biotreatment of different pollutants in wastewater.

Compound	Extraction source	Analysis used	Efficiency	Ref
Oily sludge	Crude oil polluted soil sample of Ankleshwar asset	GC and ASTM D7169	92.97 ± 0.92 %	[161]
PAH	Coking wastewater	HPLC	(HWM) PAHs (reduction from 9141.02 to 5117.16 µg/L	[162]
Hydrocarbons	Contaminated seawater is taken from the fishing harbour of Sfax, Tunisia	GC–MS	24 %, 84 %, and 99 % of naphthalene after 3, 5, and 7 days of culture	[163]
N-hexadecane, nonadecane, fluorene, phenanthrene, and pyrene	Isolated from alkaline cutting oil	GC-MS	80%, 98%, 96%, 50% and 41% respectively	[153]

2.3.6 Heavy metals bioremediation

The direct source of heavy metals pollution is caused by effluent discharges from industries, refineries, and waste treatment facilities. Indirect heavy metal pollution is caused by contaminants that enter water supplies through soil, groundwater systems, and rains from the atmosphere. Cadmium (Cd) is one of the heavy metals that are well known for being a pervasive environmental contaminant and a strong toxin that could be harmful to human health. To effectively remove or detoxify heavy metals, mostly from the soil, water, and sediments, microbial remediation has been used. At least six different manifestations of microbial Cd resistance were found. These include alternation of the

cell wall plasma membrane complex, altered accumulation of the toxic material, and deposition of the toxic metal in the cell wall. Through gene amplification, active Cd efflux increased transcription of metallothionein genes, and divalent cation absorption systems like Mn2+ or Zn2+, Cd can enter bacterial cells [164], [165]. Sinha and Mukherjee et al, [166] reported high Cd bioremediation under in vitro aerobic conditions using *Pseudomonas aeruginosa* strains. The same medium containing 3 mM of Cd was infected with TMMG's 12-hour-grown cell suspension (4 log CFU.ml-1), which was then incubated at 37° in a shaking incubator. At 24, 36, 48, 72, and 96 hours of incubation, cells were collected by centrifugation (11000 x g for 10 minutes at 4 °C.The results revealed that during the active growth phase, the isolate showed a substantial ability to remove more than 75% and 89% of the soluble cadmium from the growth medium and Cd-added industrial effluent, respectively. Energy dispersive X-ray spectroscopy (EDXS) and transmission electron microscopy (TEM) reveal that Cd has been present in the cells since the mid-stationary phase. Imron et al, [167] studied the removal of Hg by *Pseudomonas aeruginosa* strain FZ-2 at different salinity levels in a batch biosorption system. Hg is considered one of the most hazardous heavy metals that have raised concerns across the globe after being discovered in groundwater near landfills at concentrations range of 0.36-3.01 g/L [168]. The Hg removal experiment was carried out in 250 mL conical flasks with 100 mL of a 5 mg/l Hg solution and NB at various salinities. Using an inductively coupled plasma optical emission spectrometry (ICP-OES), the results revealed that up to 99.7% of Hg was removed by *Pseudomonas aeruginosa* [167]. Additionally, L. Neneng and Y. Gunawan [169] reported that *Pseudomonas aeruginosa* KHY2 and Klebsiella pneumonia KHY3 isolated from gold mine effluent had the ability to remove up to 60% of 1000 mg/l of Hg. The potential of *Pseudomonas aeruginosa* in aluminium removal and recovery from wastewater was reported by Purwanti et al, [170].

The removal of aluminum at initial concentrations of 50 and 100 mg/l was evaluated. The results revealed that the isolated *Pseudomonas aeruginosa* removed up to 46.08-1.95% of wastewater at an initial concentration of 50 mg/l of aluminum. Table 10 summarizes several studies on the biological treatment of several heavy metals in wastewater using *Pseudomonas aeruginosa*.

Table 10: A summary of various studies of *Pseudomonas aeruginosa* application for biotreatment of heavy metals

Compound	Extraction source	Analysis used	Efficiency	Ref
Cadmium	Industrial wastewater	Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDXS)	More than 75% and 89%	[166], [171]
Sludge contains heavy metals like lead and copper	Industrial sludge nearby areas of textile industries	Colorimeter	Lead 20%, and copper 30%	[172]
Na, Ca, Mg, Cu, K, Ni, Zn	Makera-Kakuri Industrial Drain in Kaduna, Nigeria	-	-	[173]
Hg, Cd, Pb, Mg, Zn, Fe, Mn, and Cu	Leachate	Inductively coupled plasma optical emission spectrometry (ICP-OES).	Hg 99.7%	[167]
Hg2+	The water around a gold mining area	Atomic Absorption Spectrophotometer (AAS) Type Shimadzu AA-6200.	60%	[169]
Hg2+	Marine sediment	Cold Vapour Atomic Absorption Spectrophotometer (CVAAS)	64%	[174]
Aluminum	The aluminum contaminated site at Jombang, Jawa Timur, Indonesia	ICP-OES	46.08±1.95%	[170]

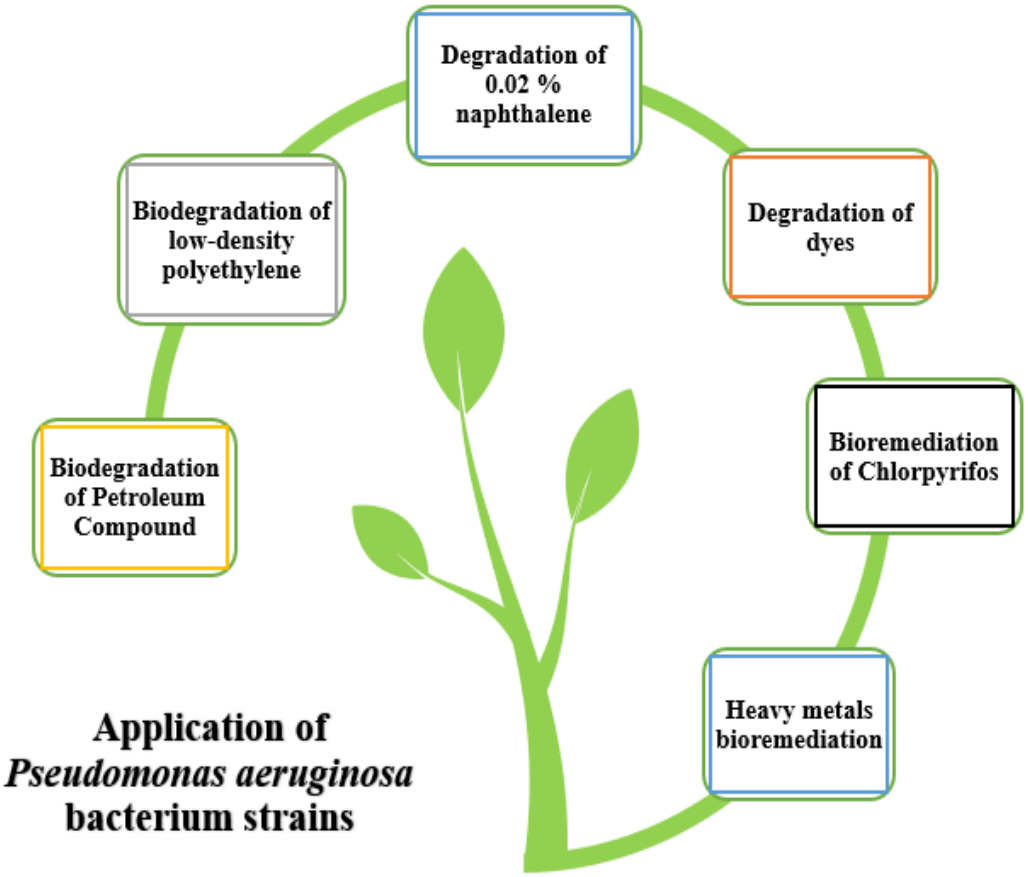


Figure 11: Application of *Pseudomonas aeruginosa* in the biotreatment of several compounds.

2.4 Free and immobilized bacteria

Traditionally, 'free' bacterial cells are used for bioremediation of various types of contaminants including pesticides. However, recently, the use of 'immobilized' bacteria has increased and gained attention as a promising technology due to several advantages including the improvement of the viability, stability, and catalytic ability of bacteria [175]. Furthermore, 'immobilized' bacteria provide high biomass, cell reuse, high tolerance to toxic compounds, high mechanical strength, and eliminate cell washout problems [176]. Immobilization refers to the technique of confining/anchoring the

enzymes or cells in or on inner support.

2.4.1 Application of biomass immobilization

The selection of proper immobilization methods for microbial cells is very critical to adapt to the various changes in the external environment. There are different types of carrier materials that can be used for biomass immobilization such as activated carbon, gel, polymers, fibers…etc. The following subsections describe the various immobilization methods, the common materials used, and the comparison among these methods.

2.4.2 Materials and techniques

The immobilization of microbial cells techniques has been continuously developed and optimized. The phenomenon in which microbial cells are attached to an inert solid material is called immobilization. The selection of the carrier is a very critical issue when dealing with immobilization technology. There are several ways in which bacterial immobilization can be done. These include adsorption, ionic bonding, covalent binding, cross-linking, and entrapment methods. The most common techniques are adsorption, ionic bonding, covalent binding, cross-linking, and entrapment in Figure 12.

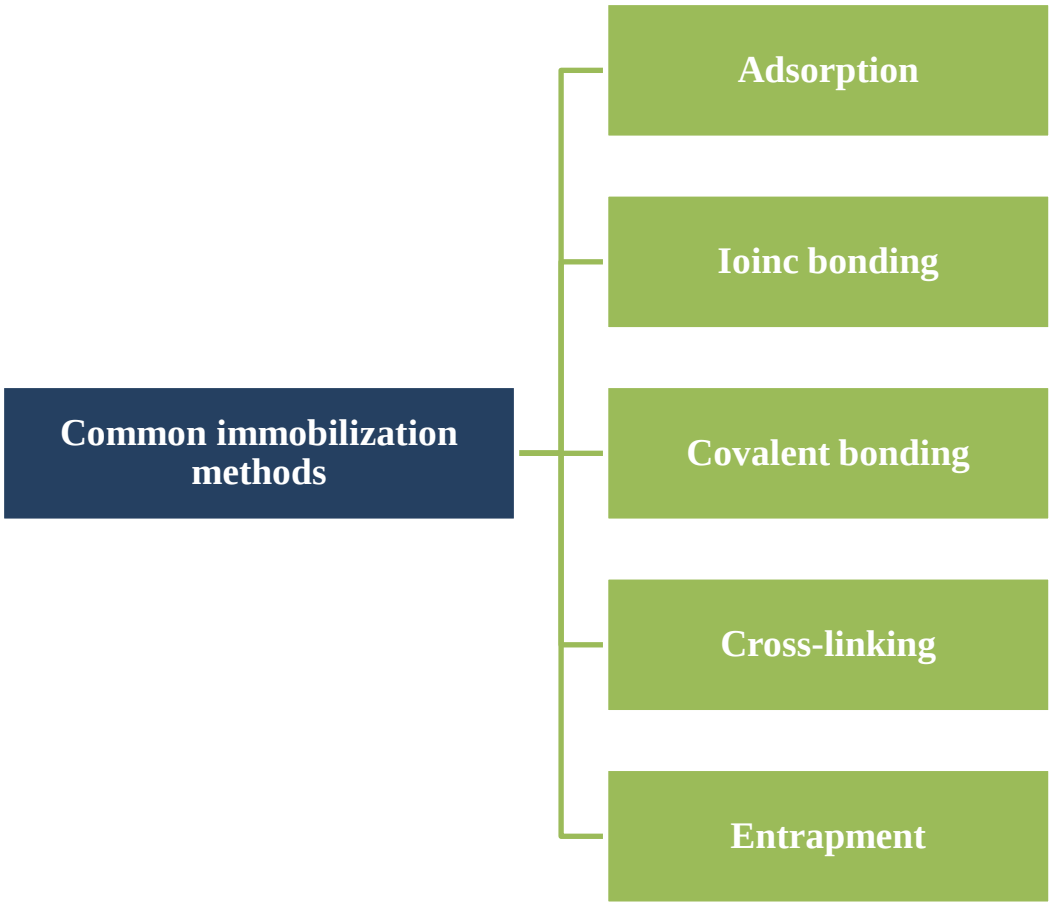


Figure 12: Common immobilization techniques.

2.4.2.1 Adsorption

Physical adsorption is the simplest well-known technique that is usually used for immobilization. The bacteria and the carrier surface, such as activated carbon, silica, calcium phosphate, starch, and clay, interact via weak binding forces. These forces are mainly hydrogen bonds, multiple salt linkages, and Van der Waal's forces. Because of this weak attractiveness, bacterial activity is not affected, however, changing pH, temperature, and ionic strength can affect bacterial binding. The adsorption technique has many advantages including simplicity, low cost, and no conformational changes or destruction of the active center of the bacteria will occur. On the other hand, the drawback

of this method is that a leakage of the adsorbed cells from the carrier during the use may ensue due to the weak binding force between the cells and the carrier as previously mentioned thus, this technique of immobilization has limited applications. One of the common applications of the adsorption technique is vinegar production (adsorption of Acetobacter sp. onto wood chips). Jesionowski et al. [177] reviewed enzyme immobilization by adsorption.

2.4.2.2 Ionic bonding

This method is a simple reversible mode of immobilization where the cells and the support have ionic interaction [178]. Ionic binding immobilization can be carried out using ionic exchange resins. These materials have positive or negative charges depending on the pH. Polysaccharides and synthetic polymers having ion-exchange centers are regularly used as support solids or carriers. Generally, the resins used are DEAE cellulose and CM cellulose. DEAE cellulose has a positive charge and can interact with cells but has a negative charge. During this process, it is necessary to maintain pH, ionic strength, and temperature, because any change in these factors can disturb the binding of enzymes [177].

2.4.2.3 Covalent bonding

Covalent bonding is a permanent method for cell immobilization. It involves covalent bond information between the functional group of the carrier and the functional group of the cell. The functional groups of the cells include amino (-NH2), carboxylic (–COOH), phenolic, hydroxyl, etc. The binding procedure of the cells to the solid carrier generally goes through two stages. The first stage is the activation of a surface using linkers like carbamides while the second stage is the covalent coupling of the biomass to the activated

support. This method is very useful due to the strong bonding, little leakage, and high uniformity; thus, the immobilized cells will not be affected by external factors such as pH and the presence of ions. However, it has the risk of cell denaturation and requires a huge amount of bioreagents to reduce the losses of cells [179].

2.4.2.4 Cross-linking

In cross-linking (also called copolymerization) method, multifunctional reagents (linkers) are connected with enzyme molecules. Unlike other methods, the cross-linking doesn't include any matrix or solid support and 3D-cross-linked aggregates are formed. The most common reagent used for crosslinking is glutaraldehyde. The cross-linking method is widely used in industrial applications and commercial applications due to its several advantages including simplicity, cost efficiency, and minimal cell leakage. On the other hand, this method has disadvantages such as cell conformation, modification, and the high risk of denaturation[180].

2.4.2.5 Entrapment

One of the most widely used methods for cell immobilization is entrapment, which is defined as the physical inclusion of cells in a narrow space. In this technique, the cells are entrapped within the lattice of a polymer matrix or membrane. The size of matrix pores is such that the cells are retained, while substrate and products are passed through [181]. The major types of entrapment are gel entrapment, microcapsule entrapment, and fiber entrapment. Gel entrapment includes natural polymer gel (e.g. agarose gel, calcium alginate, gelatin, K-carrageenan, and chitosan) and synthetic polymer gel (e.g. polyacrylamide, light-cured resin, and polyvinyl alcohol) [181]. In microcapsule entrapment, the cells are enfolded inside a microcapsule of the semipermeable polymer

membrane. However, in fiber entrapment, the bacterial cell solution is emulsified in an organic solvent of cellulose acetate. After that, it is sprayed into fibers, which are interlaced into cloth or form other shapes based on the reactor used. The entrapment technique is cost-effective as the gel can be reused many times and the recovery of the cells after the reaction is complete is easy. According to Bouabidi, El-Naas and Zhang. [179] the entrapment of cell biomass in polyvinyl alcohol (PVA) and cellulosic substance is very efficient as it provides superior biosorption characteristics.

2.4.2.6 Comparison among different bacterial immobilization methods

Comparing different bacterial immobilization methods in Table 11, it was found that adsorption is the simplest, cheapest, and most common technique. However, it has some limitations such as weak binding strength between cells and the carrier which causes the absorbed cells to leak out of the carrier. Thus, reducing the efficiency, applicability, and overall stability of the method. On the other hand, covalent bonding was adopted as an immobilization method to overcome the limitation of the adsorption technique. It provides a strong bonding between the cells and carrier, high uniformity, high stability, and a wide range of applicability. The disadvantages of covalent bonding are the risk of cell denaturation and the huge amount of chemical and bioreagents that are cytotoxic and might lead to the death of the immobilized bacteria or reduction of its metabolic activity. One of the most appropriate and efficient immobilization methods is ionic bonding. The ionic bonding method is characterized by its simplicity and inexpensive cost. However, it is very sensitive to pH, ionic strength, and temperature change which might lead to disturbing the binding of cells. Cross-linking is a simple and cost-effective technique with minimal cell leakage. However, cell conformation and modification, and the risk of denaturation are involved in this process. The last immobilization method is entrapment,

and its advantages include cost-efficiency, gel reusability, complete and easy recovery of the cells after the reaction, and fast immobilization rate. Conversely, this method has potential leakage, pore diffusion limitation, and a high probability of biomass contamination.

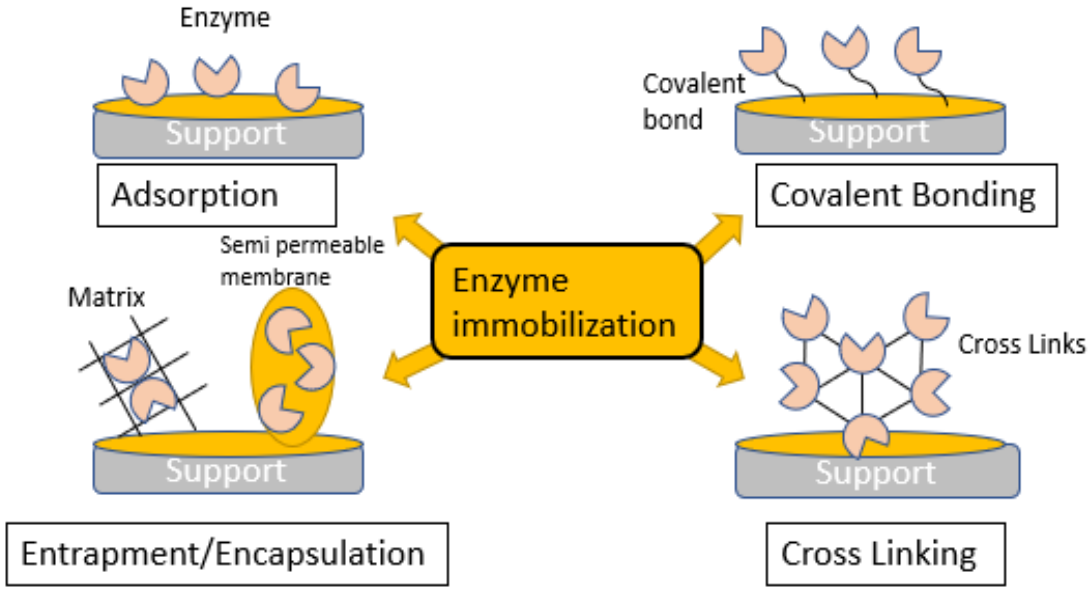


Figure 13: Enzyme immobilzation methods.

Table 11: A summary table of advantages and disadvantages of different immobilization methods.

Immobilization method	Advantages	Disadvantages	Ref
Adsorption	• Simplicity • low cost • No conformational change or destruction of the active center of the bacteria • No pore diffusion limitation	• Adsorbed cells may leak from the carrier • Limited applications • Less efficiency	[182]
Ionic bonding	• Simplicity • low cost	• pH, ionic strength, and temperature need to be maintained because any change in these factors can disturb the binding of enzymes	[183]
Covalent bonding	• Strong bonding • No leakage or desorption problem • High uniformity • Wide applicability	• The risk of cell denaturation • Requires a huge amount of bioreagents	[184]
Cross-linking	• Simplicity • Cost efficiency • Minimal cells leakage	• Cell conformation • Cell modification • High risk of denaturation	[184], [185]
Entrapment	• Cost-effective • The gel can be reused many times • The recovery of the cells after the reaction is complete and easy • Fast immobilization • Mild conditions are required	• Potential leakage • Pore diffusion limitation • High probability of biomass contamination	[182]

Recent studies for pesticide degradation using immobilized cells, and various types of reactors, and the main results of these studies are shown in Table 12.

Table 12: The recent studies for pesticide degradation using immobilized cells and various types of reactors.

Pesticide	Microorganism	Carrier	Research results	Ref
Chlorpyrifos	*Pseudomonas kilonensis, Serra-tia marcescens, Bacillus pumilus, Achromobacterxylosoxidans, and Klebsiellasp.*	Calcium alginate microspheres	• Complete biotreatment of Chlorpyrifos (100–600 mg L−1) was reached using calcium alginate microspheres • The degradation was achieved within 18 h	[186]
Methyl parathion	*Burkholderia sp.*	Powdered zeolite and Opuntia sp. and Agave sp. fibers	• The immobilized cells increased the degradation and hydrolysis of Methyl parathion when compared to free cell culture	[187]
Tebuconazole	*Alcaligenes faecalisWZ-2*	Biochar	• Biochar-immobilized WZ-2 enhanced the degradation of tebuconazole; however, it reduced the half-life of tebuconazole from 40.8 to 18.7 days.	[188]
Atrazine, propazine, simazine, simetryn, terbuthylazine, terbumeton., prometryn, Prometon, atraton, and ametryn	*Leucobacter sp. JW-1*	Polyvinyl alcohol-sodium alginate (PVA-SA)	• Immobilization time of 24–36 h. • The degradation achieved was 99.9%, 98.9%, 31.6%, 97.8%, 77.9%, 98.9%, 95.2%, 99.9%, and 100.0% of atrazine, atraton, terbumeton, propazine, simazine, terbuthylazine, prometon, ametryn, and simetryn respectively.	[189]

Pesticide	Microorganism	Carrier	Research results	Ref
Atrazine, propazine, simazine, simetryn, terbuthylazine, terbumeton., prometryn, Prometon, atraton, and ametryn	*Leucobacter sp. JW-1*	Polyvinyl alcohol-sodium alginate (PVA-SA)	• Immobilization time of 24–36 h. • The degradation achieved was 99.9%, 98.9%, 31.6%, 97.8%, 77.9%, 98.9%, 95.2%, 99.9%, and 100.0% of atrazine, atraton, terbumeton, propazine, simazine, terbuthylazine, prometon, ametryn, and simetryn respectively.	[189]
Oxon, coumaphos, and chlorpyrifos	*phingomonassp. andBrevundimonassp.*	Ca-alginate beads	• The removal of 75.4% of chlorpyrifos was achieved • The degradation was achieved after 21 days by immobilized cells in a batch system • Complete degradation of OP was achieved within 17 h	[190]
S-triazine	*Pseudomonas stutzeriY2*	4% polyvinyl alcohol (PVA), 1–3%sodium alginate (SA), 2% activated carbon (AC), and 1–2% Y2 cells (PSC-Y2	• 100% degradation of atrazine and terbuthylazine, and 96% of propazine was achieved using *Pseudomonas stutzeriY2* at an initial concentration of 50 mg L−1 • The degradation was achieved in 4 days within 24 h.	[191]

Pesticide	Microorganism	Carrier	Research results	Ref
Metribuzin	*Rhodococcus rhodochrousAQ1, Bacillus tequilensisAQ2, Bacillus ar-yabhattaiAQ3 andBacillus safensisAQ*	Biochar	• MB3R immobilized on biochar achieved up to 96% degradation of metribuzin compared to only 29.3% for free cells.	[192]
Carbofuran	*Stenotrophomonassp., Pseudomonasfulva, Comamonas jiangduensis, andThermolithobactersp*	Agar plates, loofah sponge	• Up to 52.5% removal for carbofuran was achieved by the acclimatized microbial consortia	[193]
Chlorpyrifos O, O-diethyl-O-(3,5,6-trichloro-2-pyridinol) phosphorothioate	*Cupriavidus nantongensis*	sodium alginate (SA), diatomite (KLG), chitosan (CTS), and polyvinyl alcohol (PVA)	• 96.6% degradation of chlorpyrifos at 20 mg/l by SC-X1T was achieved. • The degradation was achieved within 24 h. • The optimum conditions for strain X1T growth were found at 37 °C and pH 7 in the LB medium.	[194]

2.5 Factors that affect the biodegradation process

The rate and efficiency of degradation processes and microbial activity are highly affected by several environmental factors such as pH, availability of inorganic nutrients, temperature, dissolved oxygen, and contaminants' degradation rate[195]. When the bacteria or their enzyme contacted the organic contaminant, some of them show chemical responses to the substrate, hence, affecting the environment. While other bacteria might keep growing towards possible substrates. This section highlights the most important factors that influence the biodegradation processes such as the following:

2.5.1 pH

One of the essential factors is the pH-value which plays an important role in the biological treatment of wastewater by measuring alkalinity or acidity range. Sudden changes in pH ($pH < 3 \; or \; pH > 9$) and extreme values of contaminated water that include bacterial cells, can affect its stability, and inhibit its growth, thus, reducing the efficiency of the biodegradation process [195]. The biotreatment of COD in GTL might occur under a wide range of pH values; however, a pH of 6.5 to 8.5 range is generally considered to be optimal for the biotreatment of COD and several organic contaminants. Still, the range between 5.0 to 9.0 is considered to be acceptable as well [196]. Jilani et al, performed a comparative assessment of growth and biodegradation potential *Pseudomonas* IES-Ps- for pesticide removal. The analysis showed that IES-Ps- can degrade Cypermethrin in a broad range of pH from 5.5 to 9.55 and optimal pH of 7.33 [197]. Eskander and Saleh et al, reported that immobilization can enhance cell stability and be able to apply protection to bacteria form the effects of extreme variation of pH [196], [198]–[201]. El-Naas and Al-Muhtaseb et al, studied the biotreatment of phenol using *Pseudomonas putida* immobilized in PVA gel. They assessed the influence of pH and temperature on the

biotreatment of phenol. The results show that the biodegradation efficiency increases with pH until reaching the optimal pH at 7 [202].

2.5.2 Availability of inorganic nutrients

Besides substrate as a carbon source, microorganisms need inorganic nutrients for their metabolic activity and growth. These nutrients contain three main elements: phosphate, nitrogen, and potassium (P, N, and K) [203]. Nutrients can easily be depleted in contaminated sites during microbial metabolism; therefore, it is important to add nutrients to stimulate the microbial population, thus, improving biodegradation efficiency. The appropriate amount of nutrients for the optimal biodegradation process has been previously assessed from the ratio C:N:P in microbial cells (range from 100:15:3 [204] and 120:10:1 [205]). However, recently several studies have obtained that the higher the C: N ratio (25:1) the more optimal biodegradation efficiency can be achieved compared to lower C: N ratios (5:1) [203].

2.5.3 Temperature

Temperature is also considered as one of the critical factors that affect the rate of biotreatment of organic contaminants via controlling the reaction rates of catalyzed enzymes [195]. Purnomo et al., mentioned that the higher the temperature, the higher enzyme activity which results in greater rates of degradation of organic pollutants. At a certain temperature, the microbes are working at the fastest possible rate, which is called the optimum temperature where the activity of microbes starts reducing to 0 after this point. The biodegradation temperature range varies from one type of microbial cell to another. However, most of the studies performed their experiments in a temperature range of 20ºC to 40ºC [124], [201], [206]–[209]. Jilani et al. [197] discussed the direct

correlation between temperature and microbial activity in the degradation of Cypermethrin pesticide. A significant removal was observed in a temperature range between 28 and 30°C, while a moderate removal was obtained at 38°C. Gao et al. [210] explored the use of an integrated anaerobic fluidized bed bioreactor for the treatment of domestic wastewater (IAFMBR). The study investigated the impact of temperature and industrial effluent strength on COD reduction and found that a 35 °C operation temperature resulted in the maximum removal of COD. Mazlan et al. [208] studied the effects of temperature and pH on immobilized Laccase activity. The results obtained showed that the immobilized laccase enhanced the stability of the optimum temperature compared to free laccase. Moreover, it provides a broader range of profile temperature (30°C and 65°C) than free laccase(40°C and 50°)[208]. Additionally, according to Efremenko et al, immobilization can enhance the storage of the cells at a temperature of -18°C for a long time (1.5 to 2 years). For example, *Escherichia coli* cells were entrapped in PVA cryogel and its activity was still can be observed after almost 1.5 years [198].

2.5.4 Dissolved oxygen

It is well known that the biotreatment of organic contaminants including degradable organics proceeds under both aerobic and anaerobic conditions. However, most of the studies have tended to focus on aerobic metabolism because studying under aerobic conditions is much easier compared with anaerobic ones [203]. This factor stands for the needed amount of oxygen by aerobic biological organisms to break down organic matter. Using A/O reactors for the actual petrochemical wastewater treatment, the effects of dissolved oxygen (DO) on the biotreatment of organic contaminants were examined, by Ding et al., [211]. The results showed that by increasing the DO from 3 mg/l to 6 mg/l, the average COD reduction efficiencies were increased from 67.0% to 68.8%,

respectively. Frederick et al., [203] reported that the supplies of oxygen uptake are significant and it often needs 3 to 4 of DO to oxidize 1 ml of hydrocarbons to CO2. Jilani et al. [197] experimented Cypermethrin degradation with an initial DO range between 1.5 and 2.6 mg/l. However, the DO wasn't sufficient and it was observed that the efficiency of biodegradation using IES-*Ps*-1 is significantly enhanced at DO of 8 to 9 mg/l [197].

2.5.5 Contaminants degradation rate

The degradation rates depend on two factors, the first factor is the concentration of contaminant, while the other is the amount of enzyme present. The initial concentration of contaminants plays a significant role in the biodegradation process. This is because most organic compounds have an inhibitory effect on the activity of microbial cells [202]. Regarding pesticides, most of the studies focus on relatively high concentrations, generally, the maximum allowed application amount in mind, which varies from 0.5 mg to 50 mg kg^{-1} [212]. Khalid et al. [186] studied the biotreatment of Chlorpyrifos with a concentration that ranges from 100 to 600 mg L^{-1} using calcium alginate microspheres, where complete removal of Chlorpyrifos was achieved. Several studies investigated the biotreatment of pesticides at initial concentrations varying from 10 to 600 mg L^{-1} [189]-[194]. Therefore, the optimum concentration of pesticides varies based on several factors including type, nature, toxicity, regulatory amount, application of pesticide, and the degraded bacteria used. Too high concentration reduces biodegradation efficiency; however, several studies approved that immobilization enhances tolerance toward high concentration, of the bacteria, thus, increasing degradation efficiency [213]–[215]. Table 13 summarizes the main factors affecting the biodegradation efficiency and the role of immobilization toward the change in these factors.

Table 13: A summary of the main factors affecting the biodegradation efficiency and the role of immobilization toward the change in these factors.

Factor	Acceptable ranges	The optimal range	The role of immobilization in the change in these factors	Ref
pH	5.0 to 9.0	6.5 to 8.5	• Enhance cell stability • Apply protection to bacteria from the effects of extreme variation of pH	[196], [198]–[201]
Temperature	Varies (20°C to 65°C)	Varies (30°C to 40°C)	• Enhance the stability of the optimum condition • Improve the storage of the cells for a long time	[198], [208]
Concentration of pollutants	Varies	Varies	• Enhances tolerance toward high pollutant concentration of the bacteria • Increase degradation efficiency	[212]–[215]
Nutrients C: N:P	Varies 100:10:1(0.5)	Varies	• Enhance cell stability	[203]
Dissolve oxygen	1 - 9 mg/l	6-9 mg/l	• Enhance cell stability	[197]

2.6 Potential reuse of treated water

2.6.1 GTL process water

Treated water from a gas-to-liquids plant has many applications including being used as irrigation water, cooling water, and general process water, or it can be discharged to the environment according to a local discharge standard. It is known that the purified water is characterized by a COD ranging from 20 to 600 mg/l, a pH ranging from 6 to 9, total dissolved solids (TDS) of < 600 mg/l, and suspended solids (SS) of < 250 mg/l. Based on the end use of the treated water, Table 14 shows the water quality for each application.

Table 14: Typical requirements for different water qualities[216].

Property	Purified water	Irrigation water	Boiler feed water	Process water	Drinking water	Cooling water
COD (mg/l)	20 - 600	-	0 - 10	0 - 75	-	0 - 30
pH	6 - 9	6.5 – 8.4	7 - 8	5 - 10	6 - 9	6.5 - 8
TDS (mg/l)	< 600	< 40	0 - 100	0 - 1600	0 – 450	0 – 450
SS (mg/l)	< 250	0 - 50	0 - 3	0 - 25	< 20	0 - 5

2.6.2 Treated Pesticides' containing water

As previously mentioned, pesticides are very toxic to human health and the environment., therefore, there is a need for promising and suitable disposal/treatment methods to reduce the scale of their risks. Al Hattab et al, [217] reported four disposal methods for pesticides contaminated wastewater including land cultivation, landfilling, usage of evaporation beds, and dumping in soil, concrete, and plastics pits, or on land, and in rare instances, in streams close to the rinse operation as shown in Table 15. However, these disposal techniques are unsafe because surface runoff can contaminate nearby streams, rivers, and lakes, and wastewater infiltration into the soil can lead to the contamination of groundwater.

Table 15: Discharge methods of pesticides contaminated wastewater [217].

Disposal method	Description
Disposal pits	Put the liquid waste into the pits that contain soil and are open to the air for subsequent weathering
Evaporation ponds	Put liquid wastes in lined ponds that are exposed to the air for future weathering.
land cultivation	To put liquid wastes in the soil's plow zone for future weathering.
landfill	Burying wastes in the ground

Activated sludge is one biological treatment method that does not need a lot of lands, has a lower capital cost than AOPs, and is more environmentally safe compared to chlorination. However, it needs a location to dispose of the sludge and qualified personnel to operate and maintain it. Furthermore, although having a small footprint and being successful at removing pesticides, membrane bioreactors have several drawbacks, including membrane fouling and roughness.

Chapter 3: Materials and Analytical Methods

3.1 Chemicals and materials

Most of the chemicals including NaOH pellets for pH adjustment and mineral salts, including MgSO4·7H2O, K2HPO4, CaCl2·2H2O, (NH4)2CO3, FeSO4·7H2O, ZnSO4·7H2O MnCl2·4H2O, CuSO4·5H2O, CoCl2·6H2O, Na2MoO4·2H2O, were obtained from Sigma Aldrich, US. However, PVA powder was obtained from BDH, UK.

3.2 Wastewater samples

3.2.1 GLT process water samples

The water samples were obtained from a local GTL plant in Qatar and pretreated using air stripping to remove volatile organic pollutants. GTL PW is characterized by high acidity and COD content. Table 16 shows the physical and chemical properties of the original and pretreated GTL process.

Table 16: Physical and chemical characteristics of GTL.

Characteristic	GTL process water	Pretreated GTL process water
COD (mg/l)	5000–7000	2000 to 4000
TOC (mg/l)	1500–1700	700–1400
pH	2.9	3.3

3.2.2 Propamocarb HCL fungicides contaminated water

The propamocarb HCL fungicide was obtained from Agri Sciences Ltd, Turkiye. Each liter of the fungicide contains 72.2% Solution propamocarb hydrochloride. In the experimental work, the concentrated fungicide was diluted in deionized water to reach a

COD concentration range of 500 to 1000 mg/l. Table 17 shows the physical and chemical characteristics of the fungicide (propamocarb hydrochloride) contaminated water.

Table 17: Physical and chemical characteristics of propamocarb HCl fungicide contaminated water.

Characteristic	Propamocarb HCl contaminated water
COD (mg/l)	500–1000
TOC (mg/l)	300–600
pH	6.8

3.3 Isolation and Immobilization of Bacterial Culture

Pseudomonas aeruginosa was isolated with other Hydrocarbon-Degrading Bacteria from different highly contaminated soils in Qatar. According to Al Disi et al, [218], at a tillage depth of 1-2 cm, random sampling was taken with a sterile spatula from various spots. The soil samples were collected and placed in clean glass bottles, which were then securely sealed, labeled, and twisted with foil to prevent contamination and prevent any further light reactions. The technique for enrichment, isolation, identification, and studying the activation of Hydrocarbon-Degrading bacteria was described thoroughly by Al Disi et al, [218]. The isolated Pseudomonas aeruginosa bacterial cells were collected in a glass jar and kept refrigerated until they were immobilized in PVA gel. At roughly 70–80 ºC, a homogenous PVA solution was made by mixing 100 g of PVA powder with 850 ml of distilled water and 50 ml of suspension, to prepared PVA with 10wt%. The solution was then mixed using glass rod to esure its homogenonity. PVA solution was

poured in ice molds and the cross linked using freezing-thwaing cycles, by freezing at -20˚ C for 20h and thawing at +20˚C for 4 h. The F-T process was repeated for four times. This prepared PVA gel is known to produce a high-porosity polymer matrix with good mechanical strength and stability [12] [23].

3.4 Biomass Acclimatization

The immobilized bacteria were slowly acclimatized to GTL PW by placing them in batch SBBR with GTL PW and meniral nutrient solution. The accilimatization process was performed by gradual increase in the GTL PW COD in the range from 500- 2000 mg/l over a period of two weeks. After this step, the bacteria were fully acclimatized to GTL-PW and were ready for the biodegradation process. [220]. Table 18 shows the composition of mineral salts added to the GTL PW solution.

Table 18: Composition of mineral salt medium [221].

Component	Concentration (mg/l)
$MgSO_4 \cdot 7H_2O$	300
K_2HPO_4	250
$CaCl_2 \cdot 2H_2O$	150
$(NH4)_2CO_3$	120
$FeSO_4 \cdot 7H_2O$	3.5
$ZnSO_4 \cdot 7H_2O$	1.3
$MnCl_2 \cdot 4H_2O$	0.13
$CuSO_4 \cdot 5H_2O$	0.018
$CoCl_2 \cdot 6H_2O$	0.015
$Na_2MoO_4 \cdot 2H_2O$	0.013
Total	824.98

3.5 Spouted Bed Bioreactor System (SBBS)

The SBBR utilized in this experiment was made of Plexiglas and had a total volume of 1.5 L. The SBBR is characterized by systematic intensive mixing caused by the cyclic

motion of particles within the bed, which is caused by a single air jet injected through an aperture in the reactor's bottom [220]. The temperature (at 32 ºC) of the bioreactor was controlled through the circular movement of the water in the water jacket surrounding the reactor. Air was continuously supplied into the reactor at a certain flow rate to improve mixing and also provide oxygen to maintain aerobic conditions [221], [222]. A schematic diagram of the SBBR is shown in Figure 14.

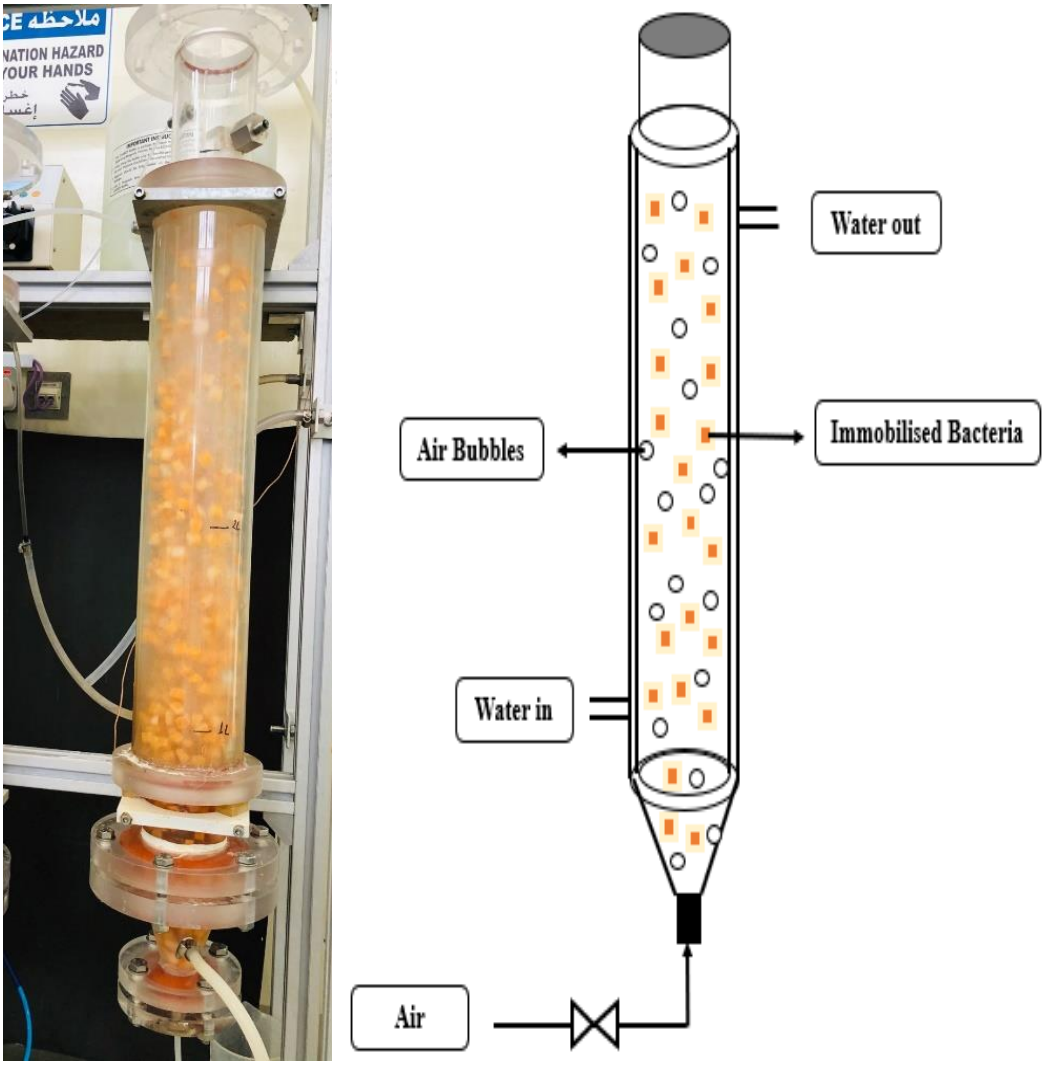


Figure 14: A photograph and a schematic diagram of the spouted bed bioreactor (SBBR).

3.6 Batch biological treatment of GTL PW

In batch experiments of GTL PW, the reactor was initially filled with the standard nutrient medium solution, as well as the biocatalyst which is the PVA gel with the immobilized bacteria, which occupied 20 to 30% of the reactor volume based on previous studies [220]. The reactor was filled with a total volume of 1.5 liters, due to the limited amount of PVA. Air was injected into the conical bottom of the bioreactor to ensure proper mixing and interaction between the substrate and the bacterial cells within the bioreactor, as well as to provide the oxygen required for biodegradation. The air flow rates, and liquid flow rates were adjusted to of 3.3 La/Lr.min and 2.4 ml min-1, respectively. The reactor temperature was held at almost 32 ºC. This temperature was found to be optimum in a past study [223], and it is in good agreement with the values mentioned in the literature [224]. The initial pH solution was kept at pH 7 using NaOH pellets. As these conditions are regarded to be the best for organic biodegradation according to El-Naas et al. [220].

3.7 Continuous biological treatment of GTL PW

The continuous experiments were performed to study the effects of air flow rates at 2, and 3.3 L_a/L_r. min, and liquid flow rates at 2.1 and 4.2 ml/min on the biotreatment of GTL PW under optimum conditions selected based on RSM. To study the response of the SBBR system to other operating factors including air and liquid flow rates, continuous experiments were carried out at constant COD of 2200 mg/l, pH of 7.29, PVA v% of 27%, and temperature of 32˚C. The stripped GTL PW mineral solution was constantly introduced to the reactor during all experimental runs utilizing a peristaltic pump at a stable liquid flow rate with an accuracy of ±1 ml/min. The samples were collected and analyzed using the COD at various periods. Tables A 4 and A 5 in the appendix, display

the continuous experiments.

3.8 Analytical Methods

A HAC-UV spectrophotometer with COD reagents was used to conduct the COD analysis as shown in Figure 15. Two mL of the water sample was added to the HAC LCK514 cuvettes and heated for 2 hours to complete the reaction between the reagent and the water sample. The COD content in mg/l was measured using the HAC DR 3900. Moreover, the characteristics and composition of the GTL process water used in this study were obtained using gas chromatography GC-MS Agilent 6890N.

Figure 15: A HAC-UV spectrophotometer and LCK514 cuvettes.

3.9 RSM modeling

The current study aimed to investigate the biotreatment of GTL process water and propamocarb HCl fungicide synthetic water by *Pseudomonas aeruginosa* bacteria, as well as the interaction between operating parameters and the optimum conditions for

maximum COD reduction efficiencies, by varying test parameters, such as initial COD concentration, immobilized bacteria volume percentage, and pH using RSM. The RSM was carried out for the biotreatment of the two types of wastewater under specific experimental conditions. The parameters were selected based on screening experiments. Using RSM, a large amount of data can be obtained with a small number of experimental operations, and there are many important advantages, such as the ability to determine not only the effects of individual parameters but also their relative importance in a given and the interactive effects of two or more variables. Tables 19 and 20 list the three variables used in this study, each of which has two levels (high and low). For propamocarb HCl fungicide, a concentration ranging from 500 to 1000 was chosen based on screening experiments.

Table 19: Variables and levels applied for the removal of COD in GTL process water.

Factor	Units	-α	Lower limit (-1)	0	Upper limit (+1)	+α
Concentration	mg/l	318.21	1000	2000	3000	3681.79
pH	-	3.98	5	6.5	8	9.02
PVA v %	-	16.59	20	25	30	33.41

Table 20: Variables and levels applied for the removal of propamocarb fungicide.

Factor	Units	-α	Lower limit (-1)	0	Upper limit (+1)	+α
Concentration	mg/l	329.55	500	750	1000	1170.45
pH	-	3.98	5	6.5	8	9.02
PVA v %	-	16.59	20	25	30	33.41

The central composite method experimental design of RSM has been chosen to find the relationship between the response functions and variables using the statistical software tool MINITAB 20. In the central composite method, a total number of 20 experiments, including center points, was augmented with a group of axial points (also called star points) to estimate curvature.

The reduction rate of COD was determined according to the following equation:

$$COD\ Reduction\ \% = \frac{C_0 - C}{C_0} \qquad 2$$

Where, C (mg/l) is the final COD concentration of the sample, and C_0 (mg/l) represents the initial COD of the water sample.

Using the optimal design factor/RSM, the coefficients were also predicted in a quadratic polynomial mathematical model to predict COD reduction efficiencies. Tables 21 and 22 list the several parameter combinations used in central composite design (CCD) by Response Surface Methodology.

Table 21: The several parameter combinations used in the design of GTL removal experiments.

RunOrder	PtType	Blocks	COD	pH	PVA Vol. %
1	0	1	2000	6.5	25
2	1	1	3000	8	20
3	1	1	1000	5	30
4	-1	1	2000	3.98	25
5	-1	1	2000	6.5	16.59
6	1	1	3000	5	20
7	1	1	3000	5	30
8	0	1	2000	6.5	25
9	-1	1	2000	9.02	25
10	-1	1	3681.79	6.5	25
11	-1	1	318.20	6.5	25
12	1	1	1000	8	20
13	0	1	2000	6.5	25
14	0	1	2000	6.5	25
15	0	1	2000	6.5	25
16	1	1	1000	8	30
17	-1	1	2000	6.5	33.40
18	1	1	1000	5	20
19	0	1	2000	6.5	25
20	1	1	3000	8	30

Table 22: The several parameter combinations used for the design of propamocarb fungicide degradation experiments.

RunOrder	PtType	Blocks	COD	pH	PVA Vol. %
1	0	1	750.00	6.50	25.00
2	0	1	750.00	6.50	25.00
3	1	1	1000.00	8.00	30.00
4	-1	1	750.00	9.02	25.00
5	-1	1	329.55	6.50	25.00
6	-1	1	750.00	3.97	25.00
7	0	1	750.00	6.50	25.00
8	1	1	500.00	8.00	30.00
9	1	1	500.00	5.00	30.00
10	1	1	1000.00	5.00	20.00
11	1	1	1000.00	8.00	20.00
12	0	1	750.00	6.50	25.00
13	1	1	1000.00	5.00	30.00
14	0	1	750.00	6.50	25.00
15	-1	1	750.00	6.50	33.41
16	-1	1	1170.45	6.50	25.00
17	1	1	500.00	8.00	20.00
18	1	1	500.00	5.00	20.00
19	-1	1	750.00	6.50	16.59

Chapter 4: Results and Discussion

4.1 Degradation of GTL PW (organic pollutants)

4.1.1 Statistical analysis

All statistical combinations of the variables were evaluated using the DOE software, which yielded the design outcomes from the experiments. *Pseudomonas aeruginosa* had high coefficients of determination R^2 of 0.8140 for biotreatment of GTL PW. RSM is used to optimize degradation conditions. The CCD method was used to investigate the effects of initial COD concentration, PVA V %, and pH on COD reduction. Table A 2 in the appendix shows the experimental findings that were used to develop an empirical model for the best response and conditions. Equation 3 shows the quadratic polynomial mathematical model to predict COD reduction efficiencies.

Regression Equation in Uncoded Units

Removal% = -304.5+0.0198 COD+37.0 pH+17.29 EB%-0.000004 COD*COD-1.654 pH*pH-0.2728 EB%*EB%-0.00077 COD*pH+0.000151 COD*EB%-0.403 pH*EB%

3

4.1.2 Effect of initial COD

The contaminant concentration is one of the most important factors that affect the biological treatment of wastewater. The increasing in the organic concentration may inhibit the biodegradation process or increase the degradation efficiency [202]. Figures 16 a and b show the effect of interaction between initial COD and other two process parameters, namely, pH, and PVA volume fraction on the removal of COD. At a constant pH of 5, a PVA v% of 20, and an initial COD of 0f 1000 mg/l, the COD reduction % was

58. However, under the same conditions, increasing the initial COD to 3000 mg/l resulted in a COD reduction% of 69.89 (around a 12% increase). Similar behavior was also noticed at a constant pH of 5, and PVA v% of 30, where an increase of initial COD from 1000 mg/l to 3000 mg/l resulted in COD reduction from 62.8% to 83.27% respectively (approximately 21% increase). This behavior reveals when the COD levels are higher, there is a greater oxygen demand. This implies that water with high COD levels likely contains more oxidizable organic material, and the microorganism can adapt to the higher organic concentration, resulted in high removal efficiency [225]. Moreover, one can observe that the biodegradation increased as COD increased from 500 to ~2600 mg/l and then decreased. It is anticipated that exposure to a high concentration of contaminants suddenly might have detrimental effects on the bacterial enzymes that are often responsible for the major stages in the biodegradation process [226]. This also implies that wastewater with high COD levels has lower dissolved oxygen (DO) values. Life forms need oxygen to survive, hence a low quantity of dissolved oxygen is dangerous. Therefore, it is advisable to increase DO concentrations by reducing COD levels in wastewater before releasing it [225]. In Figure 17, it can be noticed that there is an optimum initial concentration for COD reduction from GTL PW which was determined by the Minitab optimizer as 2595 mg/l.

4.1.3 Effect of pH

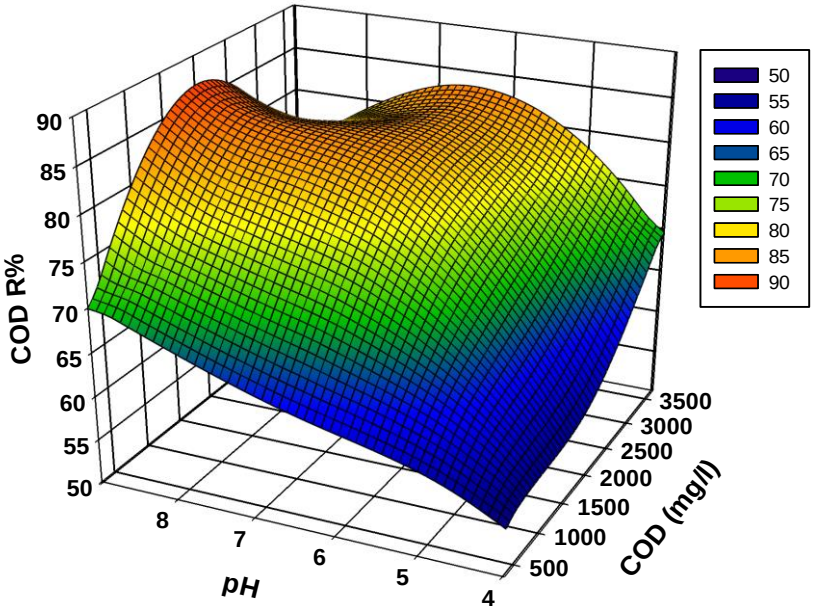
The initial pH of the solution has a big impact on microbial growth and enzyme activity, thus it's a big deal when it comes to developing biological treatment methods. Similarly, the effects of interaction relation between pH with initial COD and PVA volume fraction on COD reduction rate were determined and the results are shown in Figures 16 a, and c. At a constant initial COD of 2000 mg/l, a PVA v% of 20, and an initial pH of 3.9, the

COD reduction % was 58.15. However, under the same conditions, increasing the pH to 6.5 resulted in a COD reduction% of 86.77 (around a 29% increase). The COD reduction efficiency reduced dramatically when the initial pH in the medium was lower than 5, but only slightly when the pH was greater than 7.3, as shown in Figure 17. Because almost all biological species seem to have optimal pH conditions, pH has a physiological effect on microbial activity similar to temperature[227]. Although some species need a restricted pH range, others are more tolerant of a larger pH range. Some species thrive in high pH environments, whereas others thrive in low pH environments. Research of *Pseudomonas aeruginosa* biotreatment of GTL-produced water mixtures found that biomass activity was entirely reduced at pH 5, 9, and 10, with pH 6- 8 being the optimal[227]. Because most bacteria are neutrophils, the optimal pH for the most efficient biotreatment of organic substances is usually about 7.5 [228].

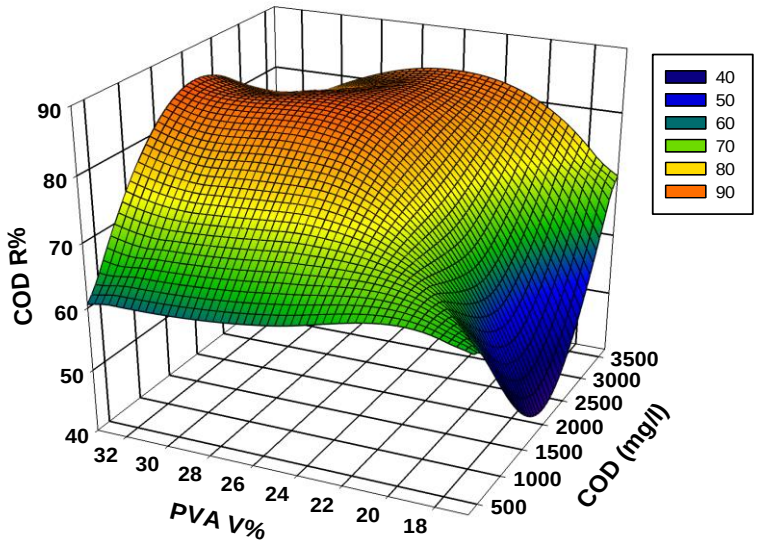
4.1.4 Effect of PVA Volume %

The rate of biodegradation of organic pollutants is significantly influenced by the volume fraction of PVA pellets, which is directly related to the quantity of active biomass cells in the bioreactor[229]. Figure 16 b and c show the effect of interactions between PVA v% with initial COD concentration, and pH respectively. The number of active biomass cells in the bioreactor is directly proportional to the volume fraction of PVA pellets, and so plays an essential role in determining the rate of COD reduction. At a constant initial COD of 2000 mg/l, pH of 6.5, and PVA v% of 16.9, the COD reduction % was 42.85. However, under the same conditions, increasing the PVA v% to 30 resulted in a COD reduction% of 86.77 (around 44% increase). Using the Minitab optimizer, the COD reduction efficiency was found to be highest at a PVA volume percentage of 27% as shown in Figure 17. The COD reduction increases as the PVA volume fraction increases.

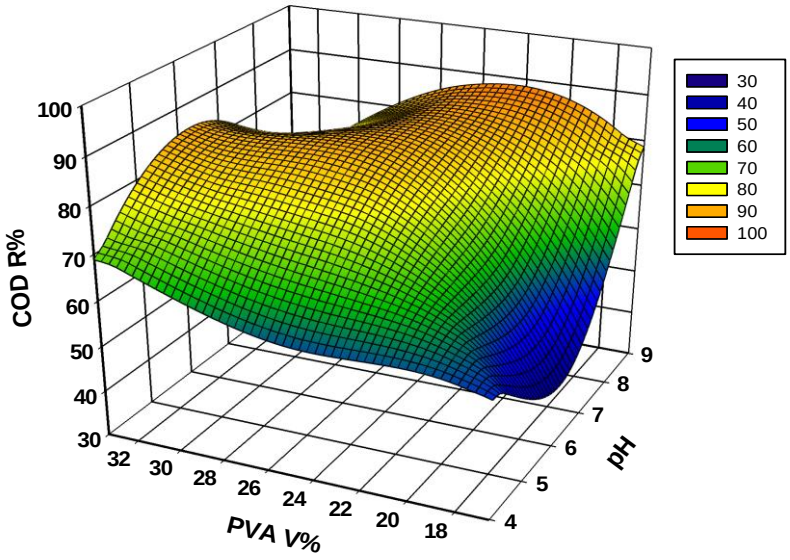
However, the removal effectiveness of PVA v% 25 and 33 % appeared to be nearly the same. This could be because 33 % have greater biomass and 25 % have better mixing. It is believed that increasing the volume fraction of PVA above 30% is likely to result in reduced mixing and, as a result, lower degradation performance[229].



a) COD reduction% vs pH and initial COD (mg/l). PVA V% is fixed at 27.



b) COD reduction% vs initial COD concentration (mg/l) and PVA volume fraction. pH is fixed at 7.3.



c) COD reduction% vs pH and PVA volume fraction. Initial COD is fixed at 2594 mg/l.

Figure 16: The interaction between experimental parameters in GTL experiment a) COD reduction% vs pH and initial COD (mg/l) b) COD reduction% vs initial COD concentration (mg/l) and PVA volume fraction c) COD reduction% vs pH and PVA volume fraction.

The optimization of the biotreatment of the GTL PW was evaluated, Figure 17 shows that the optimum conditions obtained from RSM to achieve maximum biotreatment efficiency of GTL PW which was predicted to occur at initial COD concentration of 2595 mg/l, PVA volume fraction of 27%, pH of 7.3.

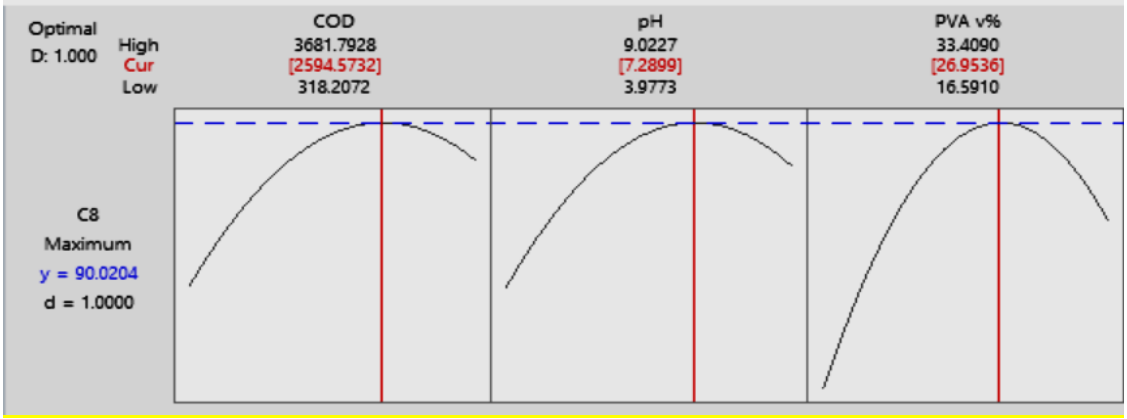


Figure 17: The optimum conditions for COD reduction % obtained using the response optimizer.

4.1.5 Model validation

The experimental response (i.e., COD Reduction %) was compared to the predicted response to validate the accuracy of RSM as shown in Figure 18. The collected experimental values, illustrated by scattered points, show a linear relationship between experimental and predicted values. . R^2 value of 0.8481 indicates a close fit between modeled and collected data. Moreover, the biodegradation experiment was carried out at optimum conditions obtained from the optimization of the COD reduction to the maximum value. Results showed that the predicted optimal COD from RSM showed has a good match with the experimental value (90% and 89%, respectively). This means that the model for the biotreatment of GTL PW was valid.

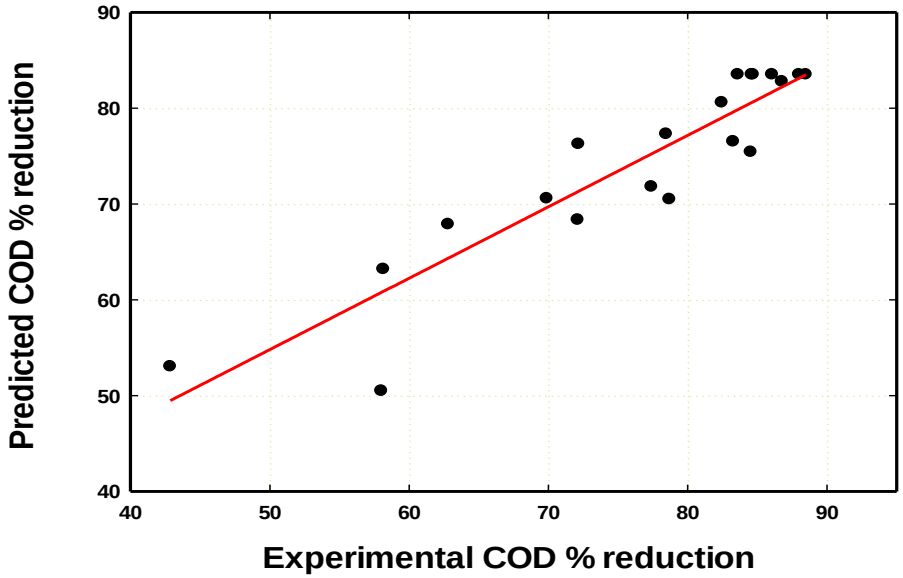


Figure 18: Predicted versus experimental COD reduction values for GTL process water.

4.2 Degradation of agricultural wastewater (propamocarb HCL fungicide)

4.2.1 Statistical analysis

Table A 3 in the appendix shows the experimental findings that were used to develop an empirical model for the best response and conditions.

4.1.1 Effect of COD

Figure 19 shows propamocarb fungicide removal% that is plotted against COD and pH while keeping PVA v% constant. Propamocarb removal% is found to be very low and a maximum removal% of ~ 42% was observed at a COD of 1000, a PVA v% of 30, and a pH of 8. The results have not been consistent and do not follow a particular trend revealing that this fungicide is relatively persistent, highly toxic, and takes a long time to degrade in the environment. These results are in agreement with previous outcomes reported by Knowles et al [149], and Myresiotis et al [150] who found little degradation of the fungicide propamocarb by all the soil microorganisms studied. This is also agreed

with a study by Kameya et al, [230] where it was stated that most compounds containing aliphatic aldehydes and amines (eg, propamocarb HCl fungicide) were hardly biodegradable.

4.1.2 Effect of pH

The effects of the initial pH of the propamocarb HCL-contaminated water and mineral nutrient solution (from 5 to 8) on the COD reduction rate were determined and the results are shown in Figure 19. At a constant initial COD of 500 mg/l, a PVA v% of 30, and initial pH of 5, the COD reduction % was 2.67. However, under the same conditions, increasing the pH to 8 resulted in a COD reduction% of 36.09 (around a 33.42% increase). When the pH drops or rises outside of the ideal pH range, their metabolic activity may decrease. A pH range of 6.5-8.5 is thought to be ideal for pesticide biodegradation in terrestrial and aquatic ecosystems, even though biodegradation can occur over a large pH range [231].

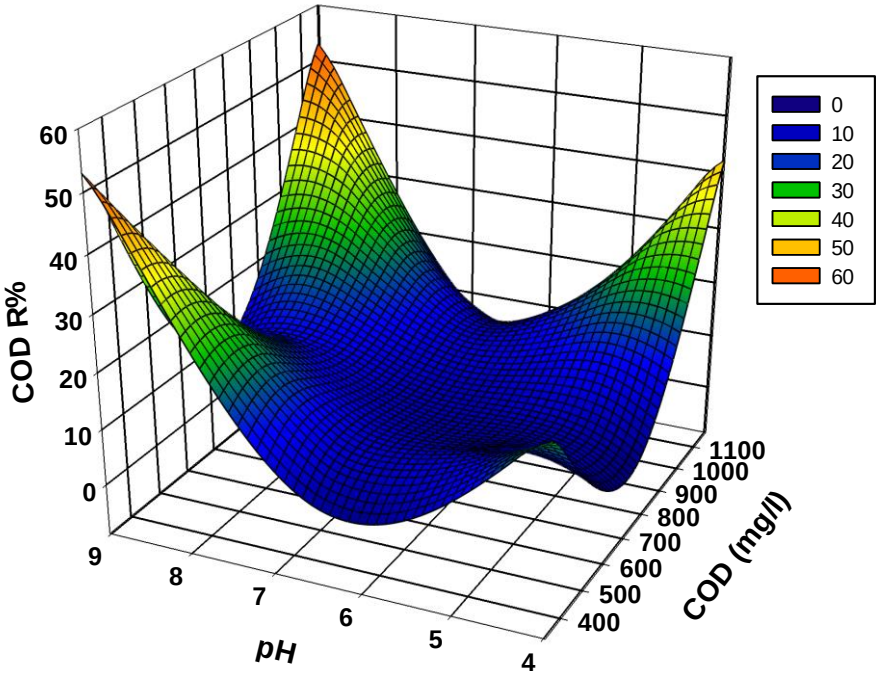
4.1.3 Effect of PVA Volume %

Figure 19 b and c show the effect of interactions between PVA v% with initial COD concentration, and pH respectively. As previously mentioned, the number of active biomass cells in the bioreactor is directly proportional to the volume fraction of PVA pellets. At a constant initial COD of 1000 mg/l, pH of 8, and PVA v% of 20, the COD reduction % was 10.67. However, under the same conditions, increasing the PVA v% to 30 resulted in a COD reduction% of 42.10 (around a 31.13% increase). The COD reduction efficiency was found to be highest at a PVA volume percentage of 30% (42.1%). In general, the COD reduction percentage increases as the PVA volume percentage increases.

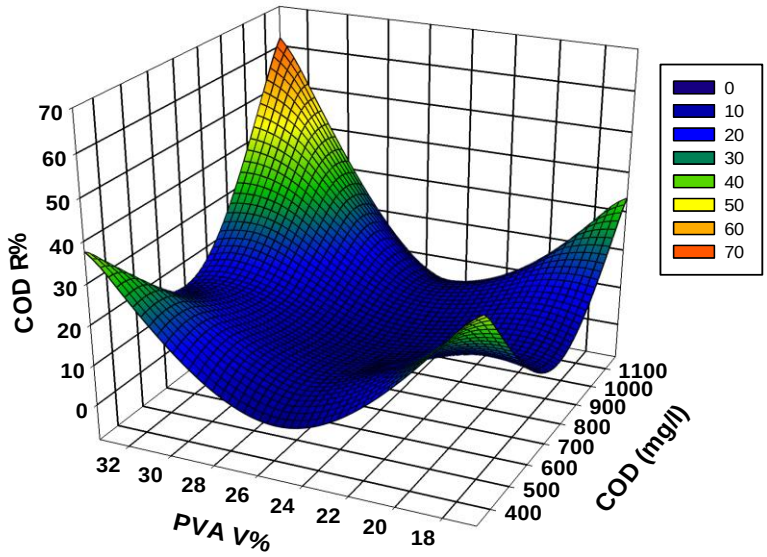
Regression Equation in Uncoded Units

Removal% = 380-0.0768 CON-38.9 pH-18.81 EB%+0.000032 CON*CON+1.11pH*

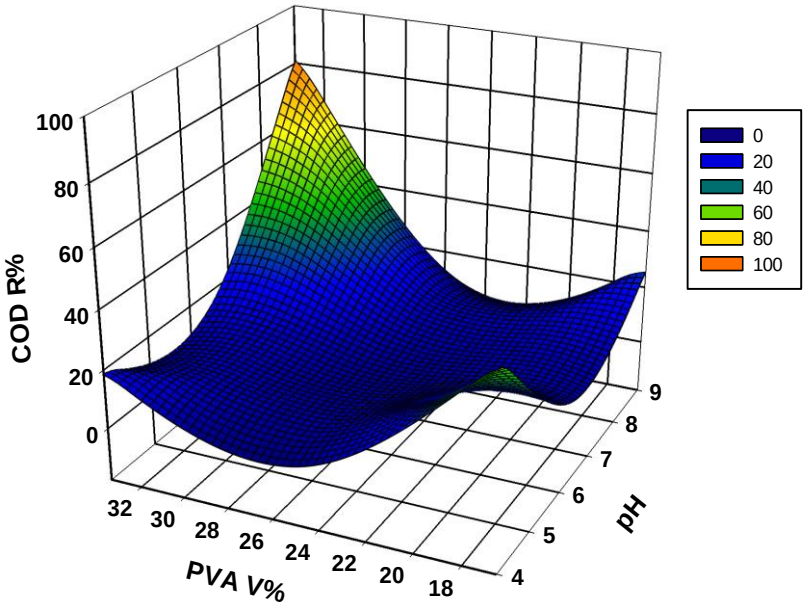
pH+0.1852 EB%*EB%-0.00529 CON*pH+0.00272 CON*EB%+1.240 pH*EB% 4



a) Propamocarb removal% vs pH and initial COD concentration (mg/l)



b) Propamocarb removal% vs initial COD concentration (mg/l) and PVA volume fraction.



c) Propamocarb removal% vs pH and PVA volume fraction.

Figure 19: The interaction between experimental parameters in propamocarb HCL experiment a) COD reduction% vs pH and initial COD (mg/l) b) COD reduction% vs initial COD concentration (mg/l) and PVA volume fraction c) COD reduction% vs pH and PVA volume fraction

The optimization of the biodegradation of the propamocarb HCl contaminated water was evaluated. Figure 20 shows that the optimum conditions obtained from RSM to achieve maximum biodegradation efficiency of the propamocarb HCl contaminated water which was predicted to occur at initial COD concentration of 1170 mg/l, PVA volume fraction of 33%, and pH of 9.

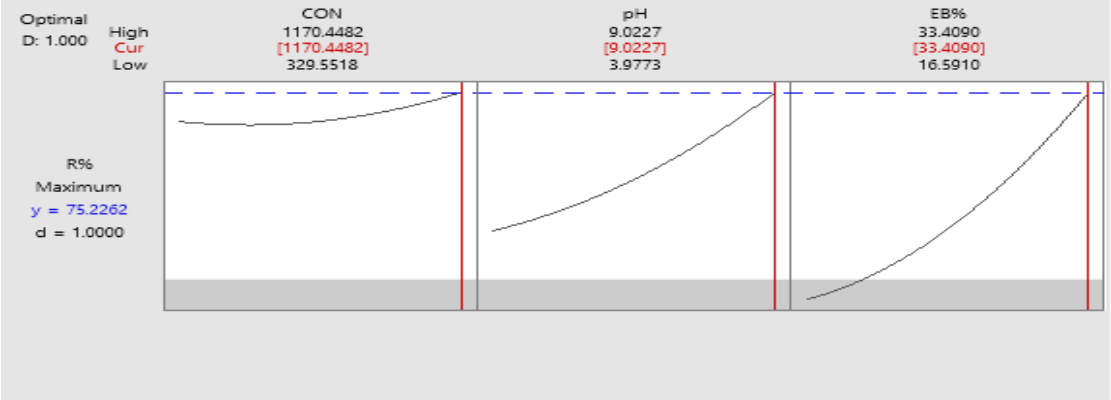


Figure 20: The optimum conditions for COD reduction % obtained using the response optimizer

4.1.4 Model validation

The experimental response (i.e., COD Reduction %) for propamocarb HCl fungicide-contaminated wastewater was compared to the predicted response to validate the obtained accuracy of RSM as shown in Figure 21 and Table A7 in the appendix. The collected experimental values do not show a good fit to the predicted values obtained from the RSM model with R^2 value of 0.7902. Moreover, the predicted optimal COD reduction obtained from RSM did not match the experimental value (75% and 12%, respectively). Which means that the model for proamocarb HCl contaminated wastewater was not valid. This could attributed to the possibility of degrading of the PVA by a certain concentration of COD.

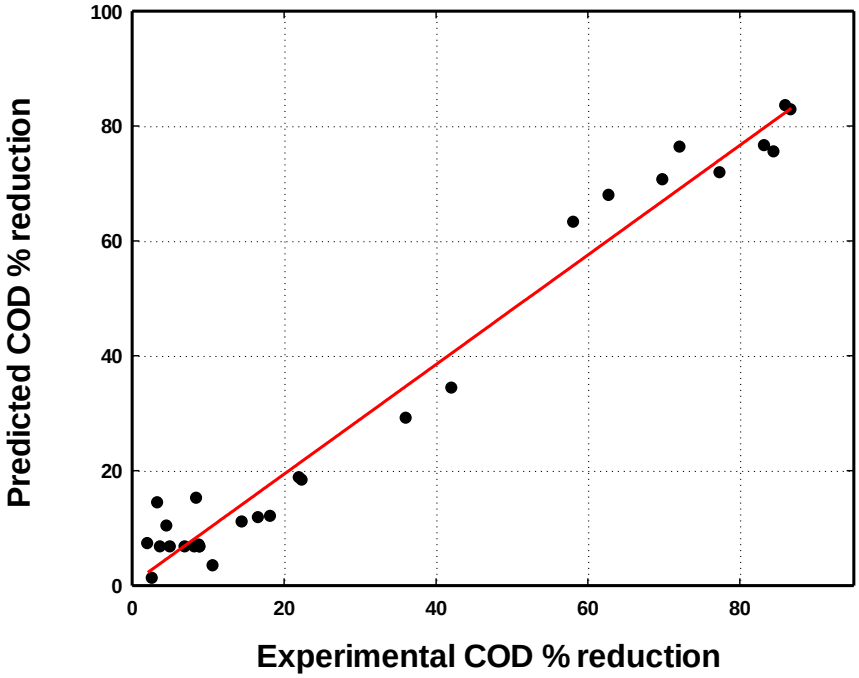


Figure 21: Predicted versus experimental COD reduction values for propamocarb fungicide-contaminated wastewater.

4.3 Comparative analysis of GTL process water and propamocarb HCl fungicide-contaminated water

By analyzing the results obtained from GTL process water and propamocarb hydrochloride fungicide-contaminated wastewater biodegradation experiments, it is obvious that the COD reduction in GTL process water is very high (88.5%) compared to that for the propamocarb HCl contaminated wastewater (42.1%). Additionally, RSM optimizer was applied for both GTL process water and propamocarb HCl contaminated wastewater, where the optimum COD reduction% was predicted to be 90 at an initial COD of 2595 mg/l, PVA volume fraction of 27%, and pH of 7.3 for GTL process water, and 75 at COD of 1170 mg/l, PVA volume fraction of 33%, and pH of 9 for propamocarb HCL contaminated wastewater; however, experimentally at optimum conditions, COD reduction% obtained were 89 (almost matching the predicted value) and 12 (very far from predicted value), respectively. Which indicates that the GTL PW model is more valid than the propamocarb HCl-contamin/ated wastewater model as shown in Figures 18 and 21.

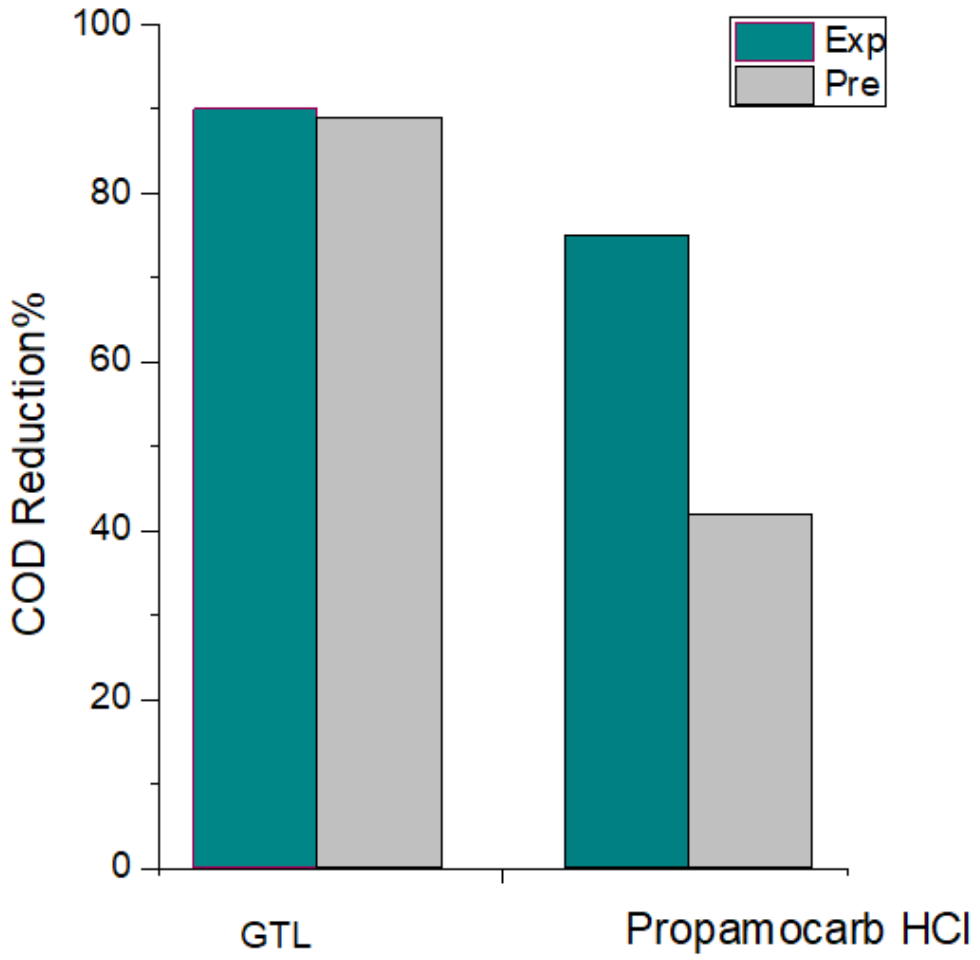


Figure 22: A comparison of experimental and predicted results for the biotreatment of GTL process water and propamocarb HCl-contaminated water.

This vast difference in the reduction of COD efficiency for the two types of wastewater is believed to be attributed to the chemical structure of the main organic contaminants in the wastewater. Propamocarb hydrochloride (Propyl [3 (dimethyl amino) propyl] carbamate-hydrogen chloride) structure contains a nitrogen atom and an amino group ($C_9H_{21}ClN_2O_2$). However, the GTL process water was mainly composed of alcohols including short-chain alcohols (methanol, ethanol, propanol, and butanol), and long-chain alcohols (3-hexanol, 2,5-dimethyl-2-hexanol, 2,5-dimethyl-2-hexanol, 4-methyl-3-heptanol, heptanol, 2-octanol, 2-butyl-1-octanol, 2,6, dimethyl-2-octanol, 3-hexadecanol, 2-methyl-2-decanol, 3-tetradecanol, 2-pentadecanol, 1-nonadecanol, 5,9-dimethyl -1-

decanol), and other components, such as fatty acids (2-propenoic acid, butanoic acid, acetoacetic acid), ketones (5-methoxy -2-pentanone, methyl ketone), esters (and 1,1-dimethyl ethyl ester, methyl ester, ethyl ester), and 4-hydroxy- cyclohexane methanol, 1-ethoxy-hexane) as shown in Table 23. It is believed that most of the aliphatic alcohols and carboxylic acids were not inhibitory and were biodegraded, but the compounds having ether bonds or branched hydrocarbon groups were biodegraded slowly [230]. According to Kameya et al, [230] the majority of the aliphatic alcohols and carboxylic acids are easily biodegradable and do not have any inhibitory effects on the microorganism. However, compounds with aliphatic aldehyde and amines, like propamocarb HCl ($C_9H_{21}ClN_2O_2$), were difficult to biodegrade.

Generally, there is a three-phase process in the metabolism of pesticides including the conversion of the primary properties of the active substance into less toxic and more water-soluble materials compared to the original compound in the first phase [125]. Moreover, the water solubility increases and the toxicity decreases by conjugation of pesticide metabolite to amino acid or sugar compounds which occurs in the second phase. While in the third phase, the metabolites produced in the second phase are converted into secondary conjugates that are also non-toxic compounds. These processes include the production of intracellular or extracellular enzymes (e.g. oxygenases, hydrolases, peroxidases, etc) by Fungi, and bacteria[126], [127]. Regarding the biodegradation mechanism of propamocarb, after a lag period of 2 weeks, propamocarb hydrochloride rapidly decomposes in mineral salt solutions containing acetate as a carbon source and is injected with a few drops of original lake water as reported by [149]. Propamocarb was converted to isothymol. Unidentified radiocarbon-containing compounds also were present in the aqueous fraction from the three carbamates. On the other hand, the

degradation mechanism for the main four compositions of GTL process water including fatty acids, alcohols, ketones, and aldehydes were described by [232]. The fatty acid is one of the important energy sources of the organism and it is converted to generate acetyl-CoA and finally to CO_2 and H_2O in the β-oxidation process, releasing much energy for the microorganism [232]. Mckinney et al, [233], also reported that in any waste disposal facility, the microorganisms' metabolic system follows define pathways. The metabolic pathways for the many types of organic chemicals used are, for the most part, quite straightforward and interrelated. The basic pathways of metabolism are the same for all organic molecules, but they each have unique preliminary processes. This includes carbohydrates, lipids, proteins, alcohols, aldehydes, ketones, and organic acids. A portion of the complex organic matter is broken down even further to provide the energy needed by the cell, while the remaining organic matter is used to create new cell tissue on the preliminary metabolic pathways. The complex organic matter is broken down by hydrolyses, and sometimes by a combination of hydrolyses and oxidation, to form the basic compounds, which then enter into the basic metabolic pathways. Isopropanol and 2-butanol are oxidized to the corresponding ketones and then to the corresponding acids, while alcohols and isobutanol are oxidized first to aldehydes and then to acids. Chemical oxidation and biological oxidation separate at the stage of acid oxidation. Acid is promptly broken down into carbon and water by chemical oxidation [233]. Furthermore, after forming a hydrate, aldehydes oxidize to carboxylic acids, whereas ketones cannot oxidize further since there is no C-H link that may be broken to generate a new C-O pi bond.

Table 23: The composition of GTL process water before and after treatment extracted using GC-MS [234].

Contaminant	Stripped GTL Water	Treated GTL water
Short Chain Alcohol		
Methanol	D	ND
Ethanol	D	ND
Propanol	D	ND
Butanol	D	ND
Long Chain Alcohol		
3-Hexanol	D	ND
2,5-dimethyl-2-Hexanol	D	D
4-methyl-3-Heptanol	D	ND
Heptanol	ND	ND
2-Octanol	D	D
2-butyl-1-Octanol	ND	ND
2,6-dimethyl-2-Octanol	D	ND
3-hexadecanol	D	ND
2-Methyl-2-decanol	D	D
3-Tetradecanol	ND	ND
2-Pentadecanol	ND	ND
1-Nonadecanol	D	ND
5,9-dimethyl -1-decanol	D	ND
Fatty Acids		
2-Propenoic acid	ND	ND
Butanoic acid	ND	ND
Acetoacetic acid	D	ND
Ketones		
5-methoxy -2-Pentanone	D	ND
methyl ketone	D	ND
Esters		
1,1-dimethy ethyl ester	ND	ND
methyl ester	ND	ND
Ethyl ester	ND	ND
Others		
4-hydroxy- Cyclohexane methanol	ND	ND
1-ethoxy-Hexane	ND	ND

The average COD for GTL process water treated in this study was found to be ~ 441 mg/l, which is considered to be purified water as reported by Luis et al, [216]. However, it cannot be used as boiler feed water, process water, drinking water, and cooling water

as shown in Table 14 in Section 2.6. Therefore, further pre/post treatment is required. Table 26 shows GTL PW characteristics after treatment. Table 24 shows the treated GTL PW characteristics.

Table 24: Physical and chemical characteristics of GTL.

Characteristic	GTL PW	Pretreated GTL PW	Treated GTL PW (batch experiments)
COD (mg/l)	5000–7000	2000 to 4000	~ 441
TOC (mg/l)	1500–1700	700–1400	~154
pH	2.9	3.3	7.2

4.4 GTL PW Continuous experiment

The RSM for the propamocarb HCl-contaminated water indicated poor degradation compared to GTL water, and hence the continuous experiments were focused on the GTL PW water. The continuous experiments were performed to study the effects of air and liquid flow rates on the biotreatment of GTL PW under optimum conditions selected based on RSM in Section 4.1.

4.4.1 Effect of air flow rate

The bioreactor's air flow rate is crucial in ensuring that there is enough oxygen for biodegradation and adequate mixing via particle movement. Different air flow rates of 1, 2, and 3.3 L_a/L_r. min (liter of air per liter of the reactor per min) were operated for 24 hrs to evaluate the impact of air flow rate on the continuous biological treatment of GTL PW. However, at 1 L_a/L_r.min the aeration and mixing of the immobilized bacteria were

limited, thus, only 2, and 3.3 L_a/L_r.min were studied. The initial COD concentration, liquid flow rate, and temperature were kept at the optimum conditions of ~ 2200 mg/l, 2.1 ml/min, and 32 ◦C, respectively. Samples were collected from the effluent for the COD analysis. Figure 23 shows COD reduction with increasing time for two different air flow rates 2, 3.3 La/Lr.min. When comparing the airflow rates of 2 and 3.3 L_a/L_r.min, the difference in DO was found to be insignificant (5.2, and 5.5 mg/l, respectively). Moreover, there was a slight difference in the mixing of immobilized bacteria between the two flow rates, which could be attributed to the lower COD reduction at 2 La/Lr.min (60.6%) compared to the air flow rate of 3.3 La/Lr. min (62%). The findings demonstrate that the air flow rate affects the biodegradation rate of organic pollutants. In general, at a specific range, the higher the airflow rate, the better the biodegradation rate which are two key factors for how the air flow rate affects the biotreatment of organic compounds by feeding the necessary amount of oxygen. [222]. Moreover, Gopalakrishnan et al, [235] reported that the excess supply of oxygen led to the higher degradation activity of the biomass, therefore, the increase in airflow rate will increase the reduction of COD. However, at a lower range, the biodegradation rate will decrease due to the fact that, after a certain limit, critical velocity occurs, causing the biomass support particles to settle down at the bottom of the reactor. As a result, there are fewer interactions between the substrate, biomass, and air, which leads to a less reduction in the COD. For the air flow rate at a lower range, oxygen is the growth-limiting factor [235].

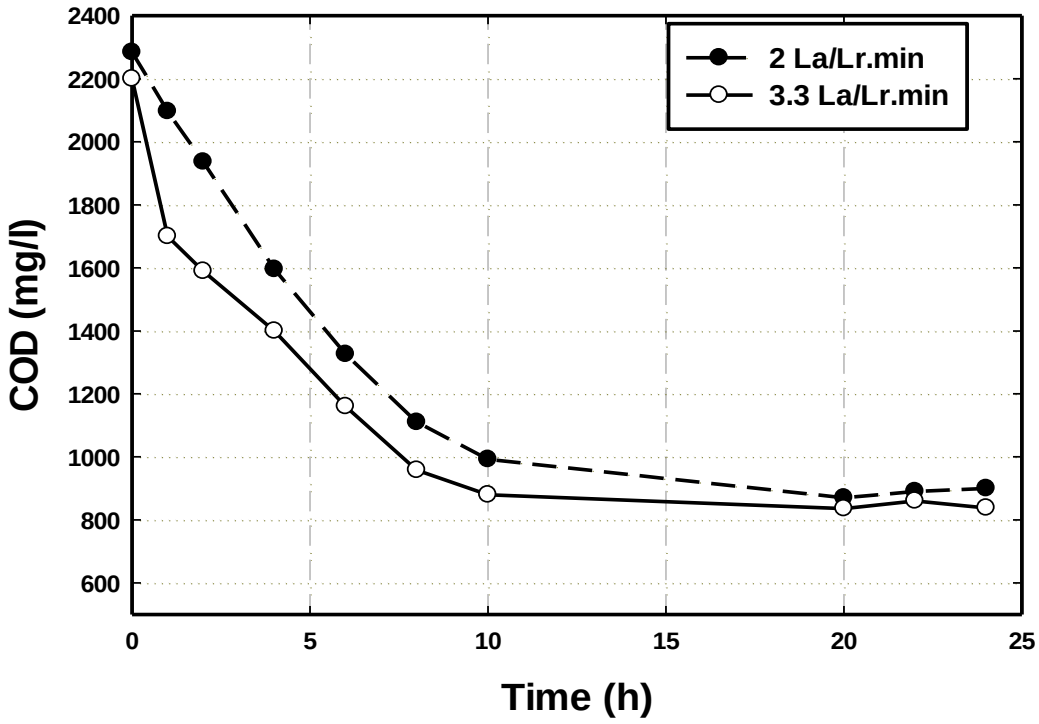


Figure 23: The concentration of GTL PW in SBBR vs time for tow airflow rates. Initial COD = ~ 2200 mg/l; PVA volume % = 27; reactor temperature = 32 ◦C; liquid flow rate = 2.1 ml/min.

4.4.2 Effect of liquid flow rate

To assess the effect of liquid flow rate step change on the biotreatment of GTL PW, a continuous experiment was carried out at the optimum conditions obtained from batch experiments in Section 4.1 (Initial COD of ~ 2200 mg/l; PVA v % of 27; reactor temperature at 32 ◦C; and an airflow rate of 2.1 l/min and Hydraulic Residense Time (HRT) of 12h). Figure 24 shows the decrease in COD reduction through these step changes in liquid flow rate . First, the experiment was carried out for around 22 hrs. to reach a steady state in COD reduction of 65.69%. Then, a step change of liquid flowrate from 2.1 to 4.2 ml/min was performed, reducing the HRT to 6h. A second steady state condition with liquid flow rate of 4.2 ml/min. where the COD reduction was declined to

38.61% COD reduction. After this time, the liquid flowrate was returned to its previous value to reach the third steady state condition with a 63.68% COD reduction. This is to be expected because a higher liquid flow rate reduces the residence time in the bioreactor HRT from 12h and to 6h at liquid flow rates of 2.1 and 4.2 ml/min, respictively. Thus, the contact time between immobilized bacteria and organic poluutanst PW reduced and resulted in lower COD reduction [222]. It is generally accepted that the inlet feed flow rate has the greatest influence on determining the efficiency of bioreactors by governing the retention time of the contaminants within the bioreactor [236], [237]. The more the HRT, the more chance for an efficient decomposition of the organic contaminant. A very low liquid flow rate, however, may also result in mass transfer constraints, which could lead to a decrease in the pollutant removal [238]. By increasing the liquid flow rate, more organic pollutants introduced to the bioreactor, thus the substrate may serve as a nutrient for the microbial biomass until a certain initial concentration, however, an increase in substrate concentration may impart the toxic effect of pollutants on the metabolic activity of microbial biomass, resulting in lower removal efficiency [238].

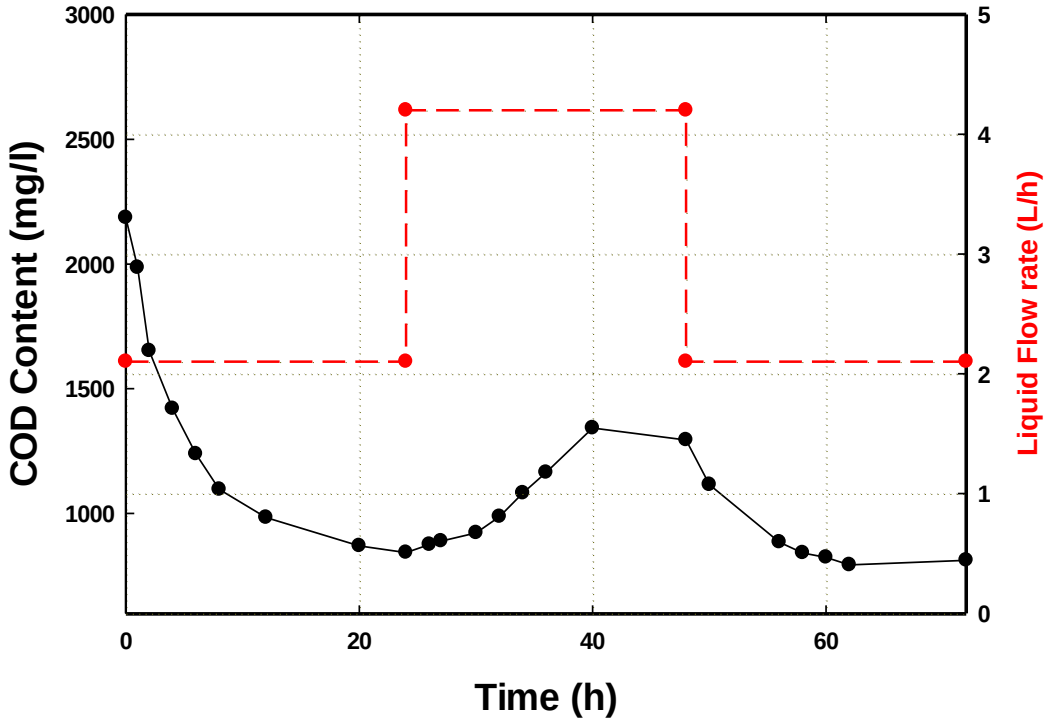


Figure 24**:** Liquid flow rate step change of (2.1-4.5 and back to 2.1 ml/min). Initial COD = ~ 2200 mg/l; temperature = 32 ◦C; air flow rate 2 l/min

Kawan et al, [239] reported that the water flow or movement in the reactor caused a high water velocity in the reactor, a short duration of contact between the organic matter, and less time for biofilm formation when the reactor was run at a high flow rate (short retention time (HRT). As a result, the capability of the organisms to metabolize organic materials was diminished. Additionally, Chen et al, [240] noted that minimizing hydraulic retention time (HRT) and lowering the pH level in the system are two ways to minimize the excessive accumulation of butyric acid and propionic acid, which is a critical component of the successful F-T wastewater treatment [240].

4.4.3 Dynamic behaviour

The variation in the load, the hydraulic characteristics of the reactor (transport and mixing), and the transformation processes are all factors that affect the dynamic, time-dependent behavior of reactors. Many effects are unreasonable and cannot be fully understood without thoughtful deliberation and analysis. A set of time constants that can be assessed depending on the rate of specific processes governs the time-dependent behavior of systems. Additionally, comparing these time constants enables the assessment of which variable has a significant or minor impact on system behavior. The reactor time constant ($\boldsymbol{\tau}_p$), which represents the reactor response to a change in liquid flowrate, and the dead time (t_d), which measures the interval between a step change and the first response of the measured COD were calculated using Equations 5 and 6, respectively [241].

$$t_d = t_1 - t_2 \quad (5)$$

$$\boldsymbol{\tau}_p = t_{63.2\%} - t_2 \quad (6)$$

where: t_1: is the time when the step change is made. t_2: representing the time when the measured COD first responds to the step change. $t_{63.2\%}$: is the time when the measured COD reaches 63.2% of its total final change. The results given in Table 25 and Figure 25 demonstrate that $t_d < \boldsymbol{\tau}_p$ in the experiments, which indicates a tight and easy overall process control [241]. It was found that the dead time is connected to the step change direction in the liquid flow rate. For instance, when the liquid flow rate was reduced, the dead time decreased. These findings are quite encouraging in terms of the adaptation and suitability of the reactor system for large-scale processes.

Table 25: Step-change in the liquid flow rate and HRT; dead time and time constant.

Condition	Step change	t_1(hr)	t_2(hr)	$t_{63.2\%}$(hr)	t_d(hr)	τ_p(hr)
Liquid flow rate	2.1 - 4.2	22	24	33.376	2	9.376
Liquid flow rate	4.2 - 2.1	48	48.5	56.848	0.5	6.848

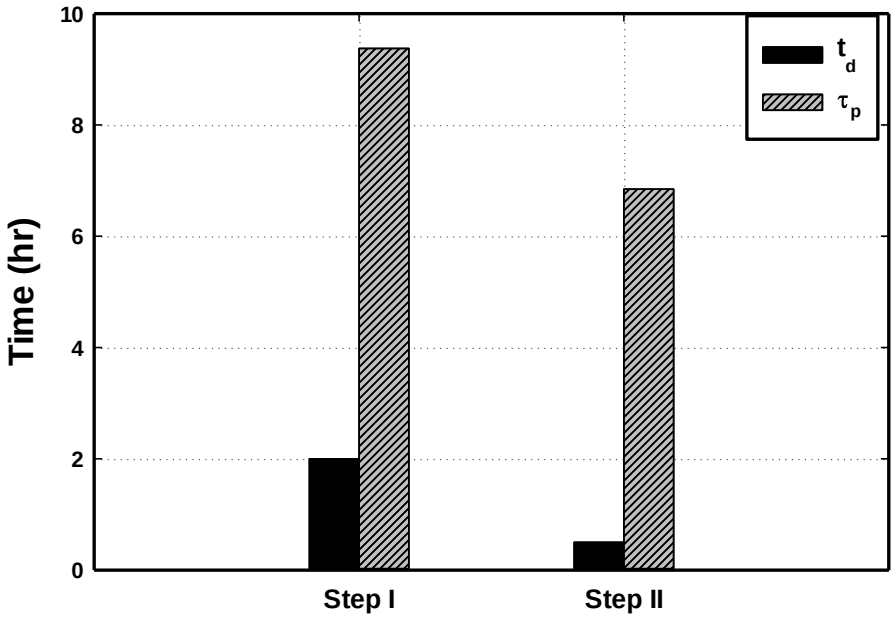


Figure 25: The dead time and reactor time constants for a step change experiment.

Finally, although these continuous experiments are limited to studying only the effect of liquid and air flow rates, other effects such as the initial COD and immobilized PVA particle size can be investigated in the future. A study of continuous biotreatment of phenol in SBBR was performed by El-Naas et al[222]. They investigated the effect of initial COD and PVA immobilized particle size on the biotreatment of phenol. It revealed that the rate of phenol reduction is stable for a longer period at high initial COD concentrations than at low initial COD concentrations, as it appears to decrease over time. Bacteria immobilized within PVA particles may have only limited access to organic compounds at low COD concentrations, which can be explained by mass transfer

limitations. In addition, the particle size of PVA has a significant effect on the continuous biotreatment of phenol, which is increased by particle size reduction, especially, for high air flow rates.

Chapter 5: Summary and Future Perspective

This study evaluated the biotreatment of organic contaminants in GTL PW and propamocarb HCl contaminated water using *Pseudomonas aeruginosa* strain in PVA gel. Among the various GTL process water and pesticide treatment approaches, biodegradation is found to be the most suitable due to its high COD reduction capability, good stability, and environmental friendliness.

In a specially designed spouted bed bioreactor system, the biotreatment of organic contaminants in GTL process water and propamocarb HCl fungicide-contaminated water was investigated. Using RSM, the second-order polynomial was found to be effective in forecasting COD reduction when three independent variables were used: initial COD concentration, pH, and PVA volume percent. All three factors had a considerable impact on GTL PW water and propamocarb HCl-contaminated water biodegradation. In the batch experiment, the maximum COD reduction for GTL PW and propamocarb HCl contaminated wastewater was found to be 88.5%, and 42.1%, respectively.

Additionally, when applying RSM optimizer for both GTL PW and propamocarb HCl contaminated wastewater, the optimal COD reduction was predicted to be 90% at an initial COD of 2595 mg/l, PVA volume fraction of 27%, and pH of 7.3, and 75% at COD of 1170 mg/l, PVA volume fraction of 33%, and pH of 9, respectively. However, experimentally at optimum conditions, only GTL PW COD reduction% matched the predicted value. This could attributed to the possibility of degrading of the PVA by a certain concentration of COD. This can be justified since propamocarb HCl fungicide is very toxic, thus, might have inhibitory effects on the bacteria.

Studying the effect of initial COD, pH, and PVA volume% on the biotreatment of organic

contaminants in GTL PW and propamocarb HCl contaminated water, the outcomes revealed that, at certain ranges, increasing the initial COD, pH, and PVA volume%, increased the COD reduction%.

To explain the biodegradation performance and variation between GTL PW and propamocarb HCl contaminated water, their structure and degradation mechanism were compared. The findings showed that GTL PW, which mainly contains alcohols, fatty acids, ketones, and esters is easily biodegradable and does not have any inhibitory effects on the microorganism. On the other hand, propamocarb HCl fungicide ($C_9H_{21}ClN_2O_2$) has compounds with aliphatic aldehyde and amines, which are hard to degrade biologically.

Continous study was carried out to investigate the effect of liquid flow rate and air flow rate on the organic removal from GTL PW. The results showed that when increasing the air flow rate from 2 to 3.3 La/Lr.min, the COD reduction, and DO of GTL PW increased from 60.6% to 62%, 5.2, and 5.5 mg/l, respectively. This domenstrates that the difference between the two flowrates is insignificant. Therefore, further studies on the effect of the air flow rate and other effects such as the initial COD and PVA particle size can be investigated in the future. A step change experiment of liquid flow rate from 2.1 to 4.2 ml/min and the back to 2.1 ml/min was performed. At liquid flow rate of 4.2 ml/min ,the COD reduction reduced due to the fact that a higher liquid flow rate reduces the residence time in the bioreactor, which reduces the amount of time the immobilized bacteria have to degrade GTL PW. The system responded quickly to the change in liquid flow rate and returned to the initial COD level. This indicates that the system is highly stable and can easily recover. Regarding the dynamic of the step change experiment, the results obtained that t_d is less than $\boldsymbol{\tau}_p$,which indicates a tight and easy overall process control. These

findings are quite encouraging in terms of the adaptation and suitability of the reactor system for large-scale processes. However, further pre/post treatment is recommended in order to discharge the treated water or using it in various application.

Nowadays, the move towards a clean, green, and environmentally friendly degradation process is significantly increasing. There is an agreement that the combined processes are the most efficient; thus, further experimental work on combined methods is required to achieve optimum performance. Finally, future work should assess other effects such as the initial COD, temperature, dissolved oxygen, and PVA particle size on the continuous biotreatment of organic contaminants in GTL PW.

REFERENCES

[1] M. N. Soliman, F. Z. Guen, S. A. Ahmed, H. Saleem, M. J. Khalil, and S. J. Zaidi, "Energy consumption and environmental impact assessment of desalination plants and brine disposal strategies," *Process Saf. Environ. Prot.*, vol. 147, 2021.

[2] R. Surkatti, M. H. El-Naas, M. C. M. Van Loosdrecht, A. Benamor, F. Al-Naemi, and U. Onwusogh, "Biotechnology for gas-to-liquid (GTL)wastewater treatment: A review," *Water (Switzerland)*, vol. 12, no. 8, Aug. 2020.

[3] G. P. Satish, D. M. Ashokrao, and S. K. Arun, "Microbial degradation of pesticide: A review," *African J. Microbiol. Res.*, vol. 11, no. 24, pp. 992–1012, 2017.

[4] D. M. Brown *et al.*, "Biodegradability assessment of complex, hydrophobic substances: Insights from gas-to-liquid (GTL) fuel and solvent testing," *Sci. Total Environ.*, vol. 727, p. 138528, Jul. 2020.

[5] ECHA, *Guidance on Information Requirements and Chemical Safety Assessment*, no. June. 2017.

[6] G. Crini and E. Lichtfouse, "Advantages and disadvantages of techniques used for wastewater treatment," *Environmental Chemistry Letters*, vol. 17, no. 1. Springer Verlag, pp. 145–155, 01-Mar-2019.

[7] A. Sonune and R. Ghate, "Developments in wastewater treatment methods," *Desalination*, vol. 167, no. 1–3, pp. 55–63, Aug. 2004.

[8] F. Gebara, "Activated sludge biofilm wastewater treatment system," *Water Res.*, vol. 33, no. 1, pp. 230–238, Jan. 1999.

[9] Y. Shimizu, K. Uryu, Y. I. Okuno, and A. Watanabe, "Cross-flow microfiltration of activated sludge using submerged membrane with air bubbling," *J. Ferment. Bioeng.*, vol. 81, no. 1, pp. 55–60, Jan. 1996.

[10] N. O. Elbashir and F. T. Eljack, “A Method to Design an Advanced Gas-to-Liquid Technology Reactor for Fischer-Tropsch Synthesis,” in *Proceedings of the 2nd Annual Gas Processing Symposium*, Elsevier, 2010, pp. 369–377.

[11] N. Pon Saravanan and M. J. Van Vuuren, “Process Wastewater Treatment and Management in Gas-to-Liquids Industries,” *SPE Oil Gas India Conf. Exhib. 2010, OGIC*, vol. 1, pp. 176–184, Jan. 2010.

[12] G. Evans and C. Smith, “Biomass to liquids technology,” *Compr. Renew. Energy*, vol. 5, pp. 155–204, 2012.

[13] S. G. Parte, A. D. Mohekar, and A. S. Kharat, “African Journal of Microbiology Research Microbial degradation of pesticide: A review,” vol. 11, no. 24, pp. 992–1012, 2017.

[14] W. Aktar, D. Sengupta, and A. Chowdhury, “Impact of pesticides use in agriculture: Their benefits and hazards,” *Interdiscip. Toxicol.*, vol. 2, no. 1, pp. 1–12, 2009.

[15] R. Chamy and F. Rosenkranz, *Biodegradation - Life of Science*. InTech, 2013.

[16] N. M. Al-Shamary, M. A. Al-Ghouti, I. Al-Shaikh, S. H. Al-Meer, and T. A. Ahmad, “Evaluation of pesticide residues of organochlorine in vegetables and fruits in Qatar: statistical analysis,” *Environ. Monit. Assess.*, vol. 188, no. 3, pp. 1–14, Mar. 2016.

[17] B. P. Shah and B. Devkota, “Obsolete Pesticides: Their Environmental and Human Health Hazards,” *J. Agric. Environ.*, vol. 10, pp. 60–66, Aug. 2009.

[18] A. Rodríguez *et al.*, “Omics Approaches to Pesticide Biodegradation,” *Current Microbiology*, vol. 77, no. 4. Springer, pp. 545–563, 01-Apr-2020.

[19] M. R. Bonner and M. C. R. Alavanja, “Pesticides, human health, and food security,” *Food Energy Secur.*, vol. 6, no. 3, pp. 89–93, Aug. 2017.

[20] O. Frank Anayo, E. Chika Scholastica, O. Chidi Peter, U. Gray Nneji, A. Obinna, and L. Oluwabusola Mistura, “The Beneficial Roles of Pseudomonas in Medicine, Industries, and Environment: A Review,” in *Pseudomonas Aeruginosa - An Armory Within*, IntechOpen, 2019.

[21] M. F. Moradali, S. Ghods, and B. H. A. Rehm, “Pseudomonas aeruginosa Lifestyle: A Paradigm for Adaptation, Survival, and Persistence,” *Front. Cell. Infect. Microbiol.*, vol. 7, no. FEB, p. 39, Feb. 2017.

[22] B. P. Retmana, S. Sitaresmi, Y. Yasman, and A. Oetari, “ARTICLES YOU MAY BE INTERESTED IN Biodegradation of 0.02 % Naphthalene by Pseudomonas aeruginosa DRK 9.1 Isolated from Volcanic Mud in Renokenongo Village, Sidoarjo,” vol. 2242, p. 50025, 2020.

[23] M. Yoshikawa, M. Zhang, and K. Toyota, “Biodegradation of Volatile Organic Compounds and Their Effects on Biodegradability under Co-Existing Conditions,” *Microbes Environ.*, vol. 32, no. 3, pp. 188–200, 2017.

[24] K. V Darsa and A. J. Thatheyus, “Biodegradation of Petroleum Compound Using Pseudomonas aeruginosa,” *OALib*, vol. 01, no. 05, pp. 1–9, 2014.

[25] S. He, Y. Ni, L. Lu, Q. Chai, H. Liu, and C. Yang, “Enhanced biodegradation of n-hexane by Pseudomonas sp. strain NEE2,” *Sci. Reports 2019 91*, vol. 9, no. 1, pp. 1–9, Nov. 2019.

[26] R. Kaur, G. K. Mavi, and S. Raghav, “Bioremediation of Sludge using Pseudomonas aeruginosa,” *Int.J.Curr.Microbiol.App.Sci*, vol. 8, no. 4, pp. 69–79, 2019.

[27] E. Brancaccio, “GTL: Small Scale and Modular Technologies for Gas to Liquid Industry,” *oil-gasportal*, 2021. [Online]. Available: http://www.oil-gasportal.com/gtl-small-scale-and-modular-technologies-for-gas-to-liquid-

industry/?print=print. [Accessed: 24-May-2022].

[28] E. Brancaccio, “GTL: Small Scale and Modular Technologies for Gas to Liquid Industry,” *Oil-Gasportal*, 2021.

[29] L. P. Dancuart and A. P. Steynberg, “Fischer-Tropsch Based GTL Technology: a New Process?,” *Stud. Surf. Sci. Catal.*, vol. 163, pp. 379–399, Jan. 2007.

[30] E. Brancaccio, “GTL: Small Scale and Modular Technologies for Gas to Liquid Industry,” *oil-gasportal*, 2021. [Online]. Available: http://www.oil-gasportal.com/gtl-small-scale-and-modular-technologies-for-gas-to-liquid-industry/?print=print. [Accessed: 26-Aug-2022].

[31] M. Höök, D. Fantazzini, A. Angelantoni, and S. Snowden, “Hydrocarbon liquefaction: Viability as a peak oil mitigation strategy,” *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, vol. 372, no. 2006, 2014.

[32] N. Pon Saravanan and M. J. Van Vuuren, “Process wastewater treatment and management in gas-to-liquids industries,” *SPE Oil Gas India Conf. Exhib. 2010, OGIC*, vol. 1, pp. 176–184, 2010.

[33] R. Dores, A. Hussain, M. Katebah, and S. Adham, “Using advanced water treatment technologies to treat produced water from the petroleum industry,” *SPE Prod. Oper. Symp. Proc.*, vol. 2, pp. 914–924, 2012.

[34] G. C. Enyi, G. G. Nasr, and M. Burby, “INTERNATIONAL JOURNAL OF ENERGY AND ENVIRONMENT Economics of wastewater treatment in GTL plant using spray technique,” *J. homepage www.IJEE.IEEFoundation.org ISSN*, vol. 4, pp. 2076–2909, 2013.

[35] S. Andre and D. Mark, “Fischer-Tropsch Technology.” Elsevier Science & Technology Books,.

[36] C.-J. Li, A. Selva, M. Boethling, and R. A. Jansen, “Greener Fischer-Tropsch

Processes for Fuels and Feedstocks," *Greener Fischer-Tropsch Process. Fuels Feed.*, Feb. 2013.

[37] D. Wang, W. Ma, H. Han, K. Li, and X. Hao, "Enhanced treatment of Fischer–Tropsch (F-T) wastewater by novel anaerobic biofilm system with scrap zero valent iron (SZVI) assisted," *Biochem. Eng. J.*, vol. 117, pp. 66–76, Jan. 2017.

[38] J. Laurinonyte, R. J. W. Meulepas, P. van den Brink, and H. Temmink, "Membrane Bioreactor (MBR) as Alternative to a Conventional Activated Sludge System Followed by Ultrafiltration (CAS-UF) for the Treatment of Fischer-Tropsch Reaction Water from Gas-to-Liquids Industries," *Water. Air. Soil Pollut.*, vol. 228, no. 4, pp. 1–13, Apr. 2017.

[39] M. Majone *et al.*, "High-rate anaerobic treatment of Fischer-Tropsch wastewater in a packed-bed biofilm reactor," *Water Res.*, vol. 44, no. 9, pp. 2745–2752, 2010.

[40] S. Chain Alcohols, "□."

[41] D. Wang, W. Ma, H. Han, K. Li, and X. Hao, "Enhanced treatment of Fischer–Tropsch (F-T) wastewater by novel anaerobic biofilm system with scrap zero valent iron (SZVI) assisted," *Biochem. Eng. J.*, vol. 117, pp. 66–76, Jan. 2017.

[42] D. Wang, H. Han, Y. Han, K. Li, and H. Zhu, "Enhanced treatment of Fischer-Tropsch (F-T) wastewater using the up-flow anaerobic sludge blanket coupled with bioelectrochemical system: Effect of electric field," *Bioresour. Technol.*, vol. 232, pp. 18–26, May 2017.

[43] D. Wang, Y. Han, H. Han, K. Li, and C. Xu, "Enhanced treatment of Fischer-Tropsch wastewater using up-flow anaerobic sludge blanket system coupled with micro-electrolysis cell: A pilot scale study," *Bioresour. Technol.*, vol. 238, pp. 333–342, Aug. 2017.

[44] S. V, M. HGJ, Z. P, T. M, R. CJ, and G. V, "Pesticide residues in European

agricultural soils - A hidden reality unfolded," *Sci. Total Environ.*, vol. 653, pp. 1532–1545, Feb. 2019.

[45] U. EPA Office of Pesticide Programs, "US EPA - Pesticides - Fact Sheet for Propamocarb."

[46] C. M. Benbrook, "Trends in glyphosate herbicide use in the United States and globally," *Environ. Sci. Eur.*, vol. 28, no. 1, pp. 1–15, Dec. 2016.

[47] R. Kaur, G. K. Mavi, S. Raghav, and I. Khan, "Pesticides Classification and its Impact on Environment," *Int. J. Curr. Microbiol. Appl. Sci.*, vol. 8, no. 03, pp. 1889–1897, Mar. 2019.

[48] WHO, *The Who recommended clasification of pesticides by hazard*. 2019.

[49] H. K. Gill and H. Garg, "Pesticides: Environmental Impacts and Management Strategies," *Pestic. - Toxic Asp.*, Feb. 2014.

[50] K. H. Kim, E. Kabir, and S. A. Jahan, "Exposure to pesticides and the associated human health effects," *Sci. Total Environ.*, vol. 575, pp. 525–535, Jan. 2017.

[51] H. D. Bailey *et al.*, "Home pesticide exposures and risk of childhood leukemia: Findings from the childhood leukemia international consortium," *Int. J. Cancer*, vol. 137, no. 11, pp. 2644–2663, Dec. 2015.

[52] J. P. Arrebola *et al.*, "Risk of female breast cancer and serum concentrations of organochlorine pesticides and polychlorinated biphenyls: A case-control study in Tunisia," *Sci. Total Environ.*, vol. 520, pp. 106–113, Jul. 2015.

[53] S. Amr *et al.*, "Pesticides, Gene Polymorphisms, and Bladder Cancer among Egyptian Agricultural Workers," *Arch. Environ. Occup. Heal.*, vol. 70, no. 1, pp. 19–26, Jan. 2015.

[54] A. F. S. Amaral, "Pesticides and asthma: Challenges for epidemiology," *Front. Public Heal.*, vol. 2, no. JAN, Jan. 2014.

[55] I. Baldi, A. Gruber, V. Rondeau, P. Lebailly, P. Brochard, and C. Fabrigoule, "Neurobehavioral effects of long-term exposure to pesticides: Results from the 4-year follow-up of the PHYTONER Study," *Occup. Environ. Med.*, vol. 68, no. 2, pp. 108–115, Feb. 2011.

[56] M. F. Bouchard *et al.*, "Prenatal exposure to organophosphate pesticides and IQ in 7-year-old children," *Environ. Health Perspect.*, vol. 119, no. 8, pp. 1189–1195, Aug. 2011.

[57] W. Aktar, D. Sengupta, and A. Chowdhury, "Impact of pesticides use in agriculture: Their benefits and hazards," *Interdiscip. Toxicol.*, vol. 2, no. 1, pp. 1–12, 2009.

[58] V. B. AHC *et al.*, "Environmental and health effects of the herbicide glyphosate," *Sci. Total Environ.*, vol. 616–617, pp. 255–268, Mar. 2018.

[59] H. Chin, P. Elefsiniotis, and N. Singhal, "Biodegradation of 2,4-dicholophenoxyacetic acid using an acidogenic anaerobic sequencing batch reactor," *J. Environ. Eng. Sci.*, vol. 4, no. 1, pp. 57–63, 2005.

[60] J. M. Salman, "Batch study for insecticide carbofuran adsorption onto palm-oil-fronds- activated carbon," *J. Chem.*, 2013.

[61] I. A. Saleh, N. Zouari, and M. A. Al-Ghouti, "Removal of pesticides from water and wastewater: Chemical, physical and biological treatment approaches," *Environ. Technol. Innov.*, vol. 19, p. 101026, 2020.

[62] S. A. C and L. EC, "Removal of emerging contaminants from the environment by adsorption," *Ecotoxicol. Environ. Saf.*, vol. 150, pp. 1–17, Apr. 2018.

[63] N. Gaur, K. Narasimhulu, and Y. PydiSetty, "Recent advances in the bio-remediation of persistent organic pollutants and its effect on environment," *Journal of Cleaner Production*, vol. 198. Elsevier Ltd, pp. 1602–1631, 10-Oct-

2018.

[64] T. Wang, C. Yu, Q. Chu, F. Wang, T. Lan, and J. Wang, “Adsorption behavior and mechanism of five pesticides on microplastics from agricultural polyethylene films,” *Chemosphere*, vol. 244, p. 125491, Apr. 2020.

[65] A. T. Shawaqfeh, “Removal of Pesticides from Water Using Anaerobic-Aerobic Biological Treatment,” *Chinese J. Chem. Eng.*, vol. 18, no. 4, pp. 672–680, Aug. 2010.

[66] R. Allabashi, M. Arkas, G. Hörmann, and D. Tsiourvas, “Removal of some organic pollutants in water employing ceramic membranes impregnated with cross-linked silylated dendritic and cyclodextrin polymers,” *Water Res.*, vol. 41, no. 2, pp. 476–486, Jan. 2007.

[67] S. A. Abdel-Gawad, A. M. Baraka, K. A. Omran, and M. M. Mokhtar, “Removal of some pesticides from the simulated waste water by electrocoagulation method using iron electrodes,” *Int. J. Electrochem. Sci.*, vol. 7, no. 8, pp. 6654–6665, 2012.

[68] M. Cycoń, A. Mrozik, and Z. Piotrowska-Seget, “Bioaugmentation as a strategy for the remediation of pesticide-polluted soil: A review,” *Chemosphere*, vol. 172, pp. 52–71, Apr. 2017.

[69] L. Goodwin, I. Carra, P. Campo, and A. Soares, “International Journal of Water and Wastewater Treatment Treatment Options for Reclaiming Wastewater Produced by the Pesticide Industry,” 2017.

[70] N. A. Baharum, H. M. Nasir, M. Y. Ishak, N. M. Isa, M. A. Hassan, and A. Z. Aris, “Highly efficient removal of diazinon pesticide from aqueous solutions by using coconut shell-modified biochar,” *Arab. J. Chem.*, vol. 13, no. 7, pp. 6106–6121, Jul. 2020.

[71] O. V. Salata, “Applications of nanoparticles in biology and medicine,” *Journal of*

Nanobiotechnology, vol. 2. 30-Apr-2004.

[72] C. B. Murray, C. R. Kagan, and M. G. Bawendi, "Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies," *Annu. Rev. Mater. Sci.*, vol. 30, no. 1, pp. 545–610, Aug. 2000.

[73] M. Rani, U. Shanker, and V. Jassal, "Recent strategies for removal and degradation of persistent & toxic organochlorine pesticides using nanoparticles: A review," *Journal of Environmental Management*, vol. 190. Academic Press, pp. 208–222, 01-Apr-2017.

[74] S. Sood, A. Umar, S. K. Mehta, and S. K. Kansal, "Highly effective Fe-doped TiO2 nanoparticles photocatalysts for visible-light driven photocatalytic degradation of toxic organic compounds," *J. Colloid Interface Sci.*, vol. 450, pp. 213–223, Jul. 2015.

[75] H. Cederlund, E. Börjesson, D. Lundberg, and J. Stenström, "Adsorption of Pesticides with Different Chemical Properties to a Wood Biochar Treated with Heat and Iron," *Water. Air. Soil Pollut.*, vol. 227, no. 6, pp. 1–12, Jun. 2016.

[76] R. J. Gilliom, "Pesticides in U.S. streams and groundwater," *Environmental Science and Technology*, vol. 41, no. 10. American Chemical Society, pp. 3409–3414, 15-May-2007.

[77] G. Z. Memon, M. I. Bhanger, M. Akhtar, F. N. Talpur, and J. R. Memon, "Adsorption of methyl parathion pesticide from water using watermelon peels as a low cost adsorbent," *Chem. Eng. J.*, vol. 138, no. 1–3, pp. 616–621, May 2008.

[78] L. San-Pedro, R. Méndez-Novelo, E. Hernández-Núñez, M. Flota-Bañuelos, J. Medina, and G. Giacomán-Vallejos, "Selection of the activated carbon type for the treatment of landfill leachate by fenton-adsorption process," *Molecules*, vol. 25, no. 13, Jul. 2020.

[79] K. C. Khulbe and T. Matsuura, “Removal of heavy metals and pollutants by membrane adsorption techniques,” *Appl. Water Sci.*, vol. 8, no. 1, p. 19, Mar. 2018.

[80] A. L. Cazetta *et al.*, “Magnetic Activated Carbon Derived from Biomass Waste by Concurrent Synthesis: Efficient Adsorbent for Toxic Dyes,” *ACS Sustain. Chem. Eng.*, vol. 4, no. 3, pp. 1058–1068, Mar. 2016.

[81] Y. Cao and X. Li, “Adsorption of graphene for the removal of inorganic pollutants in water purification: A review,” *Adsorption*, vol. 20, no. 5–6. Kluwer Academic Publishers, pp. 713–727, 25-Jun-2014.

[82] K. Madej, K. Janiga, and W. Piekoszewski, “The potential of graphene as an adsorbent for five pesticides from different classes in rape oil samples using dispersive solid-phase extraction,” *J. Anal. Methods Chem.*, vol. 2018, 2018.

[83] C. Zhang *et al.*, “Preparation of cellulose/graphene composite and its applications for triazine pesticides adsorption from water,” *ACS Sustain. Chem. Eng.*, vol. 3, no. 3, pp. 396–405, Mar. 2015.

[84] N. Cândido Homem *et al.*, “Surface Modification of Microfiltration Membrane with GO Nanosheets for Dyes Removal from Aqueous Solutions TSSiPRO-Technologies for Sustainable and Smart Innovative Products View project Modeling, simulation and optimization of sodium bicarbonate production in ethanol distilleries View project Surface Modification of Microfiltration Membrane with GO Nanosheets for Dyes Removal from Aqueous Solutions,” in *CHEMICAL ENGINEERING TRANSACTIONS*, 2017, vol. 60, p. 2017.

[85] G. Enaime, A. Baçaoui, A. Yaacoubi, and M. Lübken, “Biochar for Wastewater Treatment—Conversion Technologies and Applications,” *Appl. Sci.*, vol. 10, no. 10, p. 3492, May 2020.

[86] S. De Gisi, G. Lofrano, M. Grassi, and M. Notarnicola, “Characteristics and

adsorption capacities of low-cost sorbents for wastewater treatment: A review," *Sustainable Materials and Technologies*, vol. 9. Elsevier B.V., pp. 10–40, 01-Sep-2016.

[87] Faheem, J. Du, S. H. Kim, M. A. Hassan, S. Irshad, and J. Bao, "Application of biochar in advanced oxidation processes: supportive, adsorptive, and catalytic role," *Environmental Science and Pollution Research*, vol. 27, no. 30. Springer Science and Business Media Deutschland GmbH, pp. 37286–37312, 01-Oct-2020.

[88] A. F. Hassan, H. Elhadidy, and A. M. Abdel-Mohsen, "Adsorption and photocatalytic detoxification of diazinon using iron and nanotitania modified activated carbons," *J. Taiwan Inst. Chem. Eng.*, vol. 75, pp. 299–306, Jun. 2017.

[89] M. M. Jacob, M. Ponnuchamy, A. Kapoor, and P. Sivaraman, "Bagasse based biochar for the adsorptive removal of chlorpyrifos from contaminated water," *J. Environ. Chem. Eng.*, vol. 8, no. 4, p. 103904, Aug. 2020.

[90] A. Mandal and N. Singh, "Optimization of atrazine and imidacloprid removal from water using biochars: Designing single or multi-staged batch adsorption systems," *Int. J. Hyg. Environ. Health*, vol. 220, no. 3, pp. 637–645, May 2017.

[91] A. I, A. OML, Alo. ZA, A.-M. AM, and A. A, "Modeling of fenuron pesticide adsorption on CNTs for mechanistic insight and removal in water," *Environ. Res.*, vol. 170, pp. 389–397, Mar. 2019.

[92] T. Liu *et al.*, "A review on removal of organophosphorus pesticides in constructed wetland: Performance, mechanism and influencing factors," *Sci. Total Environ.*, vol. 651, pp. 2247–2268, Feb. 2019.

[93] S. S. Hassan, M. A. Al-Ghouti, M. Abu-Dieyeh, and G. McKay, "Novel bioadsorbents based on date pits for organophosphorus pesticide remediation from water," *J. Environ. Chem. Eng.*, vol. 8, no. 1, p. 103593, Feb. 2020.

[94] F. Suo *et al.*, “Mesoporous activated carbon from starch for superior rapid pesticides removal,” *Int. J. Biol. Macromol.*, vol. 121, pp. 806–813, Jan. 2019.

[95] M. Behloul, H. Grib, N. Drouiche, N. Abdi, H. Lounici, and N. Mameri, “Removal of Malathion Pesticide from Polluted Solutions by Electrocoagulation: Modeling of Experimental Results using Response Surface Methodology,” *Sep. Sci. Technol.*, vol. 48, no. 4, pp. 664–672, Jan. 2013.

[96] S. Mostafalou and M. Abdollahi, “Pesticides and human chronic diseases: Evidences, mechanisms, and perspectives,” *Toxicology and Applied Pharmacology*, vol. 268, no. 2. pp. 157–177, 05-Apr-2013.

[97] N. M. Ghalwa and N. B. Farhat, “Removal of Imidacloprid Pesticide by Electrocoagulation Process using Iron and aluminum Electrodes,” 2015.

[98] M. Behloul, H. Grib, N. Drouiche, N. Abdi, H. Lounici, and N. Mameri, “Removal of Malathion Pesticide from Polluted Solutions by Electrocoagulation: Modeling of Experimental Results using Response Surface Methodology,” *Sep. Sci. Technol.*, vol. 48, no. 4, pp. 664–672, Jan. 2013.

[99] M. S. Ramya Sankar and V. Sivasubramanian, “Optimization and evaluation of malathion removal by electrocoagulation process and sludge management,” *J. Environ. Chem. Eng.*, vol. 9, no. 5, p. 106147, Oct. 2021.

[100] S. B. and Z. B. K. Benahmed Daij, “Comparative experimental study on the COD removal in aqueous solution of pesticides by the electrocoagulation process using monopolar iron electrodes,” pp. 420–427, 2019.

[101] M. Muñoz, J. Llanos, A. Raschitor, P. Cañizares, and M. A. Rodrigo, “Electrocoagulation as the Key for an Efficient Concentration and Removal of Oxyfluorfen from Liquid Wastes,” *Ind. Eng. Chem. Res.*, vol. 56, no. 11, pp. 3091–3097, Mar. 2017.

[102] S. John, P. A. Soloman, and P. A. Fasnabi, “Study on Removal of Acetamiprid from Wastewater by Electrocoagulation,” *Procedia Technol.*, vol. 24, pp. 619–630, Jan. 2016.

[103] N. Ghalwa MA, “Removal of Imidacloprid Pesticide by Electrocoagulation Process using Iron and aluminum Electrodes,” *J. Environ. Anal. Chem.*, vol. 02, no. 04, 2015.

[104] G. A and N. M, “Removal of Abamectin Pesticide by Electrocoagulation Process Using Stainless Steel and Iron Electrodes,” *J. Environ. Anal. Chem.*, vol. 02, no. 03, 2015.

[105] H. D. Burrows, M. Canle, J. A. Santaballa, and S. Steenken, “Invited Review R eaction pathways and mechanisms of photodegradation of pesticides,” 2002.

[106] S. Kumar, W. Ahlawat, G. Bhanjana, S. Heydarifard, M. M. Nazhad, and N. Dilbaghi, “Nanotechnology-based water treatment strategies,” *Journal of Nanoscience and Nanotechnology*, vol. 14, no. 2. pp. 1838–1858, Feb-2014.

[107] K. Sivagami, R. R. Krishna, and T. Swaminathan, “Photo catalytic degradation of pesticides in immobilized bead photo reactor under solar irradiation,” *Sol. Energy*, vol. 103, pp. 488–493, May 2014.

[108] M. Mahalakshmi, B. Arabindoo, M. Palanichamy, and V. Murugesan, “Photocatalytic degradation of carbofuran using semiconductor oxides,” *J. Hazard. Mater.*, vol. 143, no. 1–2, pp. 240–245, May 2007.

[109] T. Katagi, “Direct photolysis mechanism of pesticides in water,” *J. Pestic. Sci.*, vol. 43, no. 2, pp. 57–72, 2018.

[110] T. Katagi, “Photodegradation of pesticides on plant and soil surfaces,” *Rev. Environ. Contam. Toxicol.*, vol. 182, pp. 1–195, 2004.

[111] T. Kromer, H. Ophoff, A. Stork, and F. Führ, “Photodegradation and volatility of

pesticides: chamber experiments.," *Environ. Sci. Pollut. Res. Int.*, vol. 11, no. 2, pp. 107–20, 2004.

[112] M. Rani, J. Yadav, Keshu, and U. Shanker, "Green synthesis of sunlight responsive zinc oxide coupled cadmium sulfide nanostructures for efficient photodegradation of pesticides," *J. Colloid Interface Sci.*, vol. 601, pp. 689–703, Nov. 2021.

[113] S. Ferhi *et al.*, "Pilot-scale direct UV-C photodegradation of pesticides in groundwater and recycled wastewater for agricultural use," *J. Environ. Chem. Eng.*, vol. 9, no. 5, p. 106120, Oct. 2021.

[114] V. K. Gupta, T. Eren, N. Atar, M. L. Yola, C. Parlak, and H. Karimi-Maleh, "CoFe2O4@TiO2 decorated reduced graphene oxide nanocomposite for photocatalytic degradation of chlorpyrifos," *J. Mol. Liq.*, vol. 208, pp. 122–129, Aug. 2015.

[115] K. Sivagami, B. Vikraman, R. R. Krishna, and T. Swaminathan, "Chlorpyrifos and Endosulfan degradation studies in an annular slurry photo reactor," *Ecotoxicol. Environ. Saf.*, vol. 134, pp. 327–331, Dec. 2016.

[116] N. Bustos, A. Cruz-Alcalde, A. Iriel, A. Fernández Cirelli, and C. Sans, "Sunlight and UVC-254 irradiation induced photodegradation of organophosphorus pesticide dichlorvos in aqueous matrices," *Sci. Total Environ.*, vol. 649, pp. 592–600, Feb. 2019.

[117] L. Lian, B. Jiang, Y. Xing, and N. Zhang, "Identification of photodegradation product of organophosphorus pesticides and elucidation of transformation mechanism under simulated sunlight irradiation," *Ecotoxicol. Environ. Saf.*, vol. 224, p. 112655, Nov. 2021.

[118] M. Cruz *et al.*, "Bare TiO2 and graphene oxide TiO2 photocatalysts on the degradation of selected pesticides and influence of the water matrix," *Appl. Surf.*

Sci., vol. 416, pp. 1013–1021, Sep. 2017.

[119] H. Lin, K. Pang, Y. Ma, and J. Hu, "Photodegradation of fluazaindolizine in water under simulated sunlight irradiation: Identification of transformation products and elucidation of transformation mechanism," *Chemosphere*, vol. 214, pp. 543–552, Jan. 2019.

[120] M. Laura, E. Snchez-Salinas, E. Dantn Gonzlez, and M. Luisa, "Pesticide Biodegradation: Mechanisms, Genetics and Strategies to Enhance the Process," in *Biodegradation - Life of Science*, InTech, 2013.

[121] J. P. Verma, D. K. Jaiswal, and R. Sagar, "Pesticide relevance and their microbial degradation: a-state-of-art," *Reviews in Environmental Science and Biotechnology*, vol. 13, no. 4. Kluwer Academic Publishers, pp. 429–466, 01-Dec-2014.

[122] M. Laura, E. Snchez-Salinas, A. Olvera-Velona, and J. Luis, "Pesticides in the Environment: Impacts and its Biodegradation as a Strategy for Residues Treatment," in *Pesticides - Formulations, Effects, Fate*, InTech, 2011.

[123] R. Chamy and F. Rosenkranz, *Biodegradation - Life of Science*. InTech, 2013.

[124] M. Laura, E. Snchez-Salinas, E. Dantn Gonzlez, and M. Luisa, "Pesticide Biodegradation: Mechanisms, Genetics and Strategies to Enhance the Process," in *Biodegradation - Life of Science*, InTech, 2013.

[125] V. I. Lushchak, T. M. Matviishyn, V. V. Husak, J. M. Storey, and K. B. Storey, "Pesticide toxicity: A mechanistic approach," *EXCLI Journal*, vol. 17. Leibniz Research Centre for Working Environment and Human Factors, pp. 1101–1136, 2018.

[126] J. J. Menn, "Comparative Aspects of Pesticide Metabolism in Plants and Animals," 1978.

[127] N. Gaur, K. Narasimhulu, and Y. PydiSetty, “Recent advances in the bio-remediation of persistent organic pollutants and its effect on environment,” *J. Clean. Prod.*, vol. 198, pp. 1602–1631, Oct. 2018.

[128] W. Tang, H. Ji, and X. Hou, “Research Progress of Microbial Degradation of Organophosphorus Pesticides 1 . The status of organophosphorus pesticides 2 . Study on Pesticide Degradation Bacteria,” pp. 29–35, 2017.

[129] R. S. Horvath, “Microbial co-metabolism and the degradation of organic compounds in nature.,” *Bacteriol. Rev.*, vol. 36, no. 2, p. 146, 1972.

[130] Y. Huang *et al.*, “Microbial degradation of pesticide residues and an emphasis on the degradation of cypermethrin and 3-phenoxy benzoic acid: A review,” *Molecules*, vol. 23, no. 9. MDPI AG, 11-Sep-2018.

[131] C. Sun, C. Chen, W. Ma, and J. Zhao, “Photodegradation of organic pollutants catalyzed by iron species under visible light irradiation,” *Phys. Chem. Chem. Phys.*, vol. 13, no. 6, pp. 1957–1969, Feb. 2011.

[132] J. Zhao *et al.*, “Mechanism of β-cypermethrin metabolism by Bacillus cereus GW-01,” *Chem. Eng. J.*, vol. 430, p. 132961, Feb. 2022.

[133] I. A. Saleh, N. Zouari, and M. A. Al-Ghouti, “Removal of pesticides from water and wastewater: Chemical, physical and biological treatment approaches,” *Environ. Technol. Innov.*, vol. 19, p. 101026, Aug. 2020.

[134] R. Avila *et al.*, “Evaluation of an outdoor pilot-scale tubular photobioreactor for removal of selected pesticides from water,” *Sci. Total Environ.*, vol. 804, Jan. 2022.

[135] B. P. Patel and A. Kumar, “Biodegradation and Co-Metabolism of Monochlorophenols and 2,4-Dichlorophenol by Microbial Consortium,” *CLEAN – Soil, Air, Water*, vol. 45, no. 9, p. 1700329, Sep. 2017.

[136] M. L. Ortiz-Hernández, E. Sánchez-Salinas, EdgarDantán-González, and M. L. Castrejón-Godínez, "Pesticide Biodegradation: Mechanisms, Genetics and Strategies to Enhance the Process," *Biodegrad. - Life Sci.*, Jun. 2013.

[137] B. S, K. PS, and V. DN, "A review on the microbial degradation of chlorpyrifos and its metabolite TCP," *Chemosphere*, vol. 283, Nov. 2021.

[138] R. Avila *et al.*, "Evaluation of an outdoor pilot-scale tubular photobioreactor for removal of selected pesticides from water," *Sci. Total Environ.*, vol. 804, p. 150040, Jan. 2022.

[139] M. H. Hussein, A. M. Abdullah, N. I. B. El Din, and E. S. I. Mishaqa, "Biosorption Potential of the Microchlorophyte Chlorella vulgaris for Some Pesticides," *J. Agric. Sci. Food Res.*, vol. 8, no. 1, pp. 1–5, 2017.

[140] A. Kumar, A. Sharma, P. Chaudhary, and S. Gangola, "Chlorpyrifos degradation using binary fungal strains isolated from industrial waste soil," *Biologia (Bratisl).*, vol. 76, no. 10, pp. 3071–3080, Oct. 2021.

[141] V. R. Góngora-Echeverría, R. García-Escalante, R. Rojas-Herrera, G. Giácoman-Vallejos, and C. Ponce-Caballero, "Pesticide bioremediation in liquid media using a microbial consortium and bacteria-pure strains isolated from a biomixture used in agricultural areas," *Ecotoxicol. Environ. Saf.*, vol. 200, p. 110734, Sep. 2020.

[142] D. M. Dash and W. J. Osborne, "Rapid biodegradation and biofilm-mediated bioremoval of organophosphorus pesticides using an indigenous Kosakonia oryzae strain -VITPSCQ3 in a Vertical-flow Packed Bed Biofilm Bioreactor," *Ecotoxicol. Environ. Saf.*, vol. 192, p. 110290, Apr. 2020.

[143] E. Bouteh, N. Ahmadi, M. Abbasi, A. Torabian, M. C. M. van Loosdrecht, and J. Ducoste, "Biodegradation of organophosphorus pesticides in moving bed biofilm reactors: Analysis of microbial community and biodegradation pathways," *J.*

Hazard. Mater., vol. 408, p. 124950, Apr. 2021.

[144] J. Nie *et al.*, "Bioremediation of water containing pesticides by microalgae: Mechanisms, methods, and prospects for future research," *Sci. Total Environ.*, vol. 707, Mar. 2020.

[145] "Agrochemicals | Agricultural Materials Co. Qatar." [Online]. Available: https://amcqa.com/pesticides-2/. [Accessed: 13-Sep-2022].

[146] S. H. Abd-Alrahman and M. M. Almaz, "Dissipation rate of different commercial formulations of propamocarb-hydrochloride applied to potatoes using HPLC–DAD," *Arab. J. Chem.*, vol. 9, pp. S1402–S1405, Nov. 2016.

[147] N. S. Sipes *et al.*, "Profiling 976 ToxCast chemicals across 331 enzymatic and receptor signaling assays," *Chem. Res. Toxicol.*, vol. 26, no. 6, pp. 878–895, Jun. 2013.

[148] U. Epa and O. of Pesticide Programs, "US EPA - Pesticides - Fact Sheet for Fluroxypyr," 1998.

[149] C. O. Knowles and H. J. Benezet, "Microbial degradation of the carbamate pesticides desmedipham, phenmedipham, promecarb, and propamocarb," *Bull. Environ. Contam. Toxicol.*, vol. 27, no. 1, pp. 529–533, 1981.

[150] C. K. Myresiotis, Z. Vryzas, and E. Papadopoulou-Mourkidou, "Biodegradation of soil-applied pesticides by selected strains of plant growth-promoting rhizobacteria (PGPR) and their effects on bacterial growth," *Biodegradation*, vol. 23, no. 2, pp. 297–310, Apr. 2012.

[151] E. Ardal, "Phycoremediation of pesticides using microalgae Möjligheter med odling av mikroalger för rening av," 2014.

[152] K. A. Kvenvolden and C. K. Cooper, "Natural seepage of crude oil into the marine environment," *Geo-Marine Lett. 2003 233*, vol. 23, no. 3, pp. 140–146, Oct. 2003.

[153] A. Medić *et al.*, “Efficient biodegradation of petroleum: N -alkanes and polycyclic aromatic hydrocarbons by polyextremophilic Pseudomonas aeruginosa san ai with multidegradative capacity,” *RSC Adv.*, vol. 10, no. 24, pp. 14060–14070, Apr. 2020.

[154] E. B. Mouafo Tamnou *et al.*, “Biodegradation of polyethylene by the bacterium Pseudomonas aeruginosa in acidic aquatic microcosm and effect of the environmental temperature,” *Environ. Challenges*, vol. 3, p. 100056, Apr. 2021.

[155] K. K. Gupta and D. Devi, “Characteristics investigation on biofilm formation and biodegradation activities of Pseudomonas aeruginosa strain ISJ14 colonizing low density polyethylene (LDPE) surface,” *Heliyon*, vol. 6, no. 7, p. e04398, Jul. 2020.

[156] M. P. Shah, “Bioremedial Application of Pseudomonas aeruginosa in Waste Water Treatment,” *Austin J. Biotechnol. Bioeng.*, vol. 4, no. 1, 2017.

[157] A. U. Khan, M. Ur Rehman, M. Zahoor, A. B. Shah, and I. Zekker, “Biodegradation of brown 706 dye by bacterial strain pseudomonas aeruginosa,” *Water (Switzerland)*, vol. 13, no. 21, p. 2959, Oct. 2021.

[158] M. H. Fulekar and M. Geetha, “Bioremediation of Chlorpyrifos by Pseudomonas aeruginosa using scale up technique,” *J. Appl. Biosci.*, vol. 12, pp. 657–660, 2008.

[159] H. A. Kharabsheh, S. Han, S. Allen, and S. L. Chao, “Metabolism of chlorpyrifos by Pseudomonas aeruginosa increases toxicity in adult zebrafish (Danio rerio),” *Int. Biodeterior. Biodegrad.*, vol. 121, pp. 114–121, Jul. 2017.

[160] A. O. Hussain Al-Janabi and H. S. Hashim, “Efficiency of Pseudomonas putida in bioremediation of chlorpyrifos toxicity,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 722, no. 1, p. 012040, Apr. 2021.

[161] S. Varjani, V. N. Upasani, and A. Pandey, “Bioremediation of oily sludge polluted soil employing a novel strain of Pseudomonas aeruginosa and phytotoxicity of

petroleum hydrocarbons for seed germination," *Sci. Total Environ.*, vol. 737, Oct. 2020.

[162] S. Sun *et al.*, "A biosurfactant-producing Pseudomonas aeruginosa S5 isolated from coking wastewater and its application for bioremediation of polycyclic aromatic hydrocarbons," *Bioresour. Technol.*, vol. 281, pp. 421–428, Jun. 2019.

[163] K. J. Rockne, J. C. Chee-Sanford, R. A. Sanford, B. P. Hedlund, J. T. Staley, and S. E. Strand, "Anaerobic Naphthalene Degradation by Microbial Pure Cultures under Nitrate-Reducing Conditions," *Appl. Environ. Microbiol.*, vol. 66, no. 4, p. 1595, Apr. 2000.

[164] E. R. Chellaiah, "Cadmium (heavy metals) bioremediation by Pseudomonas aeruginosa: a minireview," *Appl. Water Sci.*, vol. 8, no. 6, pp. 1–10, Sep. 2018.

[165] S. Lata, T. Mishra, and H. P. Kaur, "CADMIUM BIOREMEDIATION: A REVIEW," *Int. J. Pharm. Sci. Res.*, vol. 10, no. 9, p. 4120, 2019.

[166] S. Sinha and S. K. Mukherjee, "Pseudomonas aeruginosa KUCd1, a possible candidate for cadmium bioremediation," *Brazilian J. Microbiol.*, vol. 40, no. 3, pp. 655–662, 2009.

[167] M. F. Imron, S. B. Kurniawan, and S. R. S. Abdullah, "Resistance of bacteria isolated from leachate to heavy metals and the removal of Hg by Pseudomonas aeruginosa strain FZ-2 at different salinity levels in a batch biosorption system," *Sustain. Environ. Res.*, vol. 31, no. 1, 2021.

[168] B. Gworek, W. Dmuchowski, D. Gozdowski, E. Koda, R. Osiecka, and J. Borzyszkowski, "Influence of a municipal waste landfill on the spatial distribution of mercury in the environment," *PLoS One*, vol. 10, no. 7, p. e0133130, Jul. 2015.

[169] L. Neneng and Y. Gunawan, "The Role of Coenzymes on Mercury (Hg2+) Bioremediation by Isolates Pseudomonas aeruginosa KHY2 and Klebsiella

pneumonia KHY3," *J. Trop. Life Sci.*, vol. 8, no. 1, pp. 16–20, Jan. 2018.

[170] I. F. Purwanti, S. B. Kurniawan, and M. F. Imron, "Potential of Pseudomonas aeruginosa isolated from aluminium-contaminated site in aluminium removal and recovery from wastewater," *Environ. Technol. Innov.*, vol. 15, Aug. 2019.

[171] S. Sinha and S. K. Mukherjee, "Cadmium-induced siderophore production by a high Cd-resistant bacterial strain relieved Cd toxicity in plants through root colonization," *Curr. Microbiol.*, vol. 56, no. 1, pp. 55–60, Jan. 2008.

[172] R. Kaur, G. K. Mavi, and S. Raghav, "Bioremediation of Sludge using Pseudomonas aeruginosa," *Int. J. Curr. Microbiol. Appl. Sci.*, vol. 8, no. 04, pp. 69–79, 2019.

[173] H. AA, K. KK, A. I, M. Y, and O. EE, "Evaluation of Heavy Metal Tolerance Level (MIC) and Bioremediation Potentials of Pseudomonas aeruginosa Isolated from Makera-Kakuri Industrial Drain in Kaduna, Nigeria," *Eur. J. Exp. Biol.*, vol. 7, no. 5, p. 28, 2017.

[174] J. De, J. Leonhäuser, and L. Vardanyan, "Removal of mercury in fixed-bed continuous upflow reactors by mercury-resistant bacteria and effect of sodium chloride on their performance," *QScience Connect*, vol. 2014, no. 1, Mar. 2014.

[175] T. Mehrotra, S. Dev, A. Banerjee, A. Chatterjee, R. Singh, and S. Aggarwal, "Use of immobilized bacteria for environmental bioremediation: A review," *J. Environ. Chem. Eng.*, vol. 9, no. 5, Oct. 2021.

[176] Z. B. Bouabidi, M. H. El-Naas, and Z. Zhang, "Immobilization of microbial cells for the biotreatment of wastewater: A review," *Environ. Chem. Lett. 2018 171*, vol. 17, no. 1, pp. 241–257, Sep. 2018.

[177] T. Jesionowski, J. Zdarta, and B. Krajewska, "Enzyme immobilization by adsorption: A review," *Adsorption*, vol. 20, no. 5–6. Kluwer Academic Publishers,

pp. 801–821, 27-Jun-2014.

[178] L. W. Powell, “Developments in Immobilized-Enzyme technology,” *Biotechnol. Genet. Eng. Rev.*, vol. 2, no. 1, pp. 409–438, 1984.

[179] Z. B. Bouabidi, M. H. El-Naas, and Z. Zhang, “Immobilization of microbial cells for the biotreatment of wastewater: A review,” *Environ. Chem. Lett. 2018 171*, vol. 17, no. 1, pp. 241–257, Sep. 2018.

[180] Y. K. Cen, Y. X. Liu, Y. P. Xue, and Y. G. Zheng, “Immobilization of Enzymes in/on Membranes and their Applications,” *Adv. Synth. Catal.*, vol. 361, no. 24, pp. 5500–5515, Dec. 2019.

[181] R. Abdel-Karim, “Sensing Materials: Nanostructured Biomaterials,” *Ref. Modul. Biomed. Sci.*, 2021.

[182] T. Jesionowski, J. Zdarta, and B. Krajewska, “Enzyme immobilization by adsorption: A review,” *Adsorption*, vol. 20, no. 5–6, pp. 801–821, Jun. 2014.

[183] E. C. Giese and E. C. Giese, “MINING APPLICATIONS OF IMMOBILIZED MICROBIAL CELLS IN AN ALGINATE MATRIX: AN OVERVIEW,” *Rev. Int. Contam. Ambient.*, vol. 36, no. 3, pp. 775–787, 2020.

[184] L. W. Powell, “Developments in Immobilized-Enzyme technology,” *Biotechnol. Genet. Eng. Rev.*, vol. 2, no. 1, pp. 409–438, 1984.

[185] T. Mehrotra, S. Dev, A. Banerjee, A. Chatterjee, R. Singh, and S. Aggarwal, “Use of immobilized bacteria for environmental bioremediation: A review,” *J. Environ. Chem. Eng.*, vol. 9, no. 5, p. 105920, Oct. 2021.

[186] S. Khalid *et al.*, “Strengthening calcium alginate microspheres using polysulfone and its performance evaluation: Preparation, characterization and application for enhanced biodegradation of chlorpyrifos,” *Sci. Total Environ.*, vol. 631–632, pp. 1046–1058, Aug. 2018.

[187] F.-L. MG *et al.*, “Enhancing methyl parathion degradation by the immobilization of Burkholderia sp. isolated from agricultural soils,” *Microbiologyopen*, vol. 6, no. 5, Oct. 2017.

[188] S. T, M. J, S. M, Z. H, Y. Y, and Z. Q, “Bacterial compatibility and immobilization with biochar improved tebuconazole degradation, soil microbiome composition and functioning,” *J. Hazard. Mater.*, vol. 398, Nov. 2020.

[189] J. Liu *et al.*, “Enhanced degradation of prometryn and other s-triazine herbicides in pure cultures and wastewater by polyvinyl alcohol-sodium alginate immobilized Leucobacter sp. JW-1,” *Sci. Total Environ.*, vol. 615, pp. 78–86, Feb. 2018.

[190] S. JY, R. NL, G. PD, N. ML, L. ES, and I. AM, “Organophosphorus compounds biodegradation by novel bacterial isolates and their potential application in bioremediation of contaminated water,” *Bioresour. Technol.*, vol. 317, Dec. 2020.

[191] Z. B *et al.*, “Bead-immobilized Pseudomonas stutzeri Y2 prolongs functions to degrade s-triazine herbicides in industrial wastewater and maize fields,” *Sci. Total Environ.*, vol. 731, Aug. 2020.

[192] W. AQ, A. S, M. JA, A. M, and I. S, “Immobilization of metribuzin degrading bacterial consortium MB3R on biochar enhances bioremediation of potato vegetated soil and restores bacterial community structure,” *J. Hazard. Mater.*, vol. 390, May 2020.

[193] C.-J. Tien, H.-J. Huang, and C. S. Chen, “Accessing the Carbofuran Degradation Ability of Cultures From Natural River Biofilms in Different Environments,” *CLEAN – Soil, Air, Water*, vol. 45, no. 5, p. 1600380, May 2017.

[194] F. L *et al.*, “Enhanced biodegradation of organophosphorus insecticides in industrial wastewater via immobilized Cupriavidus nantongensis X1 T,” *Sci. Total Environ.*, vol. 755, no. Pt 1, Feb. 2021.

[195] A. S. Purnomo, “Microbe-Assisted Degradation of Aldrin and Dieldrin,” *Environ. Sci. Eng. (Subseries Environ. Sci.*, no. 9783319451558, pp. 1–22, 2017.

[196] S. B. Eskander and H. M. Saleh, “Biodegradation : Process Mechanism,” *Biodegrad. Bioremediat.*, vol. 8, no. January, pp. 1–31, 2017.

[197] S. Jilani, “Comparative assessment of growth and biodegradation potential of soil isolate in the presence of pesticides,” *Saudi J. Biol. Sci.*, vol. 20, no. 3, p. 257, Jul. 2013.

[198] D. Berillo, A. Al-Jwaid, and J. Caplin, “Polymeric materials used for immobilisation of bacteria for the bioremediation of contaminants in water,” *Polymers (Basel).*, vol. 13, no. 7, 2021.

[199] M. K. Yazdi *et al.*, “Hydrogel membranes: A review,” *Mater. Sci. Eng. C*, vol. 114, p. 111023, Sep. 2020.

[200] W. W. Anku, M. A. Mamo, and P. P. Govender, “Phenolic Compounds in Water: Sources, Reactivity, Toxicity and Treatment Methods,” *Phenolic Compd. - Nat. Sources, Importance Appl.*, Mar. 2017.

[201] S. Cláudia, S. Martins, C. M. Martins, L. M. Cidrão, G. Fiúza, and S. T. Santaella, “Immobilization of microbial cells: A promising tool for treatment of toxic pollutants in industrial wastewater,” *African J. Biotechnol.*, vol. 12, no. 28, p. 4473, Apr. 2016.

[202] M. H. El-Naas, S. A. Al-Muhtaseb, and S. Makhlouf, “Biodegradation of phenol by Pseudomonas putida immobilized in polyvinyl alcohol (PVA) gel,” *J. Hazard. Mater.*, vol. 164, no. 2–3, pp. 720–725, May 2009.

[203] and D. P. J. S Sihag, H Pathak., “Factors Affecting the Rate of Biodegradation of Polyaromatic Hydrocarbons,” *Int. J. Pure Appl. Biosci.*, vol. 2, no. 3, pp. 185–202, 2014.

[204] L. R. Frederick, “Introduction to Soil Microbiology,” *Agron. J.*, vol. 54, no. 3, pp. 280–280, May 1962.

[205] B. W. Bogan, B. Schoenike, R. T. Lamar, and D. Cullen, “Expression of lip genes during growth in soil and oxidation of anthracene by Phanerochaete chrysosporium,” *Appl. Environ. Microbiol.*, vol. 62, no. 10, pp. 3697–3703, 1996.

[206] G. Yañez-Ocampo, E. Sanchez-Salinas, G. A. Jimenez-Tobon, M. Penninckx, and M. L. Ortiz-Hernández, “Removal of two organophosphate pesticides by a bacterial consortium immobilized in alginate or tezontle,” *J. Hazard. Mater.*, vol. 168, no. 2–3, pp. 1554–1561, Sep. 2009.

[207] Z. Arbeli and C. L. Fuentes, “Accelerated biodegradation of pesticides: An overview of the phenomenon, its basis and possible solutions; and a discussion on the tropical dimension,” *Crop Protection*, vol. 26, no. 12. Elsevier, pp. 1733–1746, 01-Dec-2007.

[208] S. Z. Mazlan and S. A. Hanifah, “Effects of Temperature and pH on Immobilized Laccase Activity in Conjugated Methacrylate-Acrylate Microspheres,” *Int. J. Polym. Sci.*, vol. 2017, 2017.

[209] S. H. Abd-Alrahman and M. M. Almaz, “Degradation of propamocarb-hydrochloride in tomatoes, potatoes and cucumber using HPLC-DAD and QuEChERS methodology,” *Bull. Environ. Contam. Toxicol.*, vol. 89, no. 2, pp. 302–305, Aug. 2012.

[210] D. W. Gao, Q. Hu, C. Yao, and N. Q. Ren, “Treatment of domestic wastewater by an integrated anaerobic fluidized-bed membrane bioreactor under moderate to low temperature conditions,” *Bioresour. Technol.*, vol. 159, pp. 193–198, May 2014.

[211] P. Ding, L. Chu, and J. Wang, “Biological treatment of actual petrochemical wastewater using anaerobic/anoxic/oxic process and the microbial diversity

analysis," *Appl. Microbiol. Biotechnol.*, vol. 100, no. 23, pp. 10193–10202, Dec. 2016.

[212] J. Wirsching *et al.*, "Biodegradation of Pesticides at the Limit: Kinetics and Microbial Substrate Use at Low Concentrations," *Front. Microbiol.*, vol. 11, p. 2107, Aug. 2020.

[213] Z. Ye, J. Song, E. Zhu, X. Song, X. Chen, and X. Hong, "Alginate adsorbent immobilization technique promotes biobutanol production by Clostridium acetobutylicum under extreme condition of high concentration of organic solvent," *Front. Microbiol.*, vol. 9, no. MAY, p. 1071, May 2018.

[214] B. Aslim and G. Alp, "The effect of immobilization on some probiotic properties of Streptococcus thermophilus strains," *Ann. Microbiol.*, vol. 59, no. 1, pp. 127–132, 2009.

[215] Q. Chen, J. Li, M. Liu, H. Sun, and M. Bao, "Study on the biodegradation of crude oil by free and immobilized bacterial consortium in marine environment," *PLoS One*, vol. 12, no. 3, p. e0174445, Mar. 2017.

[216] K. Luis, D. Francois, and P. Trevor, "Method for purifying Fischer-Tropsch derived water." pp. 1–25, 2003.

[217] M. T. Al Hattab and A. E. Ghaly, "Disposal and Treatment Methods for Pesticide Containing Wastewaters: Critical Review and Comparative Analysis," *J. Environ. Prot. (Irvine,. Calif).*, vol. 03, no. 05, pp. 431–453, May 2012.

[218] Z. Al Disi, S. Jaoua, D. Al-Thani, S. Al-Meer, and N. Zouari, "Considering the Specific Impact of Harsh Conditions and Oil Weathering on Diversity, Adaptation, and Activity of Hydrocarbon-Degrading Bacteria in Strategies of Bioremediation of Harsh Oily-Polluted Soils," *Biomed Res. Int.*, vol. 2017, 2017.

[219] R. Surkatti, M. H. El-Naas, M. C. M. Van Loosdrecht, A. Benamor, F. Al-Naemi,

and U. Onwusogh, “Biotechnology for gas-to-liquid (GTL)wastewater treatment: A review,” *Water (Switzerland)*, vol. 12, no. 8. MDPI AG, 01-Aug-2020.

[220] M. H. El-Naas, A. H. I. Mourad, and R. Surkatti, “Evaluation of the characteristics of polyvinyl alcohol (PVA) as matrices for the immobilization of Pseudomonas putida,” *Int. Biodeterior. Biodegrad.*, vol. 85, pp. 413–420, Nov. 2013.

[221] M. H. El-Naas, S. Al-Zuhair, and S. Makhlouf, “Batch degradation of phenol in a spouted bed bioreactor system,” *J. Ind. Eng. Chem.*, vol. 16, no. 2, pp. 267–272, Mar. 2010.

[222] M. H. El-Naas, S. Al-Zuhair, and S. Makhlouf, “Continuous biodegradation of phenol in a spouted bed bioreactor (SBBR),” *Chem. Eng. J.*, vol. 160, no. 2, pp. 565–570, Jun. 2010.

[223] M. H. El-Naas, S. Al-Zuhair, and M. A. Alhaija, “Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon,” *Chem. Eng. J.*, vol. 162, no. 3, pp. 997–1005, Sep. 2010.

[224] A. Kumar, S. Kumar, and S. Kumar, “Biodegradation kinetics of phenol and catechol using Pseudomonas putida MTCC 1194,” *Biochem. Eng. J.*, vol. 22, no. 2, pp. 151–159, Jan. 2005.

[225] T. Burns, “How to Reduce COD in Water | bioprocessH2O,” 2021. [Online]. Available: https://www.bioprocessh2o.com/blog/cod. [Accessed: 11-Sep-2022].

[226] M. H. El-Naas, S. Al-Zuhair, A. Al-Lobaney, and S. Makhlouf, “Assessment of electrocoagulation for the treatment of petroleum refinery wastewater,” *J. Environ. Manage.*, vol. 91, no. 1, pp. 180–185, Oct. 2009.

[227] C. You *et al.*, “Coordination of bacterial proteome with metabolism by cyclic AMP signalling,” *Nature*, vol. 500, no. 7462, pp. 301–306, 2013.

[228] M. Achrem *et al.*, “Role of epigenetic mechanisms in plant response to low

temperature," *Acta Biol. Cracoviensia Ser. Bot.*, vol. 54, no. 1, pp. 7–15, 2012.

[229] A. E. El Telib, M. H. El-Naas, and J. A. Acio, "Biodegradation of BTEX: Optimization through Response Surface Methodology," *Am. J. Eng. Appl. Sci. Orig. Res. Pap.*, 2017.

[230] T. Kameya, T. Murayama, K. Urano, and M. Kitano, "Biodegradation ranks of priority organic compounds under anaerobic conditions," *Sci. Total Environ.*, vol. 170, no. 1–2, pp. 43–51, Aug. 1995.

[231] S. Gangola *et al.*, "Biotechnological tools to elucidate the mechanism of pesticide degradation in the environment," *Chemosphere*, vol. 296, p. 133916, Jun. 2022.

[232] M. Cai, J. Yao, H. Yang, R. Wang, and K. Masakorala, "Aerobic biodegradation process of petroleum and pathway of main compounds in water flooding well of Dagang oil field," *Bioresour. Technol.*, vol. 144, pp. 100–106, Sep. 2013.

[233] R. E. Mckinney, J. S. Jeris, B. R. E. Mckinney, and J. S. Jeris, "Metabolism of Low Molecular Weight Alcohols by Activated Sludge Stable," *Sewage Ind. Waste.*, vol. 27, no. 6, pp. 728–735, 1955.

[234] M. H. El-Naas and R. Surkatti, "Nano-biomaterial for GTL process water treatment," 5600234.00500, 2022.

[235] B. Gopalakrishnan, A. Muthukumarapandian, S. Sujatha, S. Raja, N. Rajamohan, and M. Rajasimman, "Statistical modeling and optimization of tannery wastewater treatment in a fluidized bed bioreactor with low density biomass support," *Model. Earth Syst. Environ.*, vol. 8, no. 1, pp. 1099–1107, Mar. 2022.

[236] N. Azimi, A. H. Hassani, G. N. Darzi, and S. M. Borghei, "Biodegradation of wastewater containing high concentration of sulfamethoxazole by antibiotic adopted biofilm in attached growth bioreactor," *Polish J. Environ. Stud.*, vol. 26, no. 6, pp. 2463–2469, Nov. 2017.

[237] M. H. El-Naas, A. H. I. Mourad, and R. Surkatti, “Evaluation of the characteristics of polyvinyl alcohol (PVA) as matrices for the immobilization of Pseudomonas putida,” *Int. Biodeterior. Biodegrad.*, vol. 85, pp. 413–420, Mar. 2013.

[238] S. S. Mohanty and H. M. Jena, “Biodegradation of Herbicide by the Immobilized Microbial Consortium SMC1 in Continuous Packed-Bed Biofilm Reactor,” *Front. Chem. Eng.*, vol. 4, p. 44, Jun. 2022.

[239] J. A. Kawan, F. Suja’, S. K. Pramanik, A. Yusof, R. A. Rahman, and H. A. Hasan, “Effect of Hydraulic Retention Time on the Performance of a Compact Moving Bed Biofilm Reactor for Effluent Polishing of Treated Sewage,” *Water (Switzerland)*, vol. 14, no. 1, Jan. 2022.

[240] Y. Chen, J. J. Cheng, and K. S. Creamer, “Inhibition of anaerobic digestion process: A review,” *Bioresour. Technol.*, vol. 99, no. 10, pp. 4044–4064, Jul. 2008.

[241] M. H. El-Naas, A. F. Mohammad, M. I. Suleiman, M. Al Musharfy, and A. H. Al-Marzouqi, “Evaluation of a novel gas-liquid contactor/reactor system for natural gas applications,” *J. Nat. Gas Sci. Eng.*, vol. 39, pp. 133–142, Mar. 2017.

[242] B. California - OEHHA, “Organochlorine Pesticides Fact Sheet.”

[243] R. Jayaraj, P. Megha, and P. Sreedev, “Review Article. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment,” *Interdisciplinary Toxicology*, vol. 9, no. 3–4. Slovak Toxicology Society, pp. 90–100, 01-Dec-2016.

[244] A. K. Greaves, R. J. Letcher, D. Chen, D. J. McGoldrick, L. T. Gauthier, and S. M. Backus, “Retrospective analysis of organophosphate flame retardants in herring gull eggs and relation to the aquatic food web in the Laurentian Great Lakes of North America,” *Environ. Res.*, vol. 150, pp. 255–263, Oct. 2016.

[245] V. M. Monsalvo, J. A. McDonald, S. J. Khan, and P. Le-Clech, “Removal of trace

organics by anaerobic membrane bioreactors," *Water Res.*, vol. 49, pp. 103–112, Feb. 2014.

[246] P. Devendar and G. F. Yang, "Sulfur-Containing Agrochemicals," *Topics in Current Chemistry*, vol. 375, no. 6. Springer International Publishing, 01-Dec-2017.

APPENDIX

Table A 1: Main pesticides use, composition, examples, and characteristics [242]–[246]

Pesticides	Main composition	characteristics	examples	Fatal dose	Use
Organochlorines	Carbon, hydrogen, and chlorine atoms and rarely oxygen.	Organochlorines are nonpolar and lipophilic. Have high persistence and toxicity that causes health effects.	DDT, Chlorobenzoate, Lindane, BHC, Aldrin, Chlordane, Heptachlor, Eldrin, Dieldrin,	Dieldrin is placed in the extremely toxic category (LD 50: 1 to 50 mg/kg) DDT, endodulfan, and lidane are highly toxic (LD 50: 51 to 500 mg/kg)	Agriculture and pest control (e.g mosquitoes)
Organophosphates	Phosphorylated hydrocarbons. Phosphorus atom (P) in the center of the molecule. They are phosphoric acid Esters or Triphosphoric Esters	Compared whit organochlorines, organophosphates are more stable and less toxic in the environment. The primary mechanism of its toxicity is inhibition of acetylcholinesterase enzyme in the central and peripheral nervous system which kills pests and might have side effects to humans exposed to it.	Dimefox, Mipafox, Methyl Parathion, Ronnel, enitrothion	Extremely toxic category (LD 50: 1 to 50 mg/kg) to highly toxic (LD 50: 51 to 500 mg/kg) such as Chlorpyriphos, Disulfoton Ethion, etc..) Moderately toxic category (LD 50: 501 to 5000 mg/kg) to slightly toxic (LD 50: < 5000 mg/kg) such as Abate, Acephate, and Crufomate, etc..)	In agriculture, home gardens, and veterinary practices.

Table A 1: Main pesticides use, composition, examples, and characteristics.

Pesticides	Main composition	characteristics	examples	Fatal dose	Use	Ref
Pyrethroids	These substances like the synthetic pyrethrins (which are alkaloids obtained from petals of *Chysanthemun cinerariefolium*)	They are usually breaking apart by sunlight and the atmosphere in one or two days. Affect nerve membranes and increase the efficiency of insecticides by inhibiting the cytochrome D450 Enzymes responsible for the breakdown of the insecticide which leads to death.	Allethrin, Bonthrin, Dimethrin	Has an LD50 of over 1 gm/kg Most cases of toxicity are the results of allergic reactions		Kills a wide range of insects like ants, fleas, mosquitoes scale, lace bugs, and mealy bugs
Biological	Viruses, microorganisms, or their metabolic products.	Have a narrow target range and a highly specific mode of action suppress pests. Restricted field persistence Generally safe to people and environmen	B. thuringiensis		-	Kills pests
Herbicides	The most significant chemical groups are chlorophenoxy acids (e.g. 2,4-D and 2,4,5-T; triazines such as atrazine, hexazinone, and simazine)	less expensive, safer, faster, and occasionally more selective when compared with other alternatives of weed control. non-selective and might affect many plants and animals that are not weeds.	Acetanilides, alachlor, Barban chlorbromuron hlorophenoxy		-	to kill or control specific species of plants considered to be pests

Pesticides	Main composition	characteristics	examples	Fatal dose	Use
Carbamates	Compounds have a chemical structure based on a plant alkaloid *Physostigma venenosum, Structurally and mechanistically similar to organophosphate insecticides* Derived from carbamic acid	Like organophosphate, the primary mechanism of its toxicity is inhibition of acetylcholinesterase enzyme with the difference that the inhibition is more rapidly reversed. Toxicity, mortality, and mobility are limited and led compared to organophosphate Very low doses are needed to kill insects. Bind tightly to soil and organic compounds (thus, not as efficient in penetrating the soil to kill underground pests); almost insoluble water.	Methyl Carbaryl, Carbanolate Thio Vernolate, Pebulate, Diallate, Dithio Methan, Thiram, Ferban	Extremely toxic category (LD 50: 1 to 50 mg/kg) to highly toxic (LD 50: 51 to 500 mg/kg) such as Aminocarb, bendiocarb, and dioxacarb, etc..) Moderately toxic category (LD 50: 501 to 5000 mg/kg) to slightly toxic (LD 50: < 5000 mg/kg) such as Aldicarb, isoprocarb, and pirimicarb, etc..)	Used on crops and in-home to kill insects like ants, fleas, mosquitoes scale, lace bugs, and mealy bugs
Organosulfur	They have a sulfur central atom in the molecule, very toxic to mites or insects	Low toxicity to humans, however, sulfur can irritate skin and eyes, and spray vapors should not be inhaled. Non-toxic to birds, bees, and fish.	sulfonylureas, sulfonamides, sulfur-containing heterocyclics, thioureas, sulfides, sulfones, sulfoxides, and sulfoximines	-	Control pests such as black spots, rusts, other ornamentals, fruits, and vegetables. It is rarely used as a miticide.

Table A 2: The COD reduction % of GTL process wastewater under several combinations of conditions based on RSM experimental design using Minitab Version 20.

Run	COD	pH	PVA V%	Experimental R%
1	3000.00	5.00000	20.0000	69.89
2	2000.00	9.02269	25.0000	86.77
3	318.21	6.50000	25.0000	62.80
4	1000.00	8.00000	30.0000	72.16
5	2000.00	3.97731	25.0000	58.15
6	3681.79	6.50000	25.0000	83.27
7	2000.00	6.50000	33.4090	84.53
8	3000.00	8.00000	20.0000	77.41
9	2000.00	6.50000	25.0000	86.06
10	1000.00	8.00000	20.0000	78.69
11	2000.00	6.50000	25.0000	84.69
12	1000.00	5.00000	20.0000	58.00
13	2000.00	6.50000	25.0000	84.60
14	2000.00	6.50000	25.0000	88.00
15	2000.00	6.50000	25.0000	83.60
16	1000.00	5.00000	30.0000	72.11
17	3000.00	8.00000	30.0000	82.45
18	2000.00	6.50000	25.0000	88.49
19	3000.00	5.00000	30.0000	78.46
20	2000.00	6.50000	16.5910	42.86

Table A 3: The COD reduction % of propamocarb fungicides contaminated wastewater under several combinations of conditions conditions based on RSM experimental design using Minitab Version 20.

Run	COD	pH	PVA V%	Experimental R%
1	750.00	6.50	25.00	5.02
2	750.00	6.50	25.00	3.73
3	1000.00	8.00	30.00	42.10
4	750.00	9.02	25.00	8.84
5	329.55	6.50	25.00	4.58
6	750.00	3.98	25.00	2.07
7	750.00	6.50	25.00	8.26
8	500.00	8.00	30.00	36.09
9	500.00	5.00	30.00	2.67
10	1000.00	5.00	20.00	22.39
11	1000.00	8.00	20.00	10.67
12	750.00	6.50	25.00	8.96
13	1000.00	5.00	30.00	18.24
14	750.00	6.50	25.00	8.93
15	750.00	6.50	33.41	14.49
16	1170.45	6.50	25.00	3.38
17	500.00	8.00	20.00	16.63
18	500.00	5.00	20.00	22.03
19	750.00	6.50	16.59	8.50
20	750.00	6.50	25.00	6.98

Table A 4: The COD analysis as a function of time for two air flow rates of 2, and 3.3 La/Lr.min at liquid flow rate of 2.1 ml/min, temperature 32ºC and pH 7.3.

Time (hr)	$COD_{@2\ La/Lr.min}$ (mg/l)	$COD_{@3.3\ La/Lr.min}$ (mg/l)
0	2284	2200
1	2096	1700
2	1936	1590
4	1596	1400
6	1326	1160
8	1110	958
10	992	880
20	870	836
22	890	860
24	900	838

Table A 5: GTL step change in liquid flow rate (2.1 to 4.2 to 2.1 ml/min) experiment at air flow rate of 3.3 La/Lr.min , temperature 32ºC and pH 7.3.

Time	COD (mg/l)	Liquid flow rate (ml/min)
0	2186	2.1
1	1986	2.1
2	1652	2.1
4	1420	2.1
6	1238	2.1
8	1096	2.1
12	984	2.1
20	870	2.1
22	750	2.1
24	775	4.2
26	875	4.2
27	889	4.2
28	961	4.2
30	922	4.2
32	925	4.2
34	1082	4.2
36	1164	4.2
40	1342	4.2
48	1294	4.2
50	1115	2.1
56	885	2.1
58	842	2.1
60	824	2.1
62	794	2.1

Table A 6: GTL process water experimental COD reduction% vs predicted COD reduction%.

Number	Experimental COD reduction%	Predicted COD reduction%
1	69.89	70.60
2	86.77	82.79
3	62.80	67.89
4	72.16	76.27
5	58.15	63.20
6	83.27	76.53
7	84.53	75.44
8	77.41	71.82
9	86.06	83.52
10	78.69	70.50
11	84.69	83.52
12	58.00	50.50
13	84.60	83.52
14	88.00	83.52
15	83.60	83.52
16	72.11	68.36
17	82.45	80.61
18	88.49	83.52
19	78.46	77.32
20	42.86	53.03

Table A 7: propamocarb fungicide experimental COD reduction% vs predicted COD reduction%

Number	Experimental COD reduction%	Predicted COD reduction%
1	5.02	6.66
2	3.73	6.66
3	42.1	34.30
4	8.84	7.00
5	4.58	10.29
6	2.07	7.25
7	8.26	6.66
8	36.09	29.06
9	2.67	1.19
10	22.39	18.28
11	10.67	3.40
12	8.96	6.66
13	18.24	11.98
14	8.93	6.66
15	14.49	11.00
16	3.38	14.34
17	16.63	11.76
18	22.03	18.71
19	8.5	15.13
20	6.98	6.66