



A COMPARATIVE STUDY OF ELECTROCOAGULATION AND
CHITOSANBIOSORPTION FOR THE TREATMENT OF OIL REFINERY
WASTEWATER

by

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The dissertation is submitted to the Department of Chemical Engineering in the Faculty of Engineering and the Built Environment at the Durban University of Technology, KwaZulu-Natal, South Africa, in fulfillment of academic requirements for the degree of Master of Engineering in Chemical Engineering.

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PREFACE

This research study was carried out under the supervision of Prof. Sudesh Rathilal at the Durban University of Technology in the Department of Chemical Engineering and Prof. Babatunde Femi Bakare from the Mangosuthu University of Technology in the Department of Chemical Engineering. Oily wastewater samples were collected from local oil recycling company, which is an oil recycling company in New Germany, Durban, South Africa. Samples testing and analysis were conducted at the Mangosuthu University of Technology-Technology Station and the Chemical Engineering Laboratory.

DECLARATION 1 - PLAGIARISM

I, Gugulethu Emmerencia (21958810) Ngcobo declare that:

- (i) The research reported in this thesis, except where otherwise indicated, is my original work.
- (ii) This thesis has not been submitted for any degree or examination at any other university.
- (iii) This thesis does not contain other persons' data, pictures, graphs, or other information unless specifically acknowledged as being sourced from different persons.
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As the candidate's supervisors, we agree to the submission of this thesis

Signed

Prof. Sudesh Rathilal

Signed..... ..

Prof. Babatunde Femi Bakare

DECLARATION 2 PUBLICATIONS

DETAILS OF CONTRIBUTIONS TO PUBLICATION(S)

Ngcobo, G. E, Khumalo, S.M., Tetteh, E.K., Bakare, B.F, Rathilal, S., 2023, November. Chemical Oxygen Demand and Colour Removal from Oil Refinery wastewater using Chitosan Biosorbent. In *Proceedings of the 39th Johannesburg International Conference on Chemical, Biological and Environmental Engineering (JCBEE-23)* November 16-17, Johannesburg, South Africa.

Contribution: I wrote the manuscript with suggestions from S. Rathilal and B.F. Bakare. I did the paper presentation during the conference. E.K. Tetteh and S.M. Khumalo assisted with data analysis and proofreading of the final draft.

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DEDICATION

I dedicate this dissertation to,

My late mother, Mrs. Florah Thungo, and my father, Mr. Sam Thungo, thank you for believing in me and encouraging me throughout my academic journey. You truly brightened my way.

And

My sons, Masiko and Qhawe, who have sacrificed family time, and I think that many years of beautiful time together will compensate for the sacrifice and loss of mother's love.

ABSTRACT

Water quality is being impacted by the rapid expansion in industrialization, particularly in the oil and gas industry. Improper treatment of industrial wastewater exacerbates the problem. Chemical coagulation has been the most widely used technology in treating oily wastewater; nevertheless, electrocoagulation (EC) has been employed effectively to some extent, with different metals serving as electrodes. On the other hand, valorising seafood waste through bioconversion into biosorbents offers the promise of an environmentally benign wastewater treatment method. This study compares the performance of electrocoagulation using aluminium electrodes with that of adsorption using chitosan derived from oyster shells as the adsorbent. It aims to address effluent from refineries while also tackling waste beneficiation. Biosorbent characterization involved analyzing functional groups, which was confirmed using Fourier-Transform Infrared (FTIR) spectroscopy. The crystal structure, surface morphology, and elemental composition of the produced chitosan were examined using Scanning Electron Microscopy (SEM) combined with Energy-Dispersive X-ray (EDX) analysis, respectively. The adsorption process study was conducted through the use of empirical adsorption models. The Langmuir isotherm was shown to have the greatest fit for equilibrium data, whereas the pseudo 2nd order model provided the best fit for kinetic data. When removing Chemical Oxygen Demand (COD), colour, and phenols, the biosorbent chitosan achieved removal rates of 88.2%, 87.5%, and 88.9%, respectively. The optimal conditions were found to be at the dosage of 15 g, a reaction time of 90 minutes, a speed of 250 rpm, and a settling time of 15 minutes. Double-blade aluminium electrodes have proven to be highly effective for the electrocoagulation process, achieving reductions of 91.41% in COD, 96.77% in colour, and 94.53% in phenols. This performance was attained by maintaining a configuration with double-blade electrodes, an electrolysis time of 80 minutes, and a magnetic stirrer speed of 250 rpm, resulting in excellent electrocoagulation results. The results of this research showed that the EC is the fastest and best technique, although the performance of the biosorbent chitosan is good and should be further evaluated.

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NOMENCLATURE

ANOVA	Analysis of variance
BP-P	Bipolar parallel
COD	Chemical oxygen demand
DB	Double blade
DC	Direct current
EDX	Energy dispersive X-ray
FT-IR	Fourier transform infrared
HCl	Hydrochloric acid
ORW	Oil refinery wastewater
RSM	Response surface methodology
SB	Single blade
SEM	Scanning electron microscopy
UV-VIS	Ultraviolet-visible

CHAPTER 1-INTRODUCTION

1.1 Background

Clean and safe water is one of the most basic needs for every human (Organization 2022; Sowby 2023; Zhou *et al.* 2023) and a shortage of safe drinking water remains one of the world's most significant health concerns (Gizaw *et al.* 2022). Communities demand clean water to maintain their physical wellness and avoid infections caused by inadequate water supply. The scarcity of clean and safe water could be due to a variety of factors, including deteriorating transmission and distribution systems, environmental pollution, conflict, or poor water resource management. It is clear that climate change, as well as human factors, are increasingly denying future generations the right to safe water and sanitation.

Efficient water resource management, and equitable access to safe water and sanitation, are critical for unleashing economic growth and productivity (Nations 2015). Clean water and sanitation are vital, and they are one of the United Nations (UN) General Assembly's Sustainable Development Goals (Abuhasel *et al.* 2021). Freshwater is crucial for sustaining aquatic ecosystems, feeding agriculture, and supporting fauna, all of which ultimately provide important resources for humans to utilize.

The agriculture sector consumes the most water in South Africa, followed by the industrial sector. Natural sources of water, such as rainwater, underground water, and surface water are available in terms of the supply of water; however, the demand for freshwater is increasing due to factors such as population growth, water pollution, economic, and technological progress, which may render the resources insufficient (Okello *et al.* 2015).

Drinking contaminated water causes illnesses such as diarrhoea, and untreated waste products contaminate groundwater and surface water used for drinking, irrigation, and household day-to-day functions (Mahagamage, Pathirage and Manage 2020). One of the most significant sources of water contamination is industrial effluent (Elehinafe *et al.* 2022b). Oil refineries use a voluminous amount of water; thus, they are the largest source of organic pollutants in wastewater. Sadly, some have no means of pre-treating their effluents; it also has ramifications for the water and the environment, and some are often located near low-income communities. According to statistics, the world contains 30 billion litres of oily wastewater (Vítězová *et al.* 2020). These large volumes of oil refinery effluent are unavoidably generated as a result of global demand for petrochemical and petroleum products (Tetteh and Rathilal 2018).

This leaves a gap in oily wastewater treatment becoming increasingly important (Sanghamitra, Mazumder and Mukherjee 2021). The 2030 Agenda for Sustainable Development aims to improve people's quality of life, offer a healthy environment, and improve social, economic, and environmental

conditions for both present and future generations. According to recent data analysis on Environmental Protection Agency regulations, oil refineries discharge billions of litres of pollutants into rivers every year (Adetunji and Olaniran 2021). This leads to humans bearing an unfair proportion of the consequences, making it necessary to implement solutions urgently.

Oily wastewater is produced by various sources, including oilfields (Sivasubramanian 2021), petroleum refineries (El-Naas and Banerjee 2022), food processing and restaurants (Nayyar *et al.* 2021), slaughterhouses (Akarsu *et al.* 2021), and tanneries (Yasmeen *et al.* 2016). Oily wastewater contains contaminants that are characterized by high chemical oxygen demand (COD) and colour intensity concentrations, indicating the presence of organic and inorganic pollutants. COD is an indicative measure of the amount of oxygen that can be consumed by reactions in a measured solution. It is expressed in mg(O₂)/L, and the higher the COD concentration, the more polluted the water is. The COD in industrial wastewater may range from 50 to 8 000 mg/L (Hasan *et al.* 2023), depending on the type of industry. For potable (drinking) water, COD concentrations are expected to range 2 – 10 mg/L (Khan *et al.* 2015). However, the acceptable limit for COD concentration in effluent water from treatment works must not exceed 250 mg/l (Standards 2000). Highly coloured water has significant effects on aquatic plants and algae growth. Light is critical for the growth of aquatic plants and coloured water can limit the penetration of light. Thus, a coloured body of water could not sustain aquatic life which could lead to the long-term impairment of the ecosystem (Aoyi *et al.* 2015).

Phenolic compounds exist in water bodies due to the discharge of polluted wastewater from industrial, agricultural, and domestic activities into water bodies. These compounds are known to be toxic and inflict both severe and long-lasting effects on both humans and animals (Anku, Mamo and Govender 2017). Phenolic compounds act as carcinogens and cause damage to the red blood cells and the liver, even at low concentrations (Anku, Mamo and Govender 2017). Interaction of these compounds with microorganisms, inorganic and other organic compounds in water can produce substituted compounds or other moieties, which may be as toxic as the original phenolic compounds (Anku, Mamo and Govender 2017).

Another major phenomenon is the piling up of seafood waste. Seafood waste contributes at least 30% of the total amount of food waste globally (Tümerkan 2021). In South Africa, a person consumes about 12 kg of seafood per year on average (Bizcommunity 2022). Mussels and oyster shells are among the most common types of crustacean waste in municipal landfills. Agricultural and natural adsorbents like bamboo dust (Latthe *et al.* 2020), barley straw (Ibrahim, Wang and Ang 2010), and sugar cane bagasse (Brandão *et al.* 2010; Ndebele 2023) have been used as a great option in wastewater treatment; so far, they have shown promising results and have a high absorption ability. Because of their biodegradability and high molecular weight, these natural flocculants have the potential to replace conventional adsorbents (Lapointe and Barbeau 2020). However, according to (Bi *et al.* 2012), some of these

materials adsorb water along with oil and have minimal oil-loading capacity. Some of the biosorbents derived from the aforementioned agricultural wastes have the disadvantage of being pH-sensitive and poor performance in removing tiny particles from aqueous solutions (Zhao *et al.* 2020). Chitosan has been proven to be a useful biosorbent component extracted from chitin, a substance found in crustacean shells (Santos *et al.* 2020). Its application as a biosorbent in water treatment has attracted the attention of many researchers due to its perceptible benefits in mitigating the environmental burden (Pal *et al.* 2021). Chitosan is a polymer that is fractionally deacetylated, hence it is usually expressed in degrees of deacetylation. It is obtained from chitin, a polysaccharide of N-glucoside found in marine cell walls (Espíndola-González *et al.* 2011).

Among other physical methods used in the treatment of oily wastewater are the demulsification process, (Daaou and Bendedouch 2012; Zolfaghari *et al.* 2016), evaporation separation (Aminmahalati, Fazlali and Safikhani 2022; Medeiros *et al.* 2022), flotation (Rocha e Silva *et al.* 2018; Rocha e Silva *et al.* 2020; Kolawole and Iyiola 2023), and coagulation (Sun *et al.* 2017; Yan *et al.* 2023). Coagulation has been the most widely utilized method of water treatment (Teh *et al.* 2016; Zhao *et al.* 2021). Most coagulants used in water treatment generate remarkable results; however, due to the difficulty of oily wastewater treatment and the degree of pollutants present in oily wastewater, only a few of them are effective. Coagulation, which utilizes power (electrocoagulation), is another promising technology that is appropriate in the field of wastewater treatment. Electrocoagulation (EC) is a simple and effective treatment approach that involves the electrode solution of sacrificed anodes and the generation of hydroxy-metal products as coagulants, while concomitant hydrogen synthesis at the cathode promotes pollutant removal by flotation (An *et al.* 2017). The efficiency of an experimental electrocoagulation method in removing oil content has been demonstrated to be effective at a low reaction time, minimal current consumption, and the best electrolysis time values. It also consumes less energy (Jasim and AlJaberi 2023a). EC also has a quick setup, a sustainable nature, and requires a small surface area (Shokri and Fard 2022).

1.2 Problem Statement

Water quality is degraded by industrial effluent carrying toxic chemicals, which endangers the ecology and depletes water supplies, thereby contributing significantly to the water crisis. These hazardous pollutants, particularly those found in wastewater streams, can occur in high concentrations as well as trace amounts and must be effectively eliminated from effluent streams before release into public water bodies. The pollutants include heavy metals, high concentrations of COD and nitrogen group pollutants, and other compounds that can kill aquatic life.

The pollution level in wastewater is reflected by the intensity of its colour (Chen, Wu and Li 2014). If the concentration of COD is high, it can react with chlorine in the final water treatment process to produce trihalomethane (THM), which is a toxic compound that can have negative health effects, such

as cancer (Hood 2005). Various techniques, such as nanofiltration (Chowdhary and Mani 2021) and electrocoagulation (Singh *et al.* 2019), have been evaluated for removing COD, colour, and phenol.

High concentration levels of COD in water bodies result in the reduction of dissolved oxygen in water thus destroying aquatic life and promoting eutrophication in water bodies. On the other hand, high colour intensity hinders any photolysis process in water bodies. Phenol is non-biodegradable, emits a bad odour, and poses threats to aquatic ecosystems and human health by reducing oxygen consumption rates. This study focuses on the use of electrocoagulation in comparison with adsorption using the biosorbent chitosan to remove COD, colour, and phenol from oil refinery wastewater.

1.3 Research aim and objectives

The study aimed to investigate the efficiency of electrocoagulation and chitosan biosorption for the treatment of oily wastewater from a motor oil recycling plant. In achieving the aim of the present study, the following objectives were investigated:

1. To evaluate the efficacy of electrocoagulation in treating water-oil emulsion by measuring the reduction rates of COD, colour, and phenol.
2. To synthesize and evaluate chitosan utilizing adsorption kinetics and isotherms, and then assess its efficacy in treating oily wastewater by evaluating COD, colour, and phenol reduction rates.
3. Optimization of the operating parameters of the electrocoagulation and chitosan biosorbent treatment options.
4. To compare electrocoagulation and chitosan techniques using the removal rates of the COD, colour, and phenol.

1.4 Scope of the study

The scope of this research is based on the treatment of oil recycling refinery wastewater using the two techniques (EC vs chitosan) in comparison. The effectiveness of each technique was measured based on the removal rate of the COD, colour, and phenol. The following effects were considered and compared:

- (a) The effect of running time for each technique
- (b) The effect of the dosage for the chitosan and the number of blades for the EC

1.5 Dissertation Organisation

Chapter 1: Introduction

The introduction section provides background information about the study. It also outlines the scope and purpose of the research, along with the aim and objectives that the study addresses.

Chapter 2: Literature Review

The literature review chapter is a collection of relevant and current research studies related to the chosen topic. It synthesizes the information into a cohesive summary of existing knowledge in the field of oily wastewater treatment using electrocoagulation and biosorbent chitosan. This provides a useful foundation for choosing an effective structure and relevant criteria to be used in conducting further research on the topic.

Chapter 3: Experimental procedures and materials

This chapter describes what and how the study was carried out. It describes every piece of equipment used, as well as the materials and experimental procedures used in the investigation, in an organized and logical manner.

Chapter 4: Results and Discussion

The results chapter contextualizes the meaning and significance of the study's findings. In the discussion, the results are interpreted considering the study's objectives and goals and the findings of other studies. It is essential to clearly articulate the relevance and implications of the results for the research topic.

Chapter 5: Conclusion and Recommendations

The conclusion summarizes the major points about the research findings, lays out the recommendations for future research, and explains how these recommendations will solve the gaps in real-world concerns.

CHAPTER 2 - LITERATURE REVIEW

2.1 Introduction

This chapter provides an overview of oily wastewater treatment methods, as well as their advantages and disadvantages. It examines the effectiveness of various techniques in reducing or eliminating pollutants from oily wastewater. The chapter delves further into the potential of coagulation, especially electrocoagulation, for purifying oily wastewater. It also explores the use of natural biosorbents, specifically focusing on the application of chitosan flakes in oily wastewater treatment. The chapter concludes with a summary of the findings reported in the literature.

2.2 The global issue of water scarcity

The quality and quantity of available freshwater resources for human consumption particularly in the Sub-Saharan region are deteriorating daily as a result of population growth, living standards demands, and rising temperatures. Additionally, the rapid rates of urbanization and industrialization have increased risks for the ecological degradation of surface water receiving bodies such as rivers and, consequently, of the derived services like effluent (Jia *et al.* 2020). Water is an essential resource that fulfils the primary needs of all living beings, it's always in high demand to sustain life. Humans require freshwater for drinking, cleaning their bodies, and watering plants that provide food. Plants and animals also depend on water for survival. Additionally, industries rely on water for their daily operations, and it plays a crucial role in generating electricity and supporting the transport industry. As the world faces water challenges, it is crucial to conserve the remaining resources and implement new techniques to save water. Severe water scarcity and diseases caused by a lack of access to clean water are some of the potential consequences of this global phenomenon.

With the recent implementation of the Sustainable Development Goals (SDGs) by the United Nations, the idea that "Ensuring the sustainable use of water resources is crucial" unites all departments linked to SDG 6 (water and sanitation) about water (World Health Organization 2017).

Radelyuk *et al.* (2021) recognized this issue and reported that the three pillars of social, environmental, and economic sustainability were the only drastic measures that could guarantee that everyone made sustainable use of water resources. In an industrial setting, sustainable water use involves several elements from the three sustainable development (SD) dimensions and how they interact, as depicted in Figure 2-1. Domestic industrial processes are employed for illuminating economic variables, and the industry utilizes technology to safely treat, and use supplied and processed water.

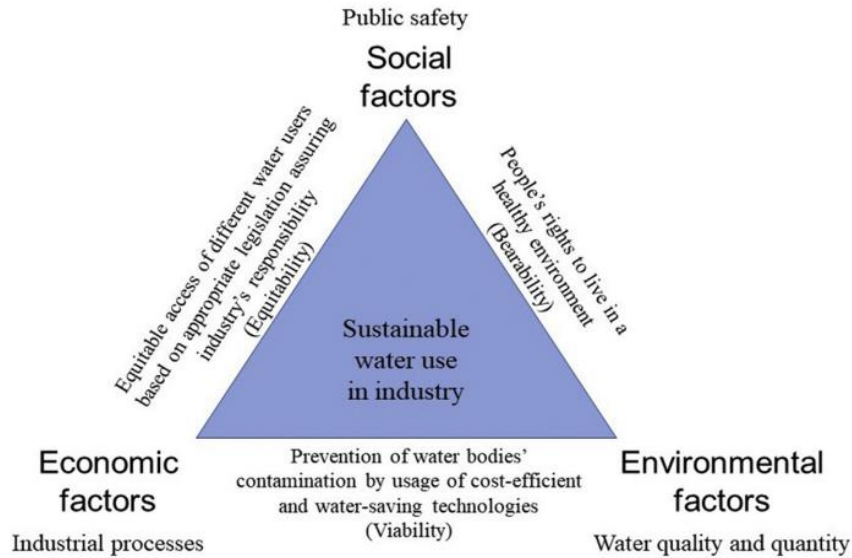


Figure 2- 1. Pillars that determine sustainable water use. Adapted from Radelyuk *et al.* (2021)

Water quality in water sources and wastewater recipients are considered by environmental factors. The use of effective technology to lessen the effects of industrial activity on water bodies and make water viable for future consumers is a hallmark of interactions between economic and environmental concerns. Public safety (such as health) is a representation of social elements that are primarily governed by the government.

2.3 Water scarcity in the South African context

South Africa is considered a semi-arid nation with an average rainfall of 500 mm (Rapholo and Diko Makia 2020) which has posed challenges in accessing water. Cape Town has been significantly affected by this issue. du Plessis (2023) suggest that South Africa's geographic location, rapid population growth, industrialization, poor water services and several other factors have contributed to water security. This means that the country's capacity to achieve other development goals will begin to be hampered by the water sector unless a combination of current plans, additional measures to tap previously unused sources of water, and some form of demand management is implemented.

The importance of scarcity in water governance was examined by Hellberg (2020) as part of the green governmentality approach, with a focus on South Africa. According to the Water Research Commission, the country's climate is characterized by variation and below-average rainfall (Le Maitre *et al.* 2018). The drought, which began in some parts of the country as early as 2014, has been declared to have produced a national disaster because of its extreme severity. Over these past years, drought conditions have challenged policy justifications for water management and changed how water scarcity is viewed. In South Africa, the drought affected industries like agriculture, one of the pillars of gross domestic product (GDP). A substantial amount of money was invested in agricultural water infrastructure during the preceding era, and a wide array of dams, reservoirs, canals, tunnels, and pumping systems were

constructed to capture and channel water to ensure access to the urban areas. Water was consequently crucial to the agricultural industry at the time. Since there were no restrictions placed on its use as a result, it became a natural part of the environment, which significantly added to the current water deficit (Hellberg 2020).

Some studies, (Elehinafe *et al.* 2022a) emphasize the availability and affordability of some of the technologies that have been investigated in South Africa as potential remedies for the country's water woes. Desalinating seawater is a promising technology (Goh, Liang and Ismail 2021). Researchers and engineers have mastered this technique, but desalination technology is prohibitively expensive for South Africa, except for very large coastal metropolises like Nelson Mandela Bay, Durban, and Cape Town. Hedden found that desalination currently only meets less than 1% of South Africa's total water demand. Desalination will probably become a more attractive choice for these large municipalities as the cost of operation is projected to drop over time. Desalination, however, will not be able to handle South Africa's inland water shortage and will not have much of an impact on the agricultural industry, so it is likely to have a minor role in the country's water status (Bessette and Winter 2022). Agriculture appears to be the sector with the highest water demand, as seen in Figure 2-2 below, which shows the three sectors with the highest water demand in South Africa. Water demand is anticipated to increase in all three sectors, namely: municipal demand, industrial demand, and agricultural demand. It is crucial to recognise that groundwater in South Africa usually has different amounts of total dissolved solids (TDS) and dissolved gases like carbon dioxide and methane. These elements, which reflect the intricate relationships within the aquifers—which frequently involve mineral leaching from nearby rocks and soils—can result from both natural geological processes and human activity. As a result, the region's groundwater rarely reaches a pure state because it may contain a variety of minerals, salts, and organic matter that can alter its overall quality and suitability for various applications. For efficient management and sustainable use, it is essential to comprehend the intrinsic qualities of this water resource (Nkosi, Mathivha and Odiyo 2021).

2.4 Industrialisation and Urbanisation Impacts on Water Resources

Human civilization has rapidly expanded over the past few decades, increasing potentially hazardous substances in water, soil, and sediments. Industrial operations and urbanization have contributed to a significant rise in pollution in the environment. As a result, there are more and more locations throughout the nation that are contaminated with numerous risks, which pose a threat to both the ecosystem and human health (Bolan *et al.* 2024). Sarker *et al.* (2021) defined contamination of groundwater as what happens when pollutants are released into the atmosphere and eventually find their way into groundwater. These contaminants not only pollute groundwater but also injure species that dwell below the surface of the groundwater. Pollution from sources includes on-site waterways, landfills, wastewater treatment plant effluent, leaking sewers, fuel stations, and excessive fertilizer use in agriculture (Sarker *et al.* 2021). Because of rising municipal and industrial discharges,

industrialization and urbanization are now the leading causes of stream degradation, behind agriculture which all result in higher nutrient loadings to urban streams.

When hazardous chemicals and compounds from companies infiltrate water streams, the water becomes unhealthy for human consumption. This is referred to as industrial water pollution. Sarker *et al.* (2021) suggest some of the reasons for the accumulation of main pollutants in industrial water pollution are that some industries still use antiquated technologies that cannot withstand modern pollutants discovered in wastewater streams.

When industrial wastewater is not properly treated before being discharged into rivers or lakes, this is especially true in small businesses that do not have the resources to invest in pollution control systems. Even while it enhances a country's economy, industrial growth is harmful to the environment, especially when unregulated. Unplanned industrial growth has some drawbacks, including the possibility of insufficient waste disposal facilities and complete contempt for pollution control standards, which may affect the ecology in the long run.

Water utilized in many industrial processes comes into touch with radioactive sludge, organic sludge, heavy metals, and toxic compounds. As a result, when such contaminated water is discharged into the ocean and/or water-receiving bodies without being treated, it becomes unfit for use in agriculture and by humans (Malik *et al.* 2022). The turbidness of the water can be made worse by industrial wastes that end up reaching aquatic life, making it difficult for those organisms to absorb dissolved oxygen from the contaminated water (Laurelta and Bright 2023).

The process of industrialization has a significant impact on water contamination. This is due to the massive production of waste that generates wastewater, particularly in developing nations like South Africa (Mahmood and Al-Musawi 2020).

Industries play a crucial role in economic growth, but they also generate wastewater that can harm the quality of water and threaten people's livelihoods. The level of water pollution varies depending on the type of wastewater. Agricultural wastewater is less toxic compared to oily contaminated wastewater, which is considered the most toxic and even mutagenic and carcinogenic (Sharma *et al.* 2020).

Dairy manufacturing operations constitute a part of the food industry and process dairy products made by farmers. Water is utilized in all stages of the dairy industry, including sterilization, cleaning, heating, cooling, and floor washing; the water demand is undoubtedly enormous and is made even more urgent by the strict requirements for hygiene. High biological oxygen demand (BOD) and chemical oxygen demand (COD) values, as well as high amounts of dissolved or suspended particles, including fats, oils, and grease, are characteristics of dairy wastewater (Meissner and Ohlhoff 2022).

According to Genghini (2021), the three areas that contribute most to high water use are the agricultural, fashion, and energy sectors. Agriculture, which is currently a key driver of the economy and the main

hope for achieving SDGs 1 and 2 (zero hunger and poverty), however, appears to be the biggest consumer of freshwater (Beharielal, Thamaga-Chitja and Schmidt 2022).

Oil-producing and recycling companies are among the biggest industries in the world, but they also represent an environmental threat, increase water contamination, and contribute to global consumption (Jafarinejad and Jiang 2019; Meese *et al.* 2021). When the chemistry of petroleum wastewater was investigated, it was discovered that crude oil, which serves as the primary raw material, contains a long chain of hydrocarbons, the relative proportions of which define the oil's qualities, and are the primary cause of water contamination (El-Naas and Banerjee 2022). Identifying effective techniques to reduce contaminants is a challenge, especially with demanding water quality regulations.

2.5 Environmental legislation and policies that apply in South Africa.

The focus of water management in South Africa is on the concept of equitable water distribution, which ensures that the needs of those who do not have access to sufficient water in their daily routines are met. Productive use of water in South Africa's economy is encouraged, and some of the regulations outlined below safeguard the environment.

2.5.1. The National Environment (standard of effluent discharge into water or land) Regulations S.I No.5/1999.

This regulation is strictly enforced to safeguard the environment. The criteria for effluent or wastewater before it is discharged into waterbodies and/or on land shall be as prescribed in the schedule to regulations.

2.5.2. Department of Water and Sanitation (Water Service Act of 1997).

The statutory mandate of the Department of Water and Sanitation (DWS) is to guarantee that the country's water resources are protected, managed, developed, conserved, and controlled sustainably for the benefit of all people and the environment Ethekwini Municipality (2011), ensures water resource safeguarding by adopting an integrated water quality management strategy to establish resource quality targets (Ethekwini Municipality 2011). This Act aims to ensure that everybody has access to basic water supply and sanitation services. In line with the United Nations Sustainable Development Goal 6 which is access to water and sanitation for all (World Health Organization 2017), this act serves to emphasize this goal which stimulates reduction of the pollution, elimination, and minimization of dangerous chemicals and materials that make water unsafe for use.

2.5.3. National Water Act 36 of 1998.

This act is an umbrella for all national water and wastewater acts and regulations. Since wastewater is currently regarded as a resource rather than a waste (Edokpayi *et al.* 2020), it plays an important role in the structure of the water cycle. This act addresses wastewater management and wastewater treatment to ensure the safety of water is adhered to by all. The wastewater discharge limits are provided by this

act, such as the limits regarding the discharge of effluent into water bodies. The limitations of some of these regulations are presented in Table 2-1.

2.5.4 Department of Water Affairs and Forestry (DWAF)

The Department of Water Affairs and Forestry (DWAF) controls South Africa's water and forestry resources, including policy development and implementation, as well as municipal government water services. The department's water sector seeks to provide clean water and healthy sanitation to all South Africans while supporting efficient resource management (Berner, Hoffman and Spangenberg 2004).

DWAF initiated the process of developing a framework that will set in motion a plan of action to ensure that South Africa has enough water, both quantitatively and qualitatively, to maintain its growth and development (Mtolo 2008). Table 2-1 lists some of the legislative bodies that govern the law and the restrictions on effluent emission.

Table 2-1. Maximum discharge limits for South African legislative bodies.

Legislation Body	PARAMETERS				REFERENCE
	COD	Colour	Phenol	pH	
National Water Act	75 mg/L	N/A	2.5 mg/L	5.5 - 9.5	(Department of Water Affairs 2013; Peng <i>et al.</i> 2020)
Industrial Effluent by Law	5000 mg/L	N/A	50 mg/L	5.5 - 12	(Law Library South Africa 2014)
DWAF	200 mg/L	N/A	2.5 mg/L	6 - 9	(Department of Water and Sanitation and Forestry 1999)
Department of Environment Affairs and Forestry in Republic of South Africa 2021	1600 mg/L	N/A	N/A	5.5 – 9.5	(Department of Water Affairs Forestry Fisheries and the Environment in the Republic of South Africa 2021)

*STD-standard

2.6 Environmental Occurrence of Oily Wastewater

Statistically, the world consists of 30 billion cubic meters of oily wastewater (Vítězová *et al.* 2020), and this volume keeps on increasing with the increasing number of refineries due to oil demand. Oily wastewater treatment is becoming an urgent need (Sanghamitra, Mazumder and Mukherjee 2021). Oil pollution brings long-term environmental damage, hazards to health, and energy loss. Flotation, coagulation, biological treatment, adsorption, membrane separation, and other approaches have been developed to separate oily wastewater (Medeiros *et al.* 2022), however, many of these techniques suffer

from low extraction efficiency, pricey electricity for long-term execution, and additional emissions such as greenhouse gas (GHG) emissions, including methane and nitrous oxide.

Oil-in-water (O/W) can be generated from different sources such as petrochemical industries, food processing, textile, steel making, and leather manufacturing industries (Chu, Feng and Seeger 2015). The oil and gas industry has a great contribution to the global economy, but its processes and its waste pose a serious threat to the environment. The swift growth of the oil industry results in a large yield of oily wastewater comprised of toxic compounds. These harmful substances are mixed with water and need to be removed by adequate water purification techniques for the wastewater to meet quality requirements for it to be discharged into communal waterbodies and/or agricultural lands. Depending on the degree of contaminants present in the wastewater, methods of purification can vary. Figure 2-2 below shows an example of how oily wastewater can throw off the balance of the environment. This figure further underlines the advantage of treatment. Studies have shown that treating wastewater contaminated with oil can be difficult, and it can be significantly more difficult when the oil particles are miscible with water (Medeiros *et al.* 2022).

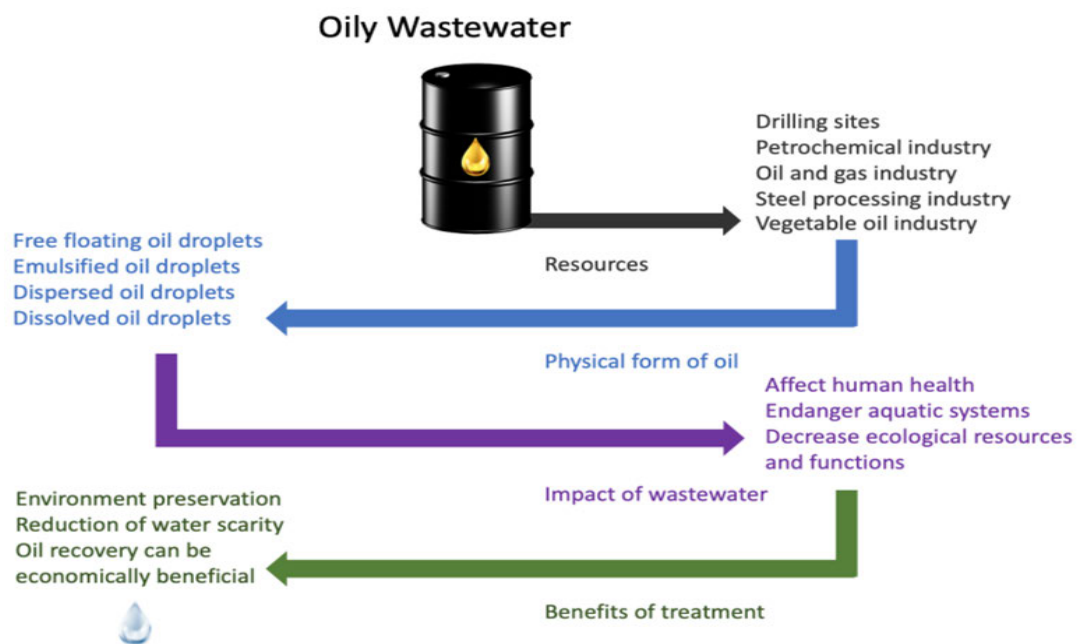


Figure 2- 2. Resources, physical form, impact and benefits of treating oil refinery (Medeiros *et al.* 2022).

The properties of crude oil have an impact on the quantity and composition of refinery effluent (Rita *et al.* 2022). Oily wastewater contains a significant volume of oil, as well as a high colour and COD (Jameel *et al.* 2011). Because these contaminants may be carcinogenic and mutagenic to people, they

must be treated and kept below the allowed limits set by South African (in the context of the present study) environmental legislation.

2.7. Oily wastewater treatment methods.

2.7.1 conventional and historical methodologies in wastewater treatment

Numerous cutting-edge treatment methods have been developed in response to the problem of oil contamination in wastewater, particularly from oil refineries and associated industries. The quality of the influent wastewater, capital and operating costs, energy consumption, and possible environmental effects are important factors that affect the choice and effectiveness of these techniques (Cardoso *et al.* 2021; Phungela *et al.* 2021). Because of benefits like automation, reduced capital needs, high chemical oxygen demand (COD) removal efficiency, and the lack of chemical agents to destabilise oil-water emulsions, membrane separation technologies have become one of the most promising approaches available (Bera, Godhaniya and Kothari 2022).

When it comes to treating oily wastewater, like that produced by olive oil mills, membrane technologies such as ultrafiltration membranes (UFMs) have shown great effectiveness, removing more than 67% of COD and significantly reducing phenolic compounds (Zulkefli *et al.* 2021) Membrane fouling is still a major operational issue that restricts long-term efficiency and raises maintenance costs in spite of these advantages (Ding *et al.* 2022).

The efficiency of RO in phenol retention from an oil refinery was examined by Bastos *et al.* (2020), at very low pressure of 2.5 bar, the use of a RO membrane led to rejections of up to 98% of phenol and 99% of COD and total organic carbon (TOC). By applying pressure to push water molecules through semi-permeable membranes, RO effectively produces high-quality effluent. The production of a concentrated waste brine, which makes disposal more difficult, high operating costs, and a high energy demand are the drawbacks of this approach is frequently used for primary treatment in vegetable oil refinery wastewater management because of its ease of use and efficiency in eliminating free oils, Othman *et al.* (2021), despite being time-consuming and requiring a large surface area. The use of traditional physical and chemical techniques, such as gravity separation, is helpful (Kaya and Hung 2021).

Another popular technique, dissolved air flotation (DAF), involves adding air bubbles to wastewater to encourage the aggregation and eventual removal of suspended solids and oil droplets from the water's surface (Abdulredha, Aslina and Luqman 2020).

2.7.2. Coagulation

Coagulation follows a simple process where tiny particles are attracted to each other by electrical forces. This attraction causes the particles to cluster together and form larger particles, known as micro-flocs. These micro-flocs then combine to create even larger particles called macro-flocs. Normally, these impurities are light and float on the surface of the water, but with the addition of a coagulant, they settle down to the bottom and leave clean water on top. The illustration of the coagulation process is demonstrated in Figure 2-3.

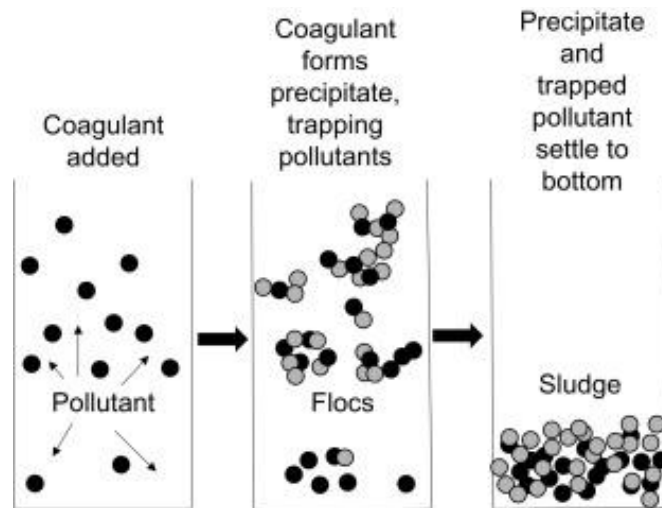


Figure 2- 3. Illustration of pollutants (particles) behaviour after the addition of a coagulant/ flocculant (Razia, Nalla and Sivaramakrishnan 2020).

A key component of wastewater treatment is coagulation, which neutralises the electrostatic charges of suspended particles to promote their aggregation and removal. This approach, which was first created in 1949 by Langelier and Ludwig, is still widely used because it is flexible and reasonably priced (Inam *et al.* 2021), But in the presence of high oil and complex organic pollutant concentrations, which are common in petrochemical and refinery effluents, conventional coagulants frequently show limited efficacy (Abuhasel *et al.* 2021). The limitations of inorganic coagulants in treating oily wastewater have prompted researchers to look into alternative agents due to advancements in coagulant technologies. Although they work best in low-turbidity waters, organic coagulants like ferric chloride, aluminium sulphate, aluminium chloride, and propylammonium chloride are affordable and suitable for a variety of wastewater types (Koul *et al.* 2022).

The most efficient method for removing oil in refinery wastewater is still chemical coagulation, especially when combined with inorganic minerals, ferric and aluminium salts, organic synthetic flocculants, and natural polymeric flocculants (Jabbar and Alatabe 2021). These compounds enhance the removal of colloidal particles and fine oil droplets from wastewater by encouraging their aggregation. According to recent studies, inorganic salt coagulants, like iron and aluminium salts, are

effective at removing up to 99.8% of oil from waters contaminated by synthetic ship oil and more than 90% of COD from refinery effluents (Othman *et al.* 2021; Zaman *et al.* 2022). Notwithstanding these achievements, the high dosages and related operating expenses continue to be major disadvantages, which has led to research into alternative and bio-based coagulants (Badawi, Salama and Mostafa 2023). Prospects for the Future Research is increasingly concentrating on the creation and application of innovative, economical coagulants, such as natural and bio-based polymers, in order to address these issues. These coagulants have the potential to lower operating costs while preserving high removal efficiencies (Diver, Nhapi and Ruziwa 2023). Additionally, to improve the overall treatment performance for oily wastewaters with complex contaminant profiles, the integration of hybrid treatment trains and advanced oxidation processes (AOPs) is being researched (Rostam and Taghizadeh 2020).

2.7.3. Electrocoagulation

Electrocoagulation was first identified in London, utilised in a sewage treatment facility, and legally patented by American researcher A. E. Dietrich in 1906 (Boinpally *et al.* 2023). This system has been utilised for wastewater treatment from many sources throughout the years, with rapid and outstanding results (Akarsu *et al.* 2021; Ebba, Asaithambi and Alemayehu 2021). Electrocoagulation is a method that employs electricity in lieu of costly chemical reagents (Gheraout 2020).

Electrocoagulation (EC) is an increasingly popular and efficient water treatment technique for the removal of various pollutants, including soluble organic compounds and emulsified oils in aqueous solutions. Sacrificial metal electrodes, usually composed of iron or aluminium, are exposed to direct electrical current, resulting in their dissolution and the formation of highly charged polymeric metal hydroxide flocs. These species facilitate the effective removal of contaminants through destabilisation and aggregation, enabling floating or sedimentation (Kadier *et al.* 2022; Ammar *et al.* 2023). The user-friendliness of EC is one of its primary features. EC is suitable for both centralised and decentralised treatment applications owing to its straightforward system design and operation, which obviates the necessity for specific technical training (Magnisali, Yan and Vayenas 2022).

Compared to conventional coagulation techniques, electrocoagulation (EC) rapidly eliminates contaminants, typically within minutes, enhancing treatment efficiency and reducing operational durations (Abuhasel *et al.* 2021). Electrocoagulation generates coagulants in situ by electrode dissolution, so markedly diminishing the necessity for chemical additives, which in turn lessens the risk of secondary pollution and risks associated with chemical storage. Moreover, the sludge generated by electrocoagulation (EC) is typically denser and more manageable than that from conventional treatments, hence facilitating disposal and reducing associated costs (Syam Babu *et al.* 2020; Ammar *et al.* 2023). Recent research indicate that electrocoagulation (EC) is both sustainable and effective in

treating wastewaters contaminated by industrial, municipal, and new pollutants (Othman *et al.* 2021; Kadier *et al.* 2022).

Ultimately, EC's swift treatment, absence of chemicals, operational simplicity, and less sludge generation underscore its promise as an environmentally sustainable solution to contemporary water treatment challenges.

Electrocoagulation (EC), an advanced water treatment technique, effectively stabilises soluble organic contaminants and emulsified oils in aqueous environments by generating highly charged polymeric metal hydroxide species. These hydroxide complexes function as coagulants, destabilising and aggregating contaminants, which facilitates their removal by flotation or sedimentation. Sacrificial metal electrodes, typically composed of iron or aluminium, are employed in the procedure. These electrodes emit metal ions into the solution upon exposure to an electric current. Reactive coagulant species are generated through the hydrolysis of these ions, eliminating the necessity for additional chemical additions. Electrocoagulation offers several significant advantages over conventional treatment methods.

EC is categorized by the straightforward operational protocols Jasim *et al.* (2023), brief treatment duration Magnisali, Yan and Vayenas (2022), and markedly reduced sludge generation Boinpally *et al.* (2023), and collectively contribute to the mitigation of secondary waste management challenges (Shahedi *et al.* 2020). This approach is more cost-effective and environmentally sustainable as it employs electrode dissolution to generate coagulants, hence minimising the requirement for external chemical dosing (Shahedi *et al.* 2020; Mao, Zhao and Cotterill 2023). Recent studies have underscored the versatility and scalability of EC for industrial and municipal wastewater applications, demonstrating its efficacy in removing a diverse array of contaminants, such as dyes, heavy metals, microplastics, and persistent organic pollutants, across various operating conditions (Chen *et al.* 2021; Kadier *et al.* 2022). Moreover, advancements in process optimisation and electrode design have enhanced removal efficiency and reduced energy usage, rendering electrocoagulation a more attractive option for sustainable wastewater and water treatment. For instance, electrocoagulation (EC) has exhibited synergistic effects when combined with other treatment methods such as membrane filtration or electro-oxidation, enhancing operational resilience and pollutant elimination (Yadav *et al.*, 2022; Wang *et al.*, 2024).

El Jery *et al.* (2023) further substantiated the efficacy of EC, attaining a 94% decrease in COD from petroleum refinery effluent, stainless-steel cathodes demonstrating best performance in this investigation. Jasim and AlJaberi (2023b) recently proved that electrocoagulation with aluminium electrodes at neutral pH efficiently diminished oil and turbidity levels. Aluminium electrode electrocoagulation has been highly effective in the treatment of effluent from oil refineries. Abbas *et al.*

(2021) investigated the elimination of phenols and chemical oxygen demand (COD), achieving a reduction of 65% in phenols and 85% in COD with sufficient detention time. (Merma *et al.* 2020; Kadier *et al.* 2022) expanded the analysis by comparing electrocoagulation efficiency across various industrial oily wastewaters, including those from petroleum, metal, nautical, food processing, and restaurant industries. Their findings underscored the significance of pH, current density, treatment duration, and electrode arrangement as critical performance variables. Recent research has investigated hybrid electrodes and surface-modified aluminium to improve pollutant removal and extend electrode lifespan (Alkurdi and Abbar 2020; Zhao *et al.* 2021). There is growing interest in integrating electrocoagulation (EC) with advanced oxidation processes (AOPs) or membrane filtration to improve the removal of oil, chemical oxygen demand (COD), and emerging contaminants (Hajalifard *et al.* 2023). Due to the complexity of oil-contaminated wastewater, recent evaluations have concentrated on actual industrial effluents, such as generated water from oil and gas fields, illustrating the adaptability of EC while underscoring the necessity for customised parameter optimisation (Tools 2024). Research has focused on improving energy efficiency and sustainability by reducing energy consumption and sludge generation. Currently, pulsed current electrocoagulation, enhanced reactor designs, and renewable energy-powered systems are undergoing pilot testing (Lu, Zhang and Li 2021).

Life Cycle and Cost Analyses: In-depth cost and environmental effect assessments significantly bolster EC's competitiveness and environmental sustainability, particularly in contrast to traditional chemical coagulation (Gasmi *et al.* 2022). This technology has been demonstrated to be highly effective for treating diverse industrial effluents (Shahedi *et al.* 2020). This method is straightforward to implement (Bajpai, Singh Katoch and Singh 2020), economically viable Merma *et al.* (2020), has a reduced treatment duration Ibrahim (2022), processes wastewater without chemicals Moneer *et al.* (2023), and generates less sludge (Gasmi *et al.* 2022).

Electrochemical coagulation has been employed as a substitute for traditional chemical coagulation. This technology is extensively utilised in municipal, industrial, and potable water treatment facilities. Electrocoagulation (EC) is a favoured technique for treating oily wastewater, yielding effective results in effluent treatment (Oden 2020). The electrochemical coagulation method employs electric current and iron or aluminium electrodes as coagulation agents, in contrast to chemical coagulants (Shahedi *et al.* 2020).

(Jasim and AlJaberi 2023a) evaluated the efficacy of electrocoagulation in treating oil refinery wastewater by analysing its oil content (OC). The study discovered that the aluminium anode elevated the concentration of H⁺ ions while the cathode employed was stainless steel, this combination resulted in a modification of the pH level. Optimal efficiency was recorded at neutral pH level, which led to diminished efficiency. The maximum removal effectiveness of OC was 99%. The study involved tests

designed using Response Surface Methodology, with independent variables including current, pH, and electrolysis duration of 60 minutes. The optimal process parameters were identified as a current density of 5 mA.cm⁻², and initial pH. Of 7.

Oily effluent from petrochemical facilities was treated via electrocoagulation employing aluminium (Al) electrodes. The findings indicated an 98.09 0% reduction of oil COD after 10 minutes of electrocoagulation time. The operating parameters wer 5A of current, 20v of voltage. The investigation was optimized usin Response Surface methodology (RSM) and received co-efficient of determination (R²) OF 0.969 (Movahhedtaher, Ojani and Raoof 2024).

Changmai, Pasawan and Purkait (2019) conducted a study examining electrocoagulation (EC) utilising aluminium electrodes, revealing that the removal rates of oil and turbidity were markedly diminished when employing EC with aluminium electrodes at a neutral pH. (Kadier *et al.* 2022) investigated the electrocoagulation efficiency in the elimination of oil and gas from diverse industrial wastewater streams, including oil-laden water, petroleum refinery effluent, metal industry wastewater, maritime industry effluent, food processing wastewater, abattoir effluent, tannery wastewater, and restaurant wastewater. This study examined various forms of oil effluent due to the inclusion of different oil types. The experimental results demonstrate that pH, current, operating duration, and electrode configuration are critical factors influencing the efficacy of the EC approach. The study by Kadier *et al.* (2022) indicated that electrocoagulation is an effective technique for the treatment of oily wastewater.

Currently, wastewater treatment systems are selected based on their ecological sustainability, cost-efficiency, energy utilisation, and overall efficacy (Wang et al. 2023). These attributes render electrocoagulation one of the most favoured methods for the treatment of greasy wastewater. Researchers analysed various configurations commonly employed in electrocoagulation, including bipolar-parallel (BP-P), monopolar parallel (MP-P), and monopolar series (MP-S). The authors' findings indicate that the BP-P arrangement is the most economically efficient therapy (Turan 2021). The BP-P configuration has proven to be exceptionally effective in energy utilisation and the elimination of wastewater pollutants, resulting in enhanced energy consumption (Moneer *et al.* 2023). Augmenting the quantity of electrodes enhances the efficacy of the electrochemical (EC) process ((Jasim *et al.* 2023)).

Table 2-2 summarises some of these separation methods utilized in oily wastewater treatment, as well as their benefits and limitations

Table 2-2. Summary of physical separation techniques investigated.

Technique	Type of wastewater used	Target pollutants	Operating parameters	% Removed (Efficiency)	Advantages	Disadvantages	References
Ultrafiltration (UF)	Olive oil wastewater	COD Total phenolic compounds	103 kPa- Pressure	61%	Easy to clean	Fouling	(Cifuentes-Cabezas <i>et al.</i> 2021)
Reverse Osmosis	Oil Refinery wastewater	COD Phenol	2.5 bar	COD-99% Phenol- 98%	Highly effective in low-pressure	Expensive	(Bastos <i>et al.</i> 2020)
Chemical coagulation	Oil Refinery wastewater	COD, TSS, colour Turbidity	coagulant dose 36.14 mg Mixing speed- 145.93 rpm	COD- 78.75% TSS- 91.21% Colour- 72.89% Turbidity- 98.10%	An efficient method of coagulation	High dosages of coagulants are required. Require a mixture of coagulants that are expensive.	(Ayhan, Aldemir and Özgüven 2024)
Electrocoagulation	Slaughterhouse oily wastewater	COD, colour	Neutral pH.	COD-94% Colour - 99%	Requires no chemicals	Cleaning electrodes can be labour-intensive	(Akarsu <i>et al.</i> 2021)
Electrocoagulation	Petroleum refinery	COD, phenol	30v	85%, 65%	Produces no sludge	(Abbas <i>et al.</i> 2021)

2.8. Biosorbents used in oily wastewater

2.8.1 Agricultural and Natural Adsorbents used in wastewater

Natural and agricultural adsorbents are becoming more and more popular as substitutes for traditional chemical coagulants in water and wastewater treatment due to the growing need for economical and ecologically friendly solutions. Naturally occurring coagulants, like biological sorbents made from marine-based materials like chitosan and agricultural by-products like husks, sawdust, and moringa, are preferred due to their low toxicity, biodegradability, and economic feasibility (Nhut *et al.* 2020; Zhao *et al.* 2020).

Rice husks have attracted significant attention as biosorbents due to their abundance and low cost Huzir *et al.* (2019), they have demonstrated that under optimal conditions (6.0 g rice husk, pH 3–6, 57 minutes settling time), chemical oxygen demand (COD) and total solids (TS) removal efficiencies reached 52.36% and 84.94%, respectively, in refinery wastewater. These findings highlight the possibility of using rice husks to remove contaminants at a reasonable cost (Rahman *et al.* 2022; Naik, Kumar and Narsaiah 2023). However, limitations such as moderate ion exchange/sorption capacity and poor physical stability restrict their broader application (Laszlo and Dintzis 1994; Naik, Kumar and Narsaiah 2023). In order to improve adsorptive performance, ongoing research aims to address these limitations through chemical or physical modifications (Rahman *et al.* 2022).

The effectiveness of barley straw in treating wastewater that contains oil has also been studied. (Ibrahim, Wang and Ang 2010) discovered that barley straw could extract up to 90.5% of emulsified oil in three hours at a pH of 6–8 using a batch isotherm technique. In addition to demonstrating the critical role pH plays in adsorption processes, their study showed that barley ash, a by-product of barley straw, has even greater efficiency.

Another promising agricultural by-product for wastewater remediation is walnut shells. Improved backwashing performance and oil removal efficiencies of roughly 89.5% have been shown by modified walnut-shell filter media, indicating their suitability for ongoing industrial use (Yin *et al.* 2021). Walnut shell-derived activated carbon shows strong adsorption of hydrocarbons like petrol and diesel, usually adhering to the Langmuir isotherm, which is a sign of monolayer adsorption (El Jery *et al.* 2024). Other studies corroborate these findings, reporting effective removal of phenol and dyes using walnut shell derived activated carbon with a well described isotherm (Uddin and Nasar 2020; Othman, Mohammed and Ismail 2023).

Sugarcane bagasse is well known for being inexpensive and highly effective at removing hydrocarbons. According to pseudo-second-order adsorption kinetics and fitting both Langmuir and Freundlich isotherms, natural bagasse removed 60.3% of the total hydrocarbons from diesel-fired power plant effluent (de la Concepción Martínez-Nodal *et al.* 2022). Large-scale industrial wastewater treatment is possible thanks to its use in pilot-scale continuous adsorption systems, especially when modified with aluminium sulphate (Janpattanapong, Piyamongkala and Von Louie 2020; Kachako *et al.* 2023).

Through pyrolysis, a variety of agricultural wastes can be converted into activated carbon, a popular adsorbent. It is valued for its high adsorption capacity, effectiveness, and potential as a substitute for commercial activated carbons due to reduced precursor costs (Lamaming *et al.* 2022). According to Remmani *et al.* (2021), a 100 mg dosage of activated carbon derived from biochar removed 97% of BOD and 95% of COD after 24 hours. Large organic molecules can be efficiently removed thanks to their adaptability in both home and commercial settings (Moosavi *et al.* 2020). Nevertheless, production challenges such as high temperature requirements, relatively small surface area, long contact times, and cost-intensive processes can hinder its widespread adoption (Jadhav and Jadhav 2021). Natural flocculants, along with conventional agricultural waste and alternative biosorbents like eggplant peels, have demonstrated remarkable effectiveness in removing pollutants due to their rich chemical composition and large surface area (Al-Jaaf *et al.* 2022). Despite their promising adsorption capabilities, these biosorbents may also co-adsorb water and oil, which could be a useful drawback (Lapointe and Barbeau 2020)

To further enhance coagulation and flocculation efficiency, natural polymeric flocculants and their modified composites have been explored. They are attractive alternatives to traditional synthetic flocculants due to their high molecular weight and biodegradability (Arman, Chen and Ahmad 2021). When combined, natural and agricultural adsorbents offer viable and efficient substitutes for treating water and wastewater. Physical stability, selective adsorption, and process optimisation are some of the issues that still exist even though each material has distinct benefits like cost-effectiveness, renewability, and high adsorption capability. The practical use of these biosorbents is being advanced by ongoing research into material modification, hybridisation, and process integration, which supports the possibility that they could replace or enhance traditional treatment technologies.

2.8.2. Chitosan

Chitosan, an alternative biosorbent, and has shown considerable promise in water and wastewater treatment (Bakshi *et al.* 2020). Chitosan was discovered by German organic chemists and researchers in 1898 (Crini 2022). It has been applied in various streams, including the food and cosmetic industry. The use of biosorbent chitosan in wastewater has recently indicated effectiveness through various applications in the removal of organic and inorganic contaminants (Chadha *et al.* 2022). Chitosan has

many appealing properties, including hydrophobicity, biocompatibility, biodegradability, non-toxicity, and the presence of highly reactive amino (-NH₂) and hydroxyl (-OH) groups in its foundation, making it a powerful adsorbent important for the elimination of wastewater harmful substances (Nechita 2017; Virmani *et al.* 2023). These functional groups are also capable of generating interactions that can bind anionic species via electrostatic attraction (Han *et al.* 2022b), which also enhances antibacterial activity (Ardean *et al.* 2021)

Chitosan has been used in water treatment for a considerable amount of time and is not a recent addition to the field, one of the earliest authors (Gidas, Garnier and Gidas 1970) contrasted its use and performance with the alum, which was the best and most acknowledged drinking water purifier at that time. It was discovered to remove 97% of the COD from the polymer and adhesive industry. In this study, copper was completely removed from drinking water after 40 mg/L of chitosan was added. Another chitosan advantage was that it produced less sludge than alum.

Chitosan is a remarkable and useful component of biosorbent that is extracted from chitin, a product of crustaceans. It is a remarkable biopolymer derived through the partial deacetylation of chitin—a complex polysaccharide made up of N-acetylglucosamine units found abundantly in the cell walls of marine organisms that has garnered considerable interest as a sustainable and effective method for water treatment. This natural substance is celebrated not only for its eco-friendly characteristics but also for its ability to enhance water clarity and quality, making it a valuable resource in the pursuit of environmental preservation. (Thambiliyagodage *et al.* 2023)

Abdullah and Jaeel (2019) studied pilot plant scale experiments. The pilot plant, which included a feeding tank, settling tank, sand filter column, chitosan mixing tank, and storage tanks, was utilized in an experiment to treat synthetic textile effluent using chitosan. This experiment was carried out using a chitosan slurry prepared with 10g chitosan and 1 litre of tap water. 30 minutes of mixing time was allowed, and thereafter, the settling time for another 30 minutes was applied before the turbidity, colour, and COD tests were performed using a single-beam UV spectrophotometer. In this study, different dosages of chitosan ranging from 10 mg/L to 50 mg/L were used for the different concentrations of dye-contaminated water. The optimum removal rate for colour and COD was obtained at a biosorbent dosage of 40mg, and removal rates were found to be 98.5% and 94.2% respectively. Chitosan has a strong potential for utilization as a natural coagulant, and as an alternative to conventional coagulants that act more efficiently since it requires a significantly lower dose than other coagulants (Maria, Mayasari and Irawati 2020).

A study by Lee and San Lee (2020) investigated the application of chitosan as a natural coagulant for treating wastewater from oil refineries, utilizing different dosages ranging from 20 to 300 mg/L. Wastewater often contains high levels of chemical oxygen demand (COD), total suspended solids

(TSS), and strong coloration. Laboratory-scale experiments demonstrated that chitosan performs optimally under acidic pH conditions, achieving removal efficiencies of up to 86.8% for COD, 35% for TSS, and 97% for color. These results highlight the potential of chitosan for effectively treating oil refinery effluents, particularly when the pH is carefully controlled. have investigated the application of chitosan as a natural coagulant for treating wastewater from oil refineries. These results underscore chitosan's potential for effective treatment of oil refinery .effluents, especially when pH is carefully monitored.

Lamanna et al. (2023) conducted a thorough evaluation of commercial chitosan as an eco-friendly flocculant for oil-water emulsions stabilised by anionic, cationic, and non-ionic surfactants. They were able to remove up to 97% of the organic fraction with only 300 ppm of chitosan that had been deacetylated by at least 80%. High performance was maintained in alkaline conditions (pH 9–11), and the material could be reused for a minimum of three cycles with no efficiency degradation, showcasing practical durability in realistic emulsion chemistries.

Srimoon and Potipat (2021) created chitosan beads (3% w/v chitosan in 5% v/v acetic acid, gelled in 2.0 M NaOH) to soak up oil. In batch experiments (0.5 g beads in 50 mL oil-in-water at pH 5; 400 rpm; 25 min), the maximum oil absorption ($q_{\text{max}} = 1667.9 \text{ mg g}^{-1}$) was very high. The kinetics and isotherms showed that the sorption pathways were efficient, which is advantageous when particulate are better than dissolved coagulants/flocculants.

Ma et al. (2023) focused on difficult-to-treat oily wastewater from steel rolling and found that magnetic chitosan-based flocculants (MCS) greatly improve demulsification. Optimised formulations attained around 95.8% oil removal while significantly decreasing turbidity, elucidating how the hydrophobic alteration of chitosan combined with magnetophoretic separation facilitates rapid solid-liquid disengagement in intricate industrial effluents.

Du et al. (2024) described a grafted cationic magnetic chitosan flocculant (FS@CTS-P(AM-DMC)) that works well in a wide range of pH levels (3–9) and with oil loads up to 3000 mg L^{-1} . In a typical jar test (10 minutes of rapid mixing at 400 rpm and 3 minutes of settling), a dose of 5000 mg L^{-1} at pH 7 removed 98.7% of turbidity and 88.9% of COD. With the help of polyacrylamide, similar results were obtained with lower concentrations of CTS. The material kept more than 79% efficiency after being used eight times, which shows that magnetisation has benefits for recovery.

Feria-Diaz, Tavera-Quiroz and Vergara-Suarez (2018) prepared chitosan from shrimp exoskeletons of the *Palaemon serratus* species obtained from a local seafood restaurant. The effectiveness of the chitosan was applied to the wastewater emanating from the cattle slaughterhouse, this wastewater had a turbidity of more than 560 NTU. Initially, glacial acetic acid was used to conduct chitosan experiments, which dissolved the biosorbent, demonstrating that chitosan dissolves in an acidic medium. As a result, all

samples were performed at neutral pH, confirming that chitosan adsorption requires an alkaline media. In the work reported by Feria-Diaz, Tavera-Quiroz and Vergara-Suarez (2018), chitosan removed 90% of turbidity and has also proven that it is possible to obtain a high-quality chitosan, which is suitable for consideration as an excellent biosorbent for oily wastewater treatment. Grem *et al.* (2013) reported that chitosan can be employed as a coagulant agent for the removal of organic species as well as an adsorbent of phenol from a variety of industrial effluents.

A study was conducted to evaluate the effectiveness of chitosan, derived from crabs and transformed into a sponge, as an adsorbent for oil and grease in wastewater generated by an automotive repair facility. Research conducted by Castañeda Olivera *et al.* (2023) demonstrated that the sponge made from chitosan, sourced from a concentration of 15 mg, achieved removal efficiencies of approximately 75.26% for oil and grease, 63.15% for biological oxygen demand (BOD), and 59.5% for chemical oxygen demand (COD). The wastewater examined had a volume of 150 ml, a circumference of 3 cm, and a height of 1 cm.

(Avryl Anna, Anusha and Lavanya 2024) conducted a thorough examination of chitosan's effectiveness as a biosorbent for the remediation of oily wastewater with elevated oil contents. The study took place in a controlled laboratory setting and lasted for 15 minutes, with a rotation speed of 180 revolutions per minute (rpm) and a pH level of 6. The results showed that the oil removal rate was an amazing 90%, which shows that chitosan has a lot of potential for quickly cleaning up greasy wastewater. The high effectiveness suggests that chitosan could be a viable option for environmental engineers seeking sustainable wastewater treatment methods.

Latest environmental matters and the swift exhaustion of petroleum-related resources made researchers turn an eye to materials like chitosan as an alternative technique in oily wastewater treatment. Chitin, from which chitosan is derived, is extracted from crustacean shells that are abundantly available in nature, mostly around seashores (Liyanage *et al.* 2023). It is preferred due to its porous structure, its unique durability, biodegradability, and its high affinity with residual oil (Bakshi *et al.* 2020).

When employed specifically in oily wastewater, it has been demonstrated to function more efficiently than other major adsorbents, activated carbon and clay. Vidal and Moraes (2019) investigated the use of various forms of chitosan in multiple types of oil effluents and reported that chitosan is one of the best adsorption biomaterials for removing phenol up to 99%, provided that pH, initial oil-water emulsion concentration, adsorbent dosage, and contact time are carefully considered. Some of the natural adsorbents are summarized in Table 2-3.

Table 2-3. Summary for natural adsorbents investigated.

Biosorbent	Type of wastewater used	Target pollutants	Operating parameters	% Removed (Efficiency)	Advantages	Disadvantages	References
Activated carbon derived from biowaste	Palm oil wastewater	BOD COD	Reaction time-24hrs, Adsorbent dose-100mg	BOD-97% COD-95%	Manufactured in high - temperatures	Requires long contact time	(Remmani <i>et al.</i> 2021)
Walnut shells	Petroleum wastewater	Oil content	Particle size 2mm	Oil content- 89.5%	Non toxicity, e	Ineffective in saturated oils	(Yin <i>et al.</i> 2021)
Sugarcane bagasse	Oil refinery wastewater (diesel)	Hydrocarbons	59.9g biosorbent in a column, pH 7.45	60.3% Hydrocarbon	The most abundant material in RSA	Ineffective in high temperatures	(de la Concepción Martínez-Nodal <i>et al.</i> 2022)
Chitosan	Oil refinery wastewater	COD, TSS, Colour	300mg/L dosage	COD – 86.8%, TSS – 35%, colour – 97%	Affordable and abundant material	Poor mechanical strength	(Lee and San Lee 2020)
Chitosan	Oil and grease wastewater	Oil and grease, BOD, COD	3cm diameter and 1cm chitosan sponge, 150ml greasy wastewater	75.26% oil and grease removal, 63.15% BOD, 59.5% COD	3D porous structure of sponge chitosan is effective in oilywasteater	Low acid stsbility	(Castañeda Olivera <i>et al.</i> 2023)

2.9 The use of adsorption isotherms in adsorption

The adsorption isotherm depicts the relationship between adsorbate in the surrounding phase and adsorbate adsorbed on the adsorbent surface at equilibrium and constant temperature (Abin-Bazaine, Trujillo and Olmos-Marquez 2022). Adsorption isotherms can broadly characterize the distribution of adsorbate in both liquid and solid phases (Ibrahim, Wang and Ang 2010). The Langmuir and Freundlich isotherms are the oldest and are still preferred and utilized by researchers around the world (Albatmi *et al.* 2019), they seem to fit well in oily wastewater (Gholamifard *et al.* 2023).

2.10. The use of Adsorption kinetics in adsorption

Adsorption kinetic models are commonly utilized for oily wastewater treatment (Mojoudi *et al.* 2019; Diaz de Tuesta *et al.* 2020). Researchers apply the adsorption kinetics to demonstrate the characteristics of the adsorption process, and they use common adsorption kinetics (Ho and McKay 1998; Grisales-Cifuentes *et al.* 2021), adsorption kinetics that are commonly used are pseudo-first-order and pseudo-second-order rate laws (Revellame *et al.* 2020; Grisales-Cifuentes *et al.* 2021) however, the trend of the authors tend to favour the second-order model (Gulistan 2014; Revellame *et al.* 2020).

2.11. Summary

The literature review demonstrated the industrial impact on diminishing water supplies. As the need for high-quality water rises, so do the methods and procedures employed, which necessitate sufficient installation and upkeep. Physical separation methods have been evaluated, with chemical coagulation being the most popular in recent decades; nevertheless, coagulants involve chemicals, and most coagulants and flocculants are expensive and generate a lot of waste. An environmentally friendly electric-based coagulation method, electrocoagulation has demonstrated another useful approach in wastewater treatment. Biological and agricultural adsorbents, on the contrary, are catching the attention of researchers. These methods are less expensive, more widely available, safer, and biodegradable. Chitosan is the most beneficial because it contains both the reactive amino group and the hydroxyl (-OH) group, making it a potent biosorbent. Chitosan production directly contributes to United Nations Goal 12.3, which advocates for reducing food waste. It also participates in the "zero waste" initiative, which is run by the South African Association for the reuse and recovery of products. Adsorption isotherms, which are known to be beneficial for assessing how adsorbate molecules or ions interact with surface adsorption sites, are being used to efficiently measure chitosan capacity. The use of FT-IR to evaluate functional groups as a technique for chitosan verification. This study will examine the usage of electrocoagulation and biosorbent chitosan in the treatment of oily wastewater as a result of advantageous strategies demonstrated in this research.

CHAPTER 3 - MATERIALS AND METHODS

3.1 Introduction

This chapter outlines the materials used in the study, including sampling methods, measurement techniques, and data analysis strategies. It details the electrocoagulation setup, the jar test arrangement for chitosan studies, and the synthesis method for chitosan. Additionally, this chapter discusses the selection of reagents and the analytical procedures employed to quantify the targeted pollutants composition such as chemical oxygen demand (COD), colour, and phenol. All samples were sourced from a waste oil recycling refinery in Durban, South Africa, and analyzed in accordance with the American Public Health Association (APHA) standards (Rice, Bridgewater and Association 2012). All reagents used in this study were of laboratory grade.

3.2. Sample collection and preparation

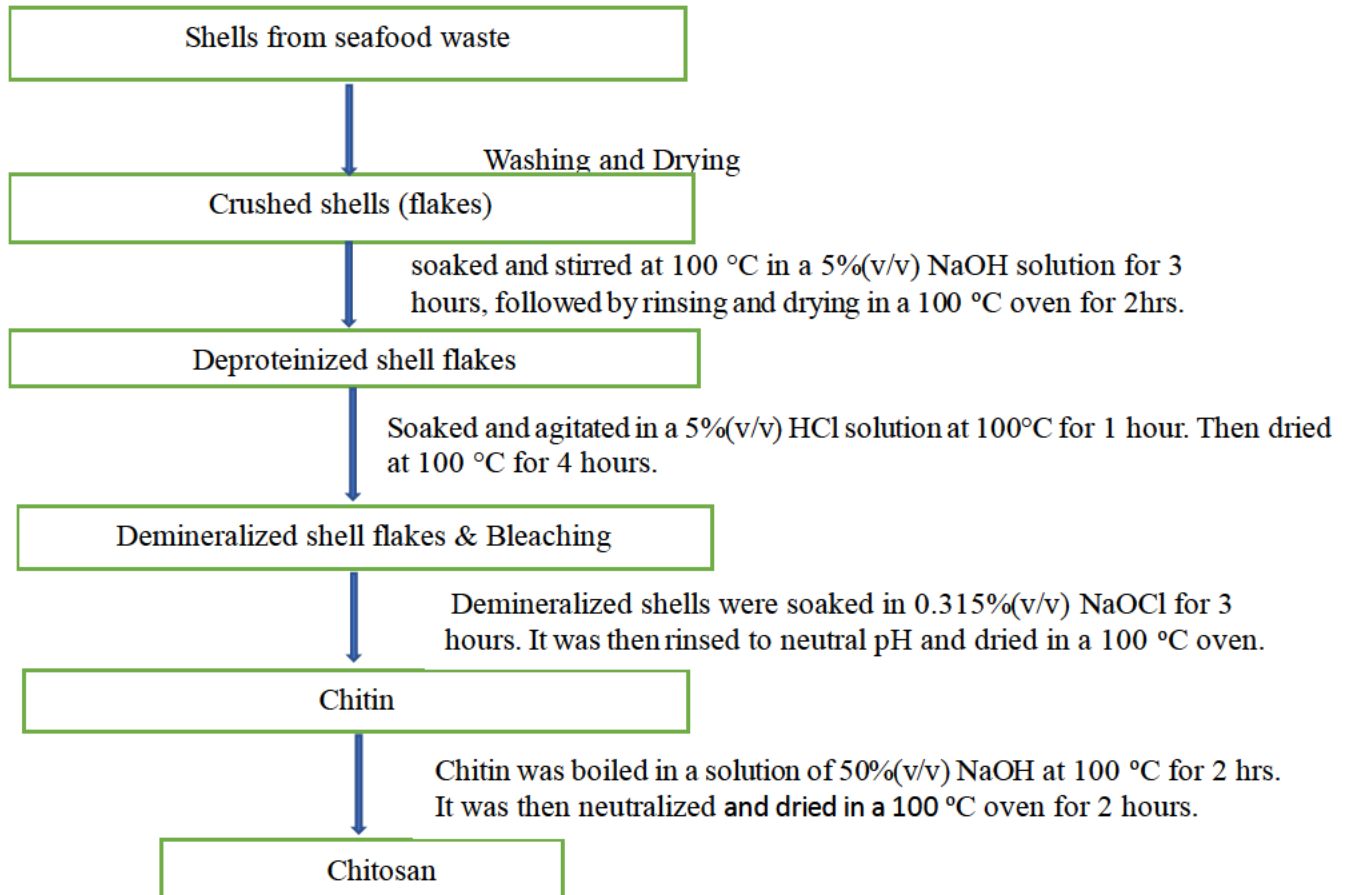
Raw wastewater samples were collected from an oil refinery plant in Durban, South Africa at the effluent stream. The sampling kit was prepared in advance to ensure optimal storage and preservation of the samples during transportation. It included a cooler box, ice cubes, and 1-liter amber bottles. The filtered samples were collected in 1-litre amber bottles to prevent photolysis and were kept in an ice-filled cooler box. This setup was designed to properly store the samples and maintain the biological conditions of the samples throughout transportation. On-site, prior to sample collection, the sampling point was flushed to remove any dirt that might have accumulated in the sampling line. Samples were collected and filtered on-site to remove debris. The samples were stored in a refrigerator maintained at ± 5 °C in the laboratory. The analysis commenced within 24 hrs of sample collection.

3.3. Biosorbent synthesis

Chitosan was synthesised by collecting oyster and mussel waste shells from a local seafood restaurant in Durban, South Africa. The shells were thoroughly cleaned using deionized water and dried before being crushed. They were crushed into a mixture of flakes and powder. Various sizes ranging from 25 to 1200 microns were obtained using sieving trays. However, samples with a particle size of 600 microns (0.6 mm) were chosen since it was predetermined to provide high removal efficiencies.

Chitosan production was done by soaking 500 g of shell powder (crushed oyster and mussel shells) in a 1 L solution of 5% sodium hydroxide (NaOH) under controlled temperature conditions of 100 °C for 3 hours. This was done to remove any protein compounds found in both oyster and mussel shells. Thereafter, the deproteinized powder was rinsed using deionized water until a pH of 7 was reached prior to drying at 100 °C for 2 hours. The dried deproteinised powder was soaked in a 1 L solution of 5% hydrochloric acid (HCl) at a temperature of 100 °C for 1 hour to produce chitin, which was then rinsed with deionized water to achieve a pH of 7. The chitin wet powder was then dried at a temperature of 100 °C for 2 hours. Dried chitin powder was then bleached by soaking it in a solution of 0.135 sodium hypochlorite NaOCl for 24 hours and rinsed with deionized water to a neutral pH. The bleached chitin

underwent deacetylation to produce chitosan by being heated in a 50% NaOH solution for 2 hours. Thereafter, the produced chitosan by deacetylation was rinsed with deionised water and dried at 65 °C for 4 hours. The steps of chitosan synthesis are further illustrated in Figure 3-1, and the produced chitosan powder is shown in Figure 3-2.



The product was rinsed to neutral pH and dried in a 65 °C oven for 4 hours to produce chitosan.

Figure 3- 1. Block diagram of the chitosan manufacturing process adapted from Hadi (2016).

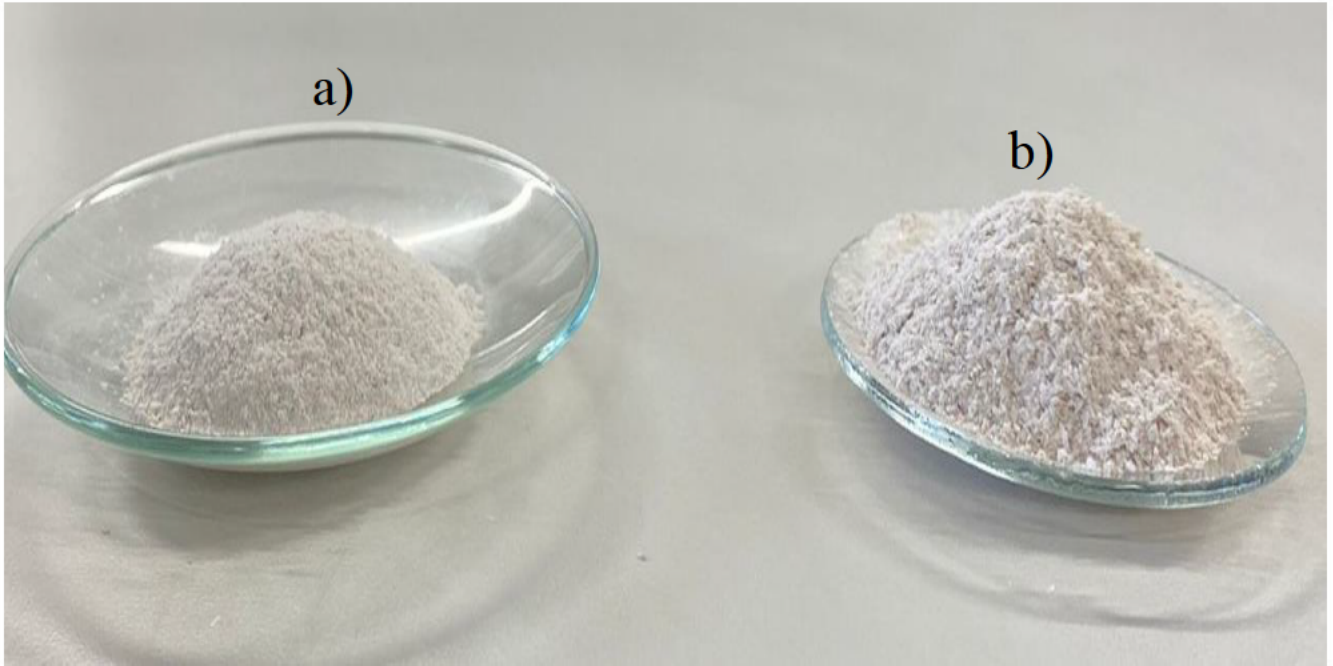


Figure 3- 2. Synthesized biosorbent (a) mussel chitosan and (b) oyster chitosan

3.3.1. Calculating the degree of deacetylation

The existence of free amino groups that remain after the removal of acetyl groups is an important aspect of chitosan manufacturing. Thus, the phase known as deacetylation defines the percentage removal of these acetyl groups, which also determines the grade of chitosan produced. The degree of deacetylation and molar mass of the synthesized chitosan was determined using the linear potentiometric titration method as outlined by Czechowska-Biskup *et al.* (2012). The degree of deacetylation (DD) was computed using the equation 3.1.

$$DD(\%) = \frac{\alpha}{W - 161. \alpha + \alpha} \times 100 \quad \text{Equation 3.1}$$

Where α is the amount of N-acetyl glucosamine and W is the mass of chitosan in g.

3.3.2. Chitosan characterization

Two methods of chitosan characterization were utilized for verification. Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray (EDX), and the Fourier Transform Infrared Spectroscopy (FTIR). SEM in conjunction with EDX was used to characterize the morphology and element distribution of chitosan. To enhance conductivity, a thin layer of carbon was employed to cover all samples throughout the examination. Upon analysis, pictures were acquired at a high voltage of 20 kV using a TESCAN Vega TC equipment linked with an X-ray detector. The EDX was retained at 5 kV and was used to determine the morphology of the components found in chitosan. The Fourier transform

infrared (FTIR) spectroscopy Perkin Elmer SP800 MIR was used to analyze and verify the presence of the chitosan functional groups in vibrations. The crystal was prepared and placed in a cleaned plate of the device, where the pinch of chitosan from the sample was added. The absorbance analysis was then conducted, and transmittance was read.

3.4. Experimental Procedure

3.4.1. Batch adsorption setup and operating procedure

Experiments were carried out using the one-factor-at-a-time (OFAT) method aimed at investigating the effect of 2 process variables, biosorbent dose and reaction time on the removal of COD, colour, and phenol from raw water originating from an oil refinery. The biosorbent setup was a simple traditional jar tester, as displayed in Figure 3-3. The jar tester (Lovibond ET 750) consisted of six paddles. Paddles were placed in each 1000 mL beaker connected to a stirrer. Chitosan dosages of 3 g, 9 g, and 15 g were prepared/measured using a top loading balance, Watch glasses were used to measure and collect chitosan, which was then added to separate beakers. Using a laboratory pipette, wastewater was measured into six sets of 1000 ml beakers, each containing a different dosage of chitosan. A timer was then set to track the duration of the experiment. While the stopwatch was observed, samples were taken from the jar test at every 15-minute intervals ranging from 15 to 90 minutes. The agitation speed was consistently maintained at 250 rpm. The pH was kept neutral because chitosan adsorption requires an alkaline or neutral environment (Bakshi *et al.* 2020). To maintain the solution pH, 1.0 M of HCl and 1.0 M NaOH were used for pH adjustments. However, during the course of the experiment, no pH adjustment was done as the adsorbent did not change the raw wastewater sample pH.



Figure 3- 3. Jar test instrument set up for chitosan experiments.

3.4.2 Electrocoagulation set-up and operating procedure

A 250 mL borosilicate glass beaker filled with 250 mL of the wastewater sample was used for the electrocoagulation tests. The bipolar-parallel (BP-P) arrangement of aluminium electrodes made up the treatment system. Each electrode was a flat, rectangular blade that measured 15 cm in height, 5 cm in width, and 0.1 cm in thickness. With polystyrene separators to prevent electrical short circuits, the number of electrodes was doubled from the original design to improve treatment efficiency. The electrode spacing was kept at 1 cm. Each electrode had an effective surface area of 150 cm² when both sides were taken into account, and the number of electrodes used determined the total active area.

The desired voltage was supplied by a regulated direct current (DC) power supply (0–30 V), and the applied current was continuously monitored during the experiment. To ensure consistent mixing throughout the treatment, the beaker was set up on a digital magnetic stirrer. Every experiment was conducted at room temperature, which is approximately 20 to 25 °C.

Depending on whether a pH increase or decrease was required, 0.1 M sodium hydroxide (NaOH) or 0.1 M hydrochloric acid (HCl) was used to bring the wastewater's pH down to the necessary level before electrocoagulation. For every run, the initial, modified, and final pH values were noted. Since the sample of oily wastewater already had adequate conductivity, the electrolyte was not investigated in this study because it would not materially improve performance or energy efficiency. Electrodes were taken out, cleaned, and dried after treatment, and the generated sludge was recovered by filtering the treated effluent. Faraday's law was used to calculate the amount of aluminium consumed.

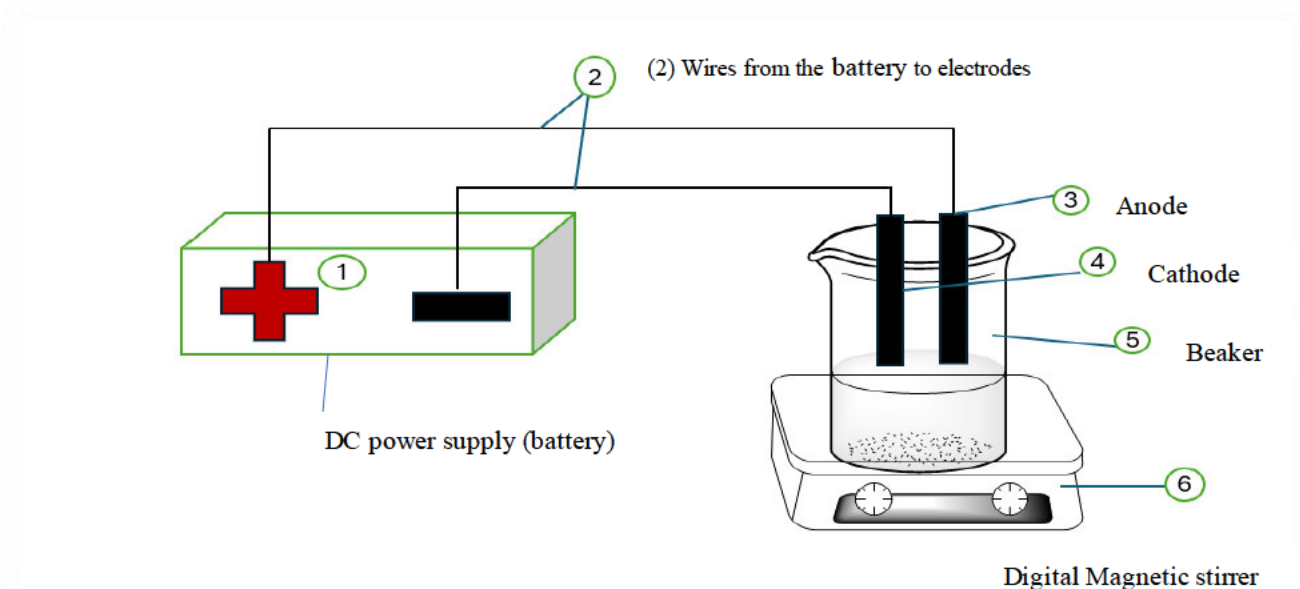


Figure 3- 4. Schematic illustration of electrocoagulation setup for experiments.

The aluminium electrodes chosen for this setup were prepared by removing the oxide coating on the metal strip. The aluminium blades were then scraped with fine sandpaper, rinsed with de-ionized water, and dried at 40°C for 2 hours. The beakers were filled with 200 ml of oily wastewater and the aluminium

blades were then immersed, separated by 1 cm polystyrene spacers. Stirring speed was kept at 250 rpm. Electrodes were connected to DC power supplier terminals. Electrodes were left to be covered by electrolytes, and the electrical circuit was turned on.

Throughout the experiments, the reactor was maintained at a constant voltage and current of 30 volts and 0.1 amps, respectively. Fresh effluent samples were provided for every run. Samples of 100 and 50 ml were collected every 10 minutes. Intervals of 10 to 90 minutes were chosen. Both single and double blades were used for the runs. This system was neutralized using 0.1 M hydrochloric acid (HCl) following each run, to prevent sample contamination and eliminate the oxides that could result in metal inactivity. The settling time for each run was 15 minutes. The instrumentation laboratory received treated samples for testing and analysis.

Since electrocoagulation (EC) uses energy, energy consumed becomes a critical parameter and the energy consumption for the EC operations needs to be measured. For this study, the energy consumption was calculated using the following equation.

$$E = UIt \quad \text{Equation 3.2}$$

Where E is the electrical energy usage (kWh), U is the voltage applied (V), I is the current (Amps), t is the electrolysis time (h).

The aluminium consumption was calculated using the equations 3.3 and 3.4:

$$m = \frac{I t M}{z F} n \quad \text{Equation 3.3}$$

Where m is the mass of electrode (g), I is the applied current (Amps), t is the electrolysis time (s), M is the molar mass of aluminium ($\text{g}\cdot\text{mol}^{-1}$), z is number of electrons exchanged = 3 ($\text{Al} \rightarrow \text{Al}^{3+}$), F is the Faraday's constant ($96485\text{C}/\text{mol}$), and n is current efficiency (=1)

$$m = nM \quad \text{Equation 3.4}$$

where m is the mass of aluminium consumed, n is the moles of electrons, and M is the molar mass of aluminium.

After each adsorption cycle, the used sorbent was regenerated to restore its ability to adsorb. Regeneration was accomplished via acid or basic desorption by rinsing the sorbent with dilute solutions of 0.1 M NaOH or HCl, depending on the experimental needs. Before being used again in the next cycle, the regenerated sorbent was cleaned with distilled water and dried. We tested the adsorption capacity after numerous regeneration cycles to see how it affected performance. This is because natural biosorbents usually lose 10–30% of their efficiency after 3–5 cycles because their structures break down and they bond to contaminants in a way that can't be undone. Final disposal was done in a controlled method, together with laboratory chemical waste.

3.5 Analytical procedure

All experiments were conducted at room temperature unless otherwise specified by the parameter test method. Before each use instruments were calibrated.

3.5.1. The use of a pH meter

The pH is a significant factor that was taken into consideration in this study. The aim was to maintain a neutral pH for electrocoagulation and biosorbent techniques. Research shows that electrocoagulation works best when the effluent is neutral. Similarly, with chitosan, the biosorbent dissolves when the effluent is acidic. Therefore, it is crucial to keep the pH of the effluent neutral or alkaline. The pH meter model EUTECH pH 700 was used in this experiment to ensure that the pH was neutral throughout the experiments.

3.5.2. Determination of COD

Chemical Oxygen Demand (COD) refers to the amount of organic and inorganic pollutants present in wastewater that decrease the amount of oxygen required in water bodies. Its high content in wastewater negatively impacts the environment, therefore by reducing the COD content the amount of contamination that enters our water supplies also decreases. In this study, reducing COD was necessary as oily wastewater is known to have high levels of COD. The HACH DR 3900 spectrometer was used to perform the COD analysis. To quantify the COD for the wastewater samples, high-range COD reagents (HI93754C-25) were used. This oxidizing agent mixture containing potassium dichromate and sulphuric acid indicates the COD content when mixed with wastewater and digested at 150 °C for 2 hours. This approach necessitates a single blank reagent adjustment for increased measuring precision.

3.5.3. Determination of colour

Wastewater colour is an indicator of the level of pollution in water. The colour in wastewater is usually caused by dissolved organic materials that can negatively affect the water's appearance. Unlike turbidity, which consists of suspended particles, colour can be challenging to remove. As a result, removing colour involves a series of processes that minimize the materials present in wastewater and restore water to its natural state. Colour removal is also necessary to comply with strict local effluent discharge limits. For this study, colour was measured using the HACH DR 3900 spectroscopy. The instrument has stored programs calibrated in colour units based on the American Public Health Association (APHA) colour index recommended standard.

3.5.4. Determination of phenol content

Phenols are a class of chemical compounds composed of an aromatic ring linked to an alcohol group. These phenolic chemicals have serious health consequences that can be both immediate and permanent. Refinery wastewaters are known to contain a high content of phenol, which highly exceeds the

allowable discharge limit of 1 mg/L. These hazardous solids pose a significant threat to the environment and removing them from our water bodies is crucial.

As a result of their metabolic and molecular characteristics, phenolic substances are ideal for quantification using UV-visible light. The ability of the phenolic ring to absorb UV light is used to quantify these chemicals, therefore, the phenolic content was determined using the ultraviolet-visible spectrometer (UV-VIS DU 640).

3.5.5. Determination of percentage removal rates

The percentage (%) removal rate for the phenol, COD, and colour, was calculated using equation 3.5.

$$\frac{C_0 - C}{C_0} \times 100 \quad \text{Equation 3.5}$$

Where: C_0 is the sample's initial concentration, and C is the final concentration after treatment.

3.6. Data Analysis

3.6.1 Adsorption Process Study

The rate at which the solute is adsorbed, and the residence time are crucial in adsorption, which is why adsorption kinetics is applied. Additionally, adsorption involves determining the optimal adsorption capacity and understanding the interaction between the adsorbate and adsorbent. This is where isotherms come into play.

3.6.1.2 Investigation of Adsorption Kinetics

Adsorption has become one of the most extensively used environmental remediation strategies. Its kinetics are critical for assessing the performance of a certain adsorbent and gaining insight into its mechanisms of operation (Qiu *et al.* 2009). Adsorption kinetic models were used in this study to evaluate adsorbents' performance and study adsorption mass exchange mechanisms. This was achieved by adding raw wastewater with known concentrations of pollutants (COD and phenol) into beakers containing 15 g of the biosorbent chitosan. A reduction in the concentration (i.e., COD and phenol) of oily wastewater was seen at varied time intervals (15 to 90 minutes). The experimental data was then fitted in linear pseudo-first-order (PFO) and pseudo-second-order (PSO) empirical adsorption kinetic models. The present study used the correlation coefficient, R^2 to identify the best fit between first-order and second-order adsorption kinetics.

Pseudo-first-order model

A pseudo-first-order (PFO) model can be used to characterize sorption kinetics. The following is the differential equation:

$$\frac{d.qt}{dt} = k_1(qe - qt) \quad \text{Equation 3.6}$$

The integrated equation in linear form yields:

$$\ln (q_e - qt) = \ln q_e \frac{k_1}{2.303} t \quad \text{Equation 3.7}$$

where:

q_e is the amount of contaminant at equilibrium, mg.g^{-1} .

qt is the amount of contaminant sorbed at time t , mg.g^{-1} .

k_1 is the equilibrium rate constant of pseudo 1st order, min^{-1} .

Pseudo-second-order model

The sorption kinetics can be characterized by a pseudo-second-order equation, a linear form for the boundary conditions is illustrated as:

$$\frac{t}{qt} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \quad \text{Equation 3.8}$$

k_2 is the equilibrium rate constant of the pseudo-second-order adsorption. All other equation terms have the same meaning as described in the pseudo-first-order model in Equation 3.7.

3.6.1.1. Investigation of Adsorption Isotherms

Adsorption isotherms are mathematical equations that describe the relationship between the amount of adsorbate adsorbed on an adsorbent and the concentration of adsorbate in solution once equilibrium is attained at a constant temperature (Abin-Bazaine, Trujillo and Olmos-Marquez 2022). For this study, batch adsorption experiments were performed by removing COD and phenol from refinery wastewater using a dosage of 15 g of chitosan in 400 ml of raw oily wastewater. This was done through the monitoring and recording of the decrease in concentration as the reaction time was increasing. The solution was agitated for 90 minutes at a constant speed of 250 rpm until equilibrium was reached. The adsorption capacity was then calculated using Equation 3.9.

$$q_e = \frac{C_i - C_o}{m} V \quad \text{Equation 3.9}$$

Where C_i and C_o are initial and final concentrations in mg/L , respectively, m is the mass of the adsorbent in g and V is the volume of wastewater used in litres. Freundlich and Langmuir's isotherms are the two most used approaches for predicting a material's adsorption capacity.

Langmuir isotherm

Isotherms are also used to calculate the amount of adsorbent material needed. The surface is homogenous according to the Langmuir adsorption isotherm if no lateral interaction occurs between the

adjacent adsorbed molecules. This is true even when a single molecule occupies a single surface location (El-Gendy and Nassar 2016). The linearised form of the Langmuir adsorption isotherm model is represented by the equation (Langmuir 1918).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad \text{Equation 3.10}$$

Where q_e (mg/g) is the amount adsorbed at equilibrium, C_e (mg/L) is the equilibrium concentration of the adsorbate, q_{max} (mg/g) is the maximum adsorption capacity, and K_L (L/mg) is the Langmuir constant related to adsorption energy. It denotes the degree of interaction between the adsorbate and the surface. If this constant has a high value, it implies a significant interaction between the adsorbent and the adsorbate. A smaller value for K_L , on the other hand, suggests a weaker contact between the surface and the adsorbate (Al-Ghouti and Da'ana 2020). Langmuir equilibrium constants are determined by plotting a slope from the intercept of the C_e/q_e vs C_e graph

The dimensionless separation factor R_L constant forecasts whether an adsorption system is “favourable” or “unfavourable”

The R_L is calculated using the equation 3.11.

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Equation 3.11}$$

R_L ranges from 0 to 1; R_L of zero indicates that the adsorption is irreversible; when $R_L=1$, the adsorption is unfavourable, when R_L is > 0 but < 1 the adsorption is favourable (Mckay, Blair and Gardner 1982).

Freundlich isotherm

The Freundlich adsorption isotherm relationship is also applicable for the concentration of the solute adsorbed onto the surface of a solid and the concentration of the solute in the liquid phase. Adsorption is a physical-chemical process involving the mass transport of adsorbate from the solution phase to the interior surface of the porous adsorbent where the adsorption occurs (Ng *et al.* 2002).

The linearised form of the Freundlich adsorption isotherm model is represented by the equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Equation 3.12}$$

Where C_e is the equilibrium concentration (mg/L), q_e is the adsorbed volume (mg/g), K_f (L/g) is an adsorption capacity constant, and $\frac{1}{n}$ is an empirical measure related to adsorption intensity. Freundlich equilibrium constants are determined by plotting a slope from the intercept of the $\ln q_e$ vs $\ln C_e$ graph. The variable n is an empirical constant related to the adsorbent surface's heterogeneity. For favourable adsorption, the value of n should be between 0 and 1 i.e., ($0 < n < 1$). $n > 1$ indicates

unfavourable adsorption, $n = 1$ represents linear adsorption. Additionally, if $n = 0$, the adsorption process is considered irreversible.

3.6.2. Process Optimization Using Response Surface Methodology (RSM)

In this study, the Design Expert 11 software program was utilized to perform RSM. It was used as a statistical approach method of optimization which in this case, was the use of the imported data from completed experiments and were custom-designed for optimization and validation purposes. One of the advantages of this tool is that it allows the selection of a minimum of two factors (input variables) when using custom-designed data, which was also applied in this study for both electrocoagulation and chitosan techniques. A series of laboratory experiments was conducted at the end to verify the optimization responses for both methods.

3.6.2.1. The application of RSM in Electrocoagulation

The scope of the investigative setup selected the two operational factors, the number of blades and the electrolysis time as the input, with their low and high values, respectively. Table 3-1 represents the input files for the electrocoagulation experimental domain.

Table 3-1. Experimental domain for electrocoagulation

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	Rn time	mins	Numeric	10.	80	-1 ↔ 10	+1 ↔ 80	45	23.66
B	No. of blades		Numeric	1	2	-1 ↔ 1	+1 ↔ 2	1.5	0.5164

3.6.2.2. The application of RSM in batch adsorption studies of Chitosan

The setup utilized two operational factors, the chitosan biosorbent dose and reaction time. The low and high values were clearly defined for an effective approach. Table 3-2 represents the input files for the chitosan experimental domain.

Table 3-2. Experimental domain for chitosan

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	Dosage	g	Numeric	3	15	-1 ↔ 3	+1 ↔ 15	9.00	5.04
B	Rxn Time	min	Numeric	15	90	-1 ↔ 15	+1 ↔ 90	52.50	26.36

3.6.2.3. Optimisation using completed experiments

The response surface methodology (RSM) used the imported data from completed experiments and were custom-designed for optimization and validation purposes. Since RSM uses independent input variables (factors) and the output (responses), this study used the completed data from completed experiments. The RSM tool, Design- Expert 11 made use of 16 proposed experiments for Electrocoagulation.

The study utilized this data as an optimization tool for factorial variables. The design used numerical factors: electrolysis time and the number of blades for the EC, and used reaction time, and biosorbent dosage for the chitosan, to evaluate the optimum conditions of the efficiency of parameters (responses) in percentages (%). The responses were COD, colour, and phenol. By fitting the responses to a second-order polynomial equation, the mathematical correlation between the operational variables and the replies was computed (AlJaberi, Ahmed and Makki 2020).

$$y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ij} X_i X_j + \varepsilon \quad \text{Equation 3.13}$$

Where: k represents the number of variables, β_0 is the constant coefficient, β_i is the linear parameter coefficient, X_i and X_j are variables, β_{ij} is the quadratic parameter coefficient, and ε is the random error of experiments.

After fitting the polynomial equation, the quality of the model is indicated by a higher value of the regression coefficient R^2 and the results of the analysis of variance (ANOVA). The p test ($p \leq 0.05$) determined the significance and the coefficients of determination (R^2 and Adjusted R^2) assessed model fit. The functional relationship between the responses was represented further by 3-dimensional plots and expected vs actual plots.

The optimal solution was represented by the ramp plot which exhibited the desirability and optimization solutions. The selected solutions were compared with the optimal solution from the experiments and validated with the repeated laboratory experiments.

CHAPTER 4 - RESULTS AND DISCUSSION

4.1. Introduction

This chapter gives comprehensive findings of the analysis conducted by contrasting the two methods i.e., electrocoagulation, and adsorption in the removal of contaminants viz. COD, colour, as well as phenol from oil wastewater. The comparison of these techniques was assessed on a laboratory scale set-up. Detailed results of the performed analysis are presented in this chapter. The results of chitosan characterization, including surface morphology and element distribution analysis and its functional groups, are provided, as well as those derived from chitosan functional group verification. Data analysis results on biosorption kinetics and isotherms, as well as optimization and verification are also presented in this chapter.

4.2. Structural and Surface Analysis

4.2.1. Raw oily wastewater

Fresh samples of oily wastewater were analyzed for the selected parameters as presented in Table 4-1 before the commencement of experimental runs. Each parameter was evaluated three times to obtain an average, and the deviation was calculated to assess data variability. From Table 4-1, it can be observed that raw wastewater used in this study recorded a turbidity of 80.5 NTU. The obtained low turbidity values suggest that wastewater emanating from oily refineries is characterized by a low composition of dissolved solids. This could be attributed to the fact that the activities within the refinery plant do not involve solid or organic material during processing. The present study's findings on turbidity are congruent with the work reported by Safo-Adu (2020) who reported a turbidity mean value of 65 NTU for wastewater emanating from an oily refinery. The chemical oxygen demand (COD) of 2029 mg/L obtained from this study confirms the classification of oily wastewater as having a high COD due to organic materials such as oil and grease. Meiramkulova *et al.* (2020) also investigated the COD value of the refinery wastewater, reporting an initial concentration of 2042 mg/L. Oily wastewater is further distinguished by its high colour intensity, the presence of various pollutants during oil processing causes high colour intensity (AlJaberi *et al.* 2020). This research yielded a colour value of 1955 Pt-Co. Ishak and Malakahmad (2013) reported the colour value of 5325 Pt-Co, which is even higher than the value obtained in this study. Phenol is a highly harmful organic substance found in wastewater and poses a significant health risk; refinery wastewater contains a high concentration of this contaminant since its processes employ crude oil and petroleum. The present research obtained 1948 mg/L, which confirms the study conducted by Saputera *et al.* (2021), which found a high phenol content value of 1600 mg/L.

Table 4-1. Oil refinery wastewater composition

Parameter	Present Study	Meiramkulova <i>et al.</i> (2020)	Bastos <i>et al.</i> (2022)
pH	7.05 – 7.8	7.4	8
COD (mg/L)	2027 - 2031	2024	1241.9
Turbidity (NTU)	80.1 – 80.5	68.7	-
Colour (Pt-Co)	1944 - 1981	552	-
Phenol Content (mg/L)	1925 -1967	-	376

4.2.2. Synthesized chitosan biosorbent

Characterization of the adsorbent was critical for this study since it detailed the effects of the biosorbent's physical, chemical, and biological properties, as well as the mechanisms, behaviour, and phenomena that occur throughout the adsorption process. It also sheds light on the qualities of the adsorbent material and its performance in various procedures. Characterization provided useful information regarding the adsorbent's chemical constituents such as identification, location, and quantity. It also showed the functional groups on the material's surface that are associated with adsorption mechanisms.

A polysaccharide's performance is often related to its membrane surface, textural qualities, complexity, film roughness, and cross-sectional morphology (Rekik, Gassara and Deratani 2023). Thus, proper characterization of the membrane structures is crucial for developing the synthetic chitosan used in this study. During characterization, scanning electron microscopy (SEM) was combined with energy-dispersive X-ray (EDX) to determine the shape of the components found in synthetic chitosan. Figures 4-1 to 4-2 show that the microstructure obtained by SEM and EDX microscopy for chitosan and its composite particles is generally well disseminated in the chitosan medium.

The SEM-EDX results displayed in Figures 4-1 and 4-2 show the spherical morphology and homogeneous size distribution of the oyster chitosan (i.e., Figure 4-1(a)) and mussel chitosan (i.e., Figure 4-2(a)). Figures 4-1(b) and 4-2(b) illustrate the elemental composition of chitosan in detail. The results of the elemental analysis highlight a notably high content of calcium within the chitosan structure. This elevated calcium level is particularly advantageous, as calcium-based adsorbents have demonstrated significant effectiveness in a variety of applications, including water purification and heavy metal removal (Chakraborty, Pandey and Pandey 2017; Han *et al.* 2022a).

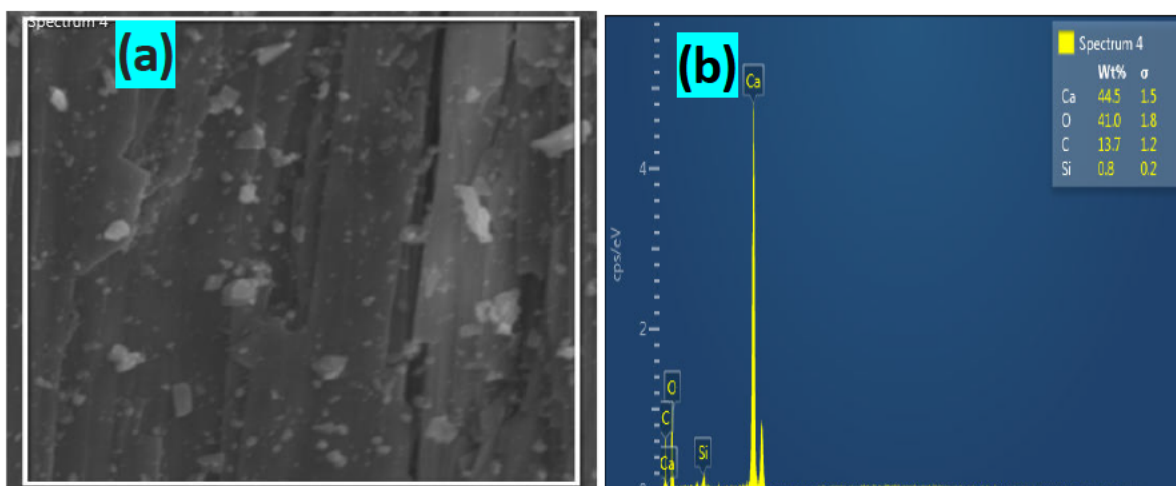


Figure 4- 1. SEM -EDX analysis image for oyster chitosan.

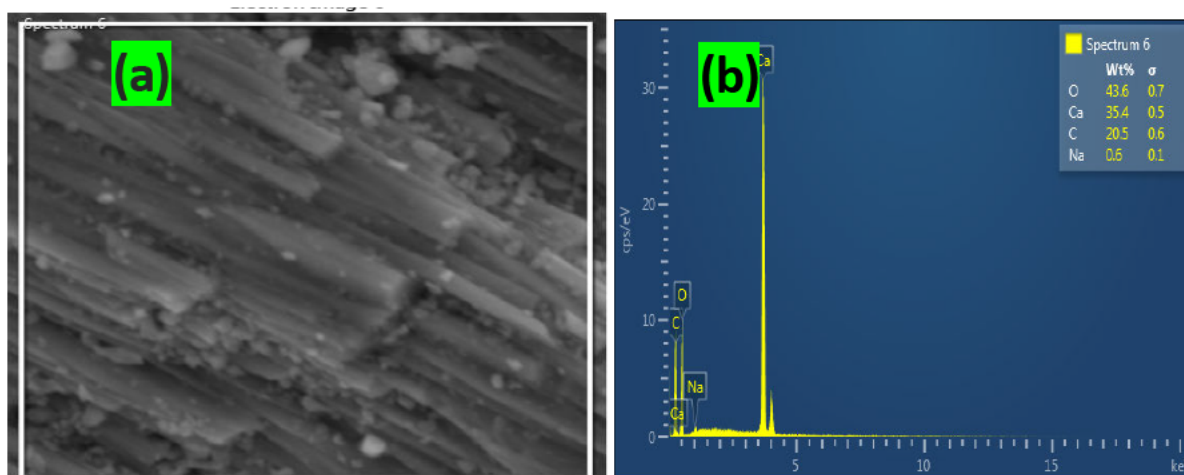


Figure 4- 2. SEM – EDX analysis image for mussel chitosan.

Furthermore, effective chitosan should possess several key properties such as hydrophobicity, biocompatibility, biodegradability, and non-toxicity (Hamed 2023). Additionally, it should contain highly reactive amino (-NH₂) and hydroxyl (OH) groups in its structure (Abourehab *et al.* 2022). These attributes make chitosan an efficient adsorbent material for removing contaminants from wastewater (Shalaby 2017; Das, Ghosh and Pramanik 2024). Thus, an FTIR spectrometer was used in this study to detect the presence of the aforementioned functional groups for the synthesized chitosan.

The FTIR vibrations measured in cm⁻¹ for the spectroscopy are shown in Figure 4-3 and Figure 4-4. In the spectrum for oyster-based chitosan in Figure 4-3, the band 3655 cm⁻¹ suggests the presence of an O-H stretching bond, 2924 cm⁻¹ attributes the N-H stretching bond, and vibration 1577 cm⁻¹ confirms N-H bending bond. There is also an indication of an O=C=O at vibrations 2349 cm⁻¹ bend which could be a possible nano chitosan. This spectroscopy is congruent with the work reported by Dias *et al.* (2022), thus suggesting chitosan properties for the synthesized adsorbent. The spectrum for mussel chitosan in Figure 4-4 also follows the above trend, however, the vibrations for the second amine group are not evident in the structure. These findings indicate that the chitin component was not completely removed.

Based on these findings, this study only continued with the utilization of oyster-based chitosan for the removal of COD, colour, and phenol in oil refinery wastewater.

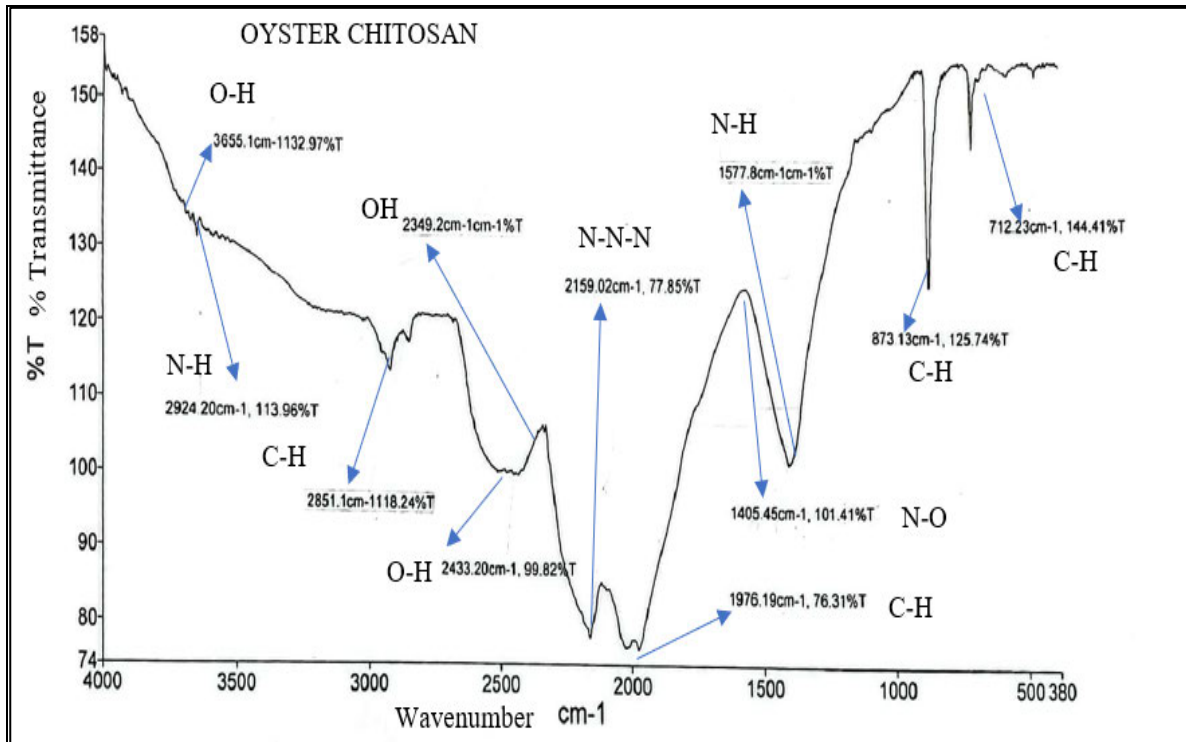


Figure 4- 3. FTIR spectrum for oyster shell-based chitosan

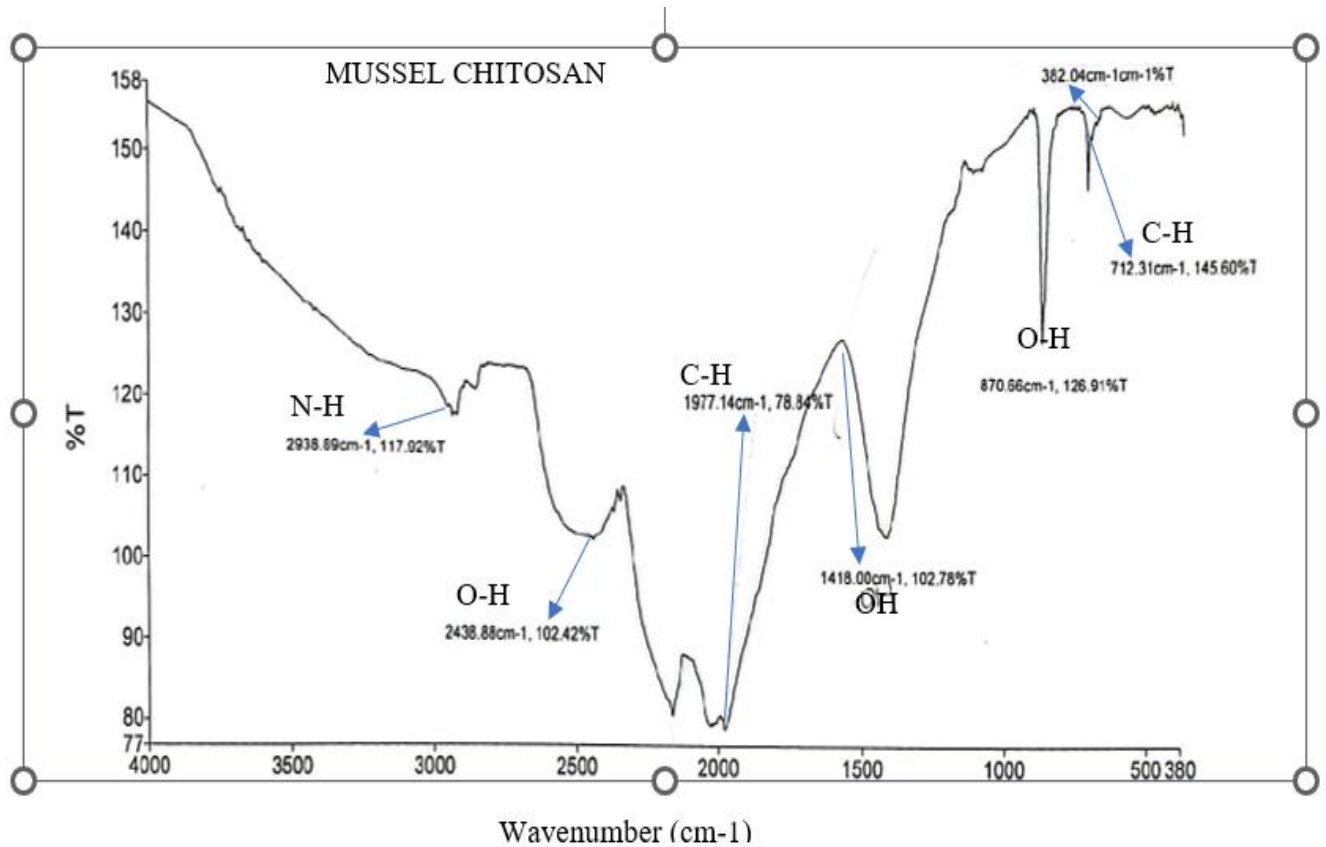


Figure 4- 4. FTIR spectrum for mussel shells-based chitosan

Following the production of the biosorbent chitosan discussed in Chapter 3, the degree of deacetylation (DD) for each chitosan species was calculated using Equation (3-2). The results revealed that the DD values for chitosan derived from mussels and oysters were 76.92% and 80.46%, respectively. These values fall within the medium deacetylation range, indicating a moderate conversion of acetyl groups to amino groups. (Carrera *et al.* 2023). Chitosan of 85-95% has a good solubility in water (Gamage *et al.* 2023).

4.3. Electrocoagulation (EC) in the treatment of oil refinery wastewater (ORW)

The selection and performance of operational factors, such as the kind of analyte, the distance between electrodes, the metal employed, and the running time, determined the effectiveness of electrocoagulation. The parameters for this investigation were selected based on the normal composition of the raw wastewater samples that are related to highly concentrated waste oil-water emulsion. The primary contaminants found in oily wastewater include phenol, however, this study also investigated COD and colour in the treatment of raw oily wastewater since these parameters are commonly found in oily wastewater (Chakawa and Aziz 2021; Thorat and Sonwani 2022).

This study was conducted at 30 volts of voltage and a current of 0.1 Amps and was kept constant throughout the experiments. However, despite the low current, gas bubbles and contaminants were spotted floating on the water's surface, and the process produced good results in electrocoagulation. Authors like Ahangarnokolaei, Ganjidoust and Ayati (2018) also considered taking current as an independent variable and kept it constant in their experiments. Conducting an EC experiment under these conditions is not novel, Amri *et al.* (2023) also conducted the study under these conditions. A series of experimental runs were conducted to investigate the use of electrocoagulation (EC) in removing COD, colour, and phenol from raw wastewater. Each run focused on one variable at a time. As the reaction time increased from 0 to 80 minutes, the satisfactory removal rates confirmed the EC process's effectiveness. Under optimal conditions, which are the double blade arrangement, and electrolysis time of 80 minutes, the experimental runs resulted in removal rates of 91.4% for COD, 96.7% for colour, and 94.5% for phenol.

The coherence and effectiveness of electrocoagulation also depend on a constituent, initial pH (Loukanov *et al.* 2020). When aluminium electrodes were employed in this study, neutral pH (pH7) produced dependable, consistent, effective, and quality findings; the pH did not fluctuate during the experiment.

4.3.1. COD removal using EC

The removal rate of COD over time is illustrated in Figure 4-5. This study conducted a comprehensive analysis of COD elimination rates over a duration of 80 minutes. At 60 minutes, the measured parameter attained equilibrium, as seen in Figure 4-5. Interestingly, the rate of COD removal responded quickly around the 30-minute mark, suggesting that this was the apex of the removal process's efficiency.

Therefore, removal rates were not significantly increased by prolonging the time past 60 minutes. During the optimal operating time of 80 minutes, the study achieved an impressive COD removal rate of 91.4%. This finding emphasizes the effectiveness of the electrocoagulation process and highlights the importance of monitoring time frames to maximize pollutant removal.

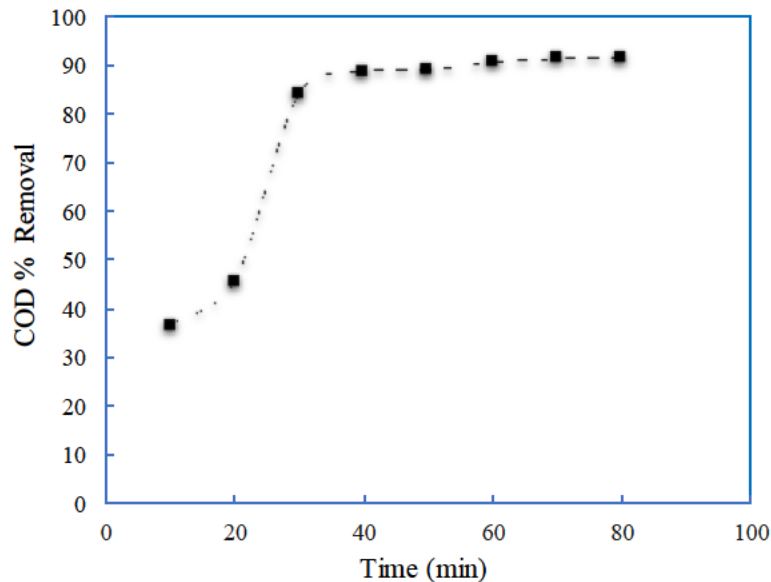


Figure 4- 5. EC effect on COD removal rate

4.3.2. Colour removal using EC

Figure 4-6 provides a detailed illustration of the dynamic response of the colour removal rate achieved through the electrocoagulation (EC) process. The data indicates that within just 10 minutes, approximately 60% of the colour was removed from the raw wastewater sample. This rapid reduction underscores the effectiveness of the method. As the process continued for 20 minutes, the colour removal rate improved significantly, reaching around 80%. Ultimately, the electrocoagulation process achieved an impressive total colour removal of 96.7%. These findings highlight the efficacy of using aluminium electrodes in electrocoagulation for colour removal in wastewater treatment. The fast rate of colour elimination suggests that this technique can be viable for industries seeking quick and efficient treatment for colour. Furthermore, this study's results align with previous research done by Beddai *et al.* (2022), which reported a remarkable 98% colour removal using aluminium electrodes, confirming the reliability and effectiveness of electrocoagulation as a solution for colour pollution.

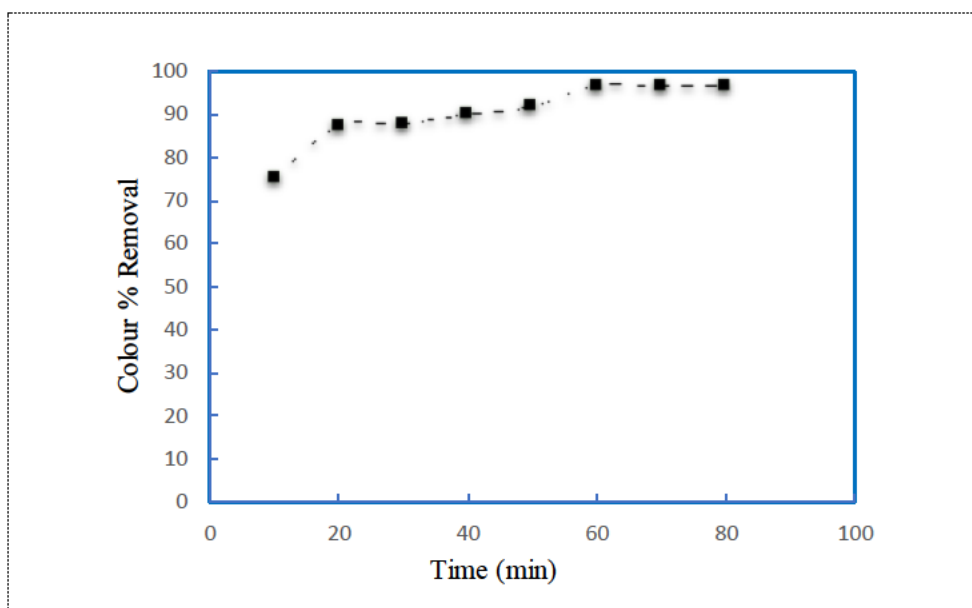


Figure 4- 6. EC effect on colour removal rate

4.3.3. Phenol removal using EC

The efficacy of electrocoagulation (EC) as a technique for the removal of phenolic chemicals from refinery wastewater was studied. The results, as depicted in Figure 4-7, demonstrate the rapid and effective response of the electrocoagulation process in eliminating phenol contaminants. In the initial phase of the experiments, it was observed that more than 80% of phenol was effectively removed within a brief reaction time of just 10 minutes. As the reaction time was progressively extended to 80 minutes, the removal efficiency improved significantly, ultimately achieving a remarkable rate of 94.5%. These results highlight electrocoagulation's potential as a dependable approach for treating phenol-containing wastewater. Furthermore, these findings align with previous research conducted by Abbas *et al.* (2021) which similarly reported substantial reductions in phenol contaminants when aluminium electrodes were employed in the electrocoagulation process. The consistency of these results highlights the robust applicability of EC in effectively addressing phenolic pollution in wastewater treatment.

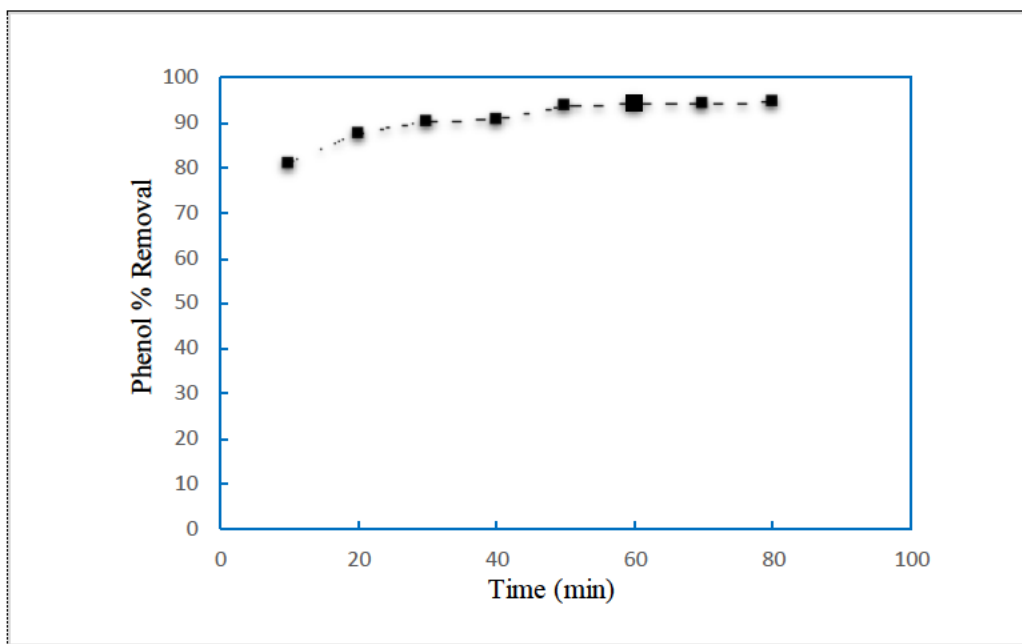


Figure 4- 7. EC effect on phenol removal rate

4.3.4. Effect of electrolysis time and double blade arrangement on removal rates.

This study thoroughly investigated the selection of electrodes, specifically analyzing the performance of single-blade (SB) and double-blade (DB) aluminium electrodes. In addition to electrode selection, the study also examined the impact of varying the duration of the electrolysis process on the overall results. The removal rates of COD, colour and phenol as a function of time are depicted in Figure 4-8. This study measured the rates of elimination for chemical oxygen demand (COD), colour, and phenol over a period of 80 minutes. However, it can be observed in Figures 4-8 that the process reached equilibrium for all measured parameters at 60 minutes. The importance of reaction time in this study is coherent with Faraday's law, which states that the amount of substance being reduced during electrocoagulation is the function of time and current. According to Faraday's law, the response contact time has a significant impact on the electrocoagulation process (Ebba, Asaithambi and Alemayehu 2021; Sankar and Sivasubramanian 2021). The experiment carefully monitored the reaction time while conducting the removal rate for the three parameters: COD, colour, and phenol. The parameters' elimination rates improved as the electrolysis time increased. The benefit of an extended electrolysis time in electrocoagulation is demonstrated by the good reduction rate of over 89% that both single and double blades achieved at the ideal electrolysis period of 80 minutes (see Table 4-2). This backs up the research done by Priya and Jeyanthi (2019) and Ebba, Asaithambi and Alemayehu (2021).

There was a noticeable, rapid response in removing COD, colour, and phenol; 50% of the contaminants were removed in 10 minutes when using double electrodes, as opposed to 30 minutes with a single electrode. Turan (2021) and Asfaha, Tekile and Zewge (2021) also observed that this arrangement is both cost-effective and enhances efficiency.

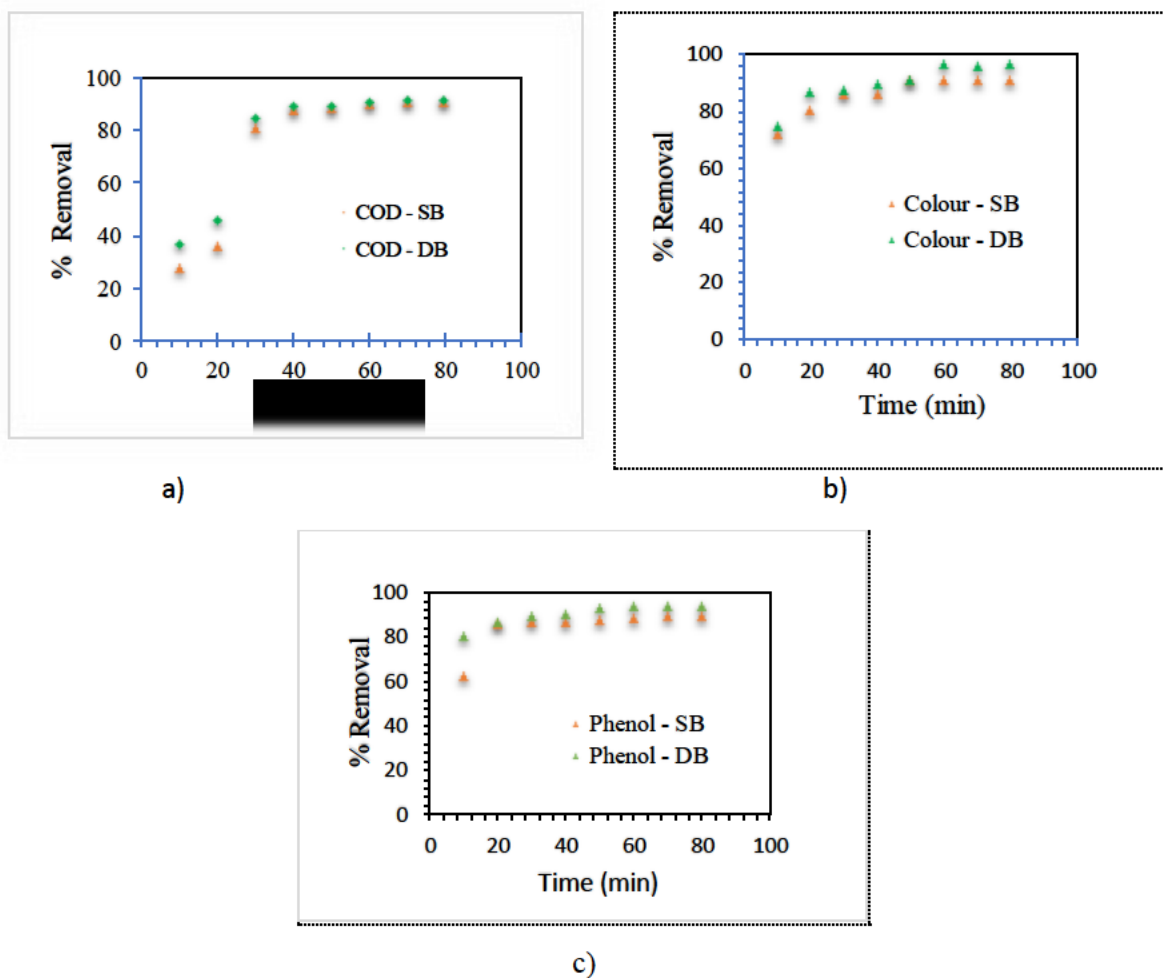


Figure 4- 8. Effect of time and electrode configuration on a) COD, b) colour, and c) phenol reduction using EC.

Table 4-2. Electrocoagulation performance at maximum time (80 minutes)

No. of blades	COD initial concentration 2029mg/L		Colour initial concentration 1955 mg/L		Phenol initial concentration 1948 mg/L	
	Final concentration	Removal Rate (%)	Final concentration	Removal Rate (%)	Final concentration	Removal Rate (%)
Single	184.1mg/L	90.9	168.3mg/L	91.4%	201.6mg/L	89.6%
Double	174.3mg/L	91.4	63mg/L	96.8%	106.5mg/L	94.5%

The use of double electrodes led to a significantly faster response time than the single-electrode design, as illustrated in Figures 4-8 and Table 4-2. Additionally, the double-blade configuration showed an enhanced rate of contaminant removal.

Moreover, this study applied the bipolar parallel (BP-P) arrangement of electrodes, which proved to be effective. This arrangement offers a simple setup and easy maintenance. When this configuration is utilized, current flows through the outer electrode and the other electrodes also become charged, resulting in reduced power consumption (Bharath, Krishna and Manoj 2018; Moneer *et al.* 2023).

In this study, a direct power supply was used to calculate the energy consumption of the electrocoagulation technique. Equation 3.1 in Chapter 3 was used to determine the power consumption of this experiment. Electrocoagulation is widely employed due to its potency and ease of usage, especially when attributed to the BP-P arrangement of electrodes due to the high surface area (Sharma and Chopra 2015; Othmani *et al.* 2022). The energy consumption for this study was compared to other research studies that used electrocoagulation with different configurations and using two distinct materials to treat oily wastewater. (Ibrahim 2022) obtained 0.062 kWh when using aluminium electrodes arranged in a bipolar series arrangement; Jasim and AlJaberi (2023a) obtained 4.342 kWh when using an aluminium anode and a stainless-steel cathode. This study's power consumption was 0.004 kWh, and it used aluminium electrodes. These findings were in line with the study conducted by Sharma and Chopra (2015) and (Igwegbe *et al.* 2021), where aluminium (Al – Al) electrodes exhibited satisfactory contaminant removal. This study also calculated aluminium consumption, which resulted in a value of 0.09 g (see Equation 3.4 and calculation in the appendix).

4.4 Biosorbent chitosan use in the treatment of oil refinery wastewater (ORW)

The effectiveness of an adsorbent in treating wastewater is primarily determined by its ability to absorb various contaminants. This study explored the performance of chitosan as an adsorbent by varying key parameters such as dosage and reaction time. The chitosan utilized in this experiment was synthesized in Chapter 3 and specifically selected for its potential to remove pollutants from oily wastewater originating from an oil refinery.

4.4.1. COD removal using chitosan

This study conducted an in-depth analysis of the rates at which COD was eliminated over a period of 90 minutes. The data presented in Figure 4-9 demonstrate that the COD removal rate experienced a significant improvement, exceeding 70% at the 30-minute mark. This suggests that the efficiency of the removal process was maximized at this specific time point.

Furthermore, during the entire 90-minute duration, the study achieved an impressive overall COD removal rate of 88% at a chitosan dosage of 15 g. This high level of removal underscores the efficacy of chitosan as an adsorbent in treating oily wastewater, making it a promising option for industries dealing with such contaminants. The findings of this research not only illustrate the rapid effectiveness of chitosan in reducing COD levels but also provide valuable insights for optimizing wastewater

treatment processes. This study aligns with El Shahawy and Heikal (2018) findings, which demonstrated an impressive 92% COD removal when treating oily wastewater with chitosan.

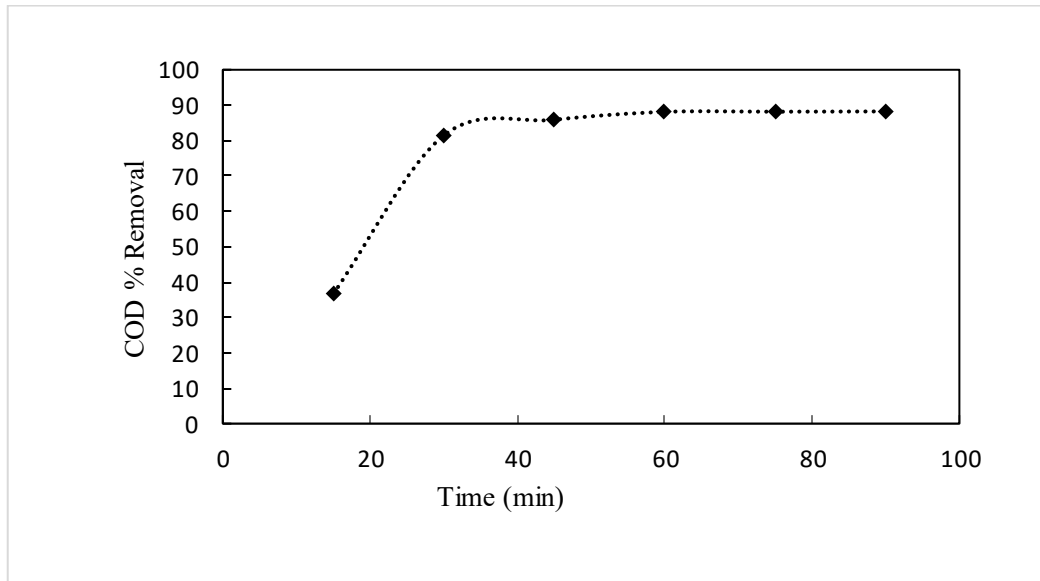


Figure 4- 9. Chitosan effect on the COD removal rate

4.4.2 Colour removal using chitosan

The colour removal rate using chitosan is shown in Figure 4-10. Chitosan has proven to be effective in removing colour contaminants from raw oily wastewater, demonstrating its potential as a viable treatment option. The study identified optimal conditions for colour removal, which were achieved with a chitosan dosage of 15 g. Under these conditions, the removal efficiency reached an impressive rate of 87.53%. This suggests that chitosan is a promising agent for treating colour in oily wastewater and can significantly improve water quality by targeting and reducing specific pollutants such as colour.

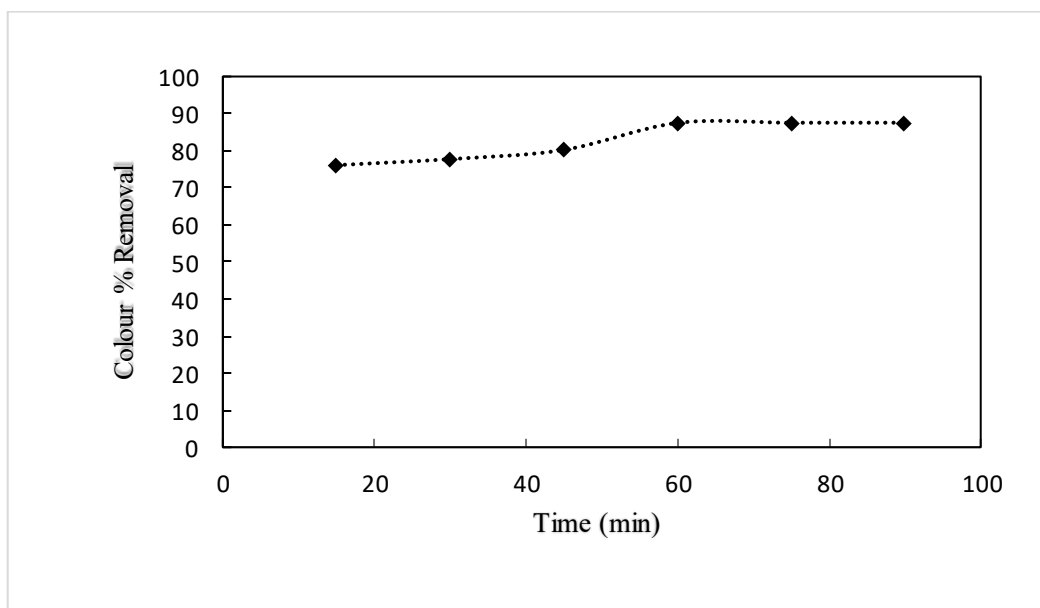


Figure 4- 10. Chitosan effect on colour removal rate

4.4.3. Phenol removal using chitosan

This study investigated the effectiveness of chitosan in removing phenol from raw oily wastewater. The results, illustrated in Figure 4-11, indicate that chitosan, as a biosorbent, successfully eliminated phenolic contaminants. Initially, it was observed that more than 85% of phenol was removed using chitosan in just 10 minutes of reaction time. As the reaction time was extended to 90 minutes, the removal efficiency increased significantly, ultimately reaching an impressive 89%. This finding emphasizes chitosan's potential as a reliable method for treating phenol, a known toxic contaminant (Singh et al., 2020). Additionally, these results align with previous research done by Salari et al. (2019), which reported phenol reductions of up to 97% when employing chitosan in oily wastewater. The consistency of these findings further emphasizes the effectiveness of chitosan in addressing phenolic pollution in wastewater treatment.

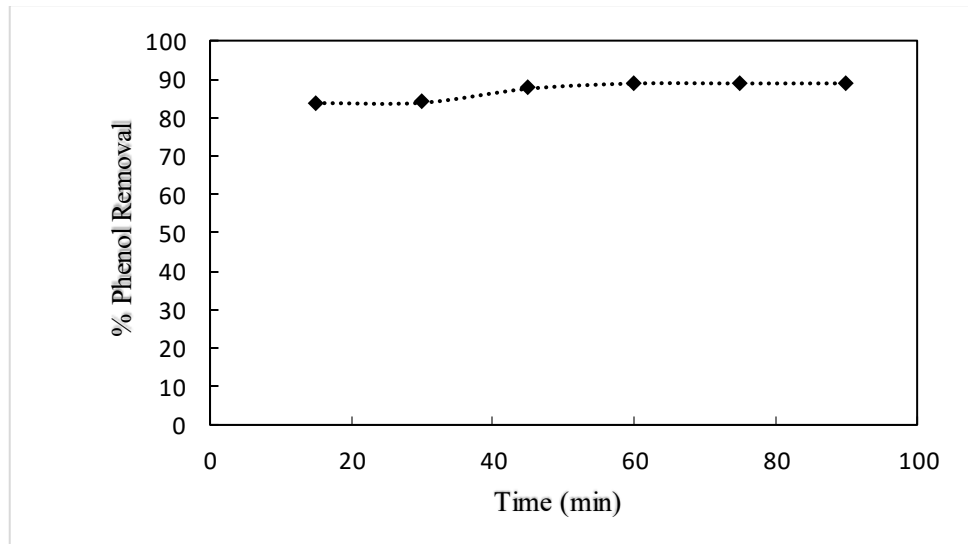


Figure 4- 11. Chitosan effect on phenol removal rate

4.4.4. Effect of biosorbent dose and contact time in the removal rates of contaminants.

This research thoroughly investigated the use of biosorbent chitosan in treating oily raw wastewater. The study concluded that the duration of adsorption time is crucial for the removal of COD, colour, and phenol. Figure 4-12 illustrates that the removal rates increase as contact time increases. A significant change was observed in the removal rates between 60 and 90 minutes of contact time for all contaminants. The duration of the treatment process played a crucial role in enhancing COD removal. For instance, when a small dosage of 3 g was used, the COD removal rate increased from 3% to 79% as the treatment duration was extended from 15 minutes to 60 minutes. Furthermore, the highest COD removal rates were achieved with dosages of both 9 g/L and 15 g/L, with only a slight difference in removal rates between the two (see Figure 4-12a) indicating that minimal adsorbent was needed for COD elimination.

Increasing the dosage of adsorbent significantly enhances the attachment of contaminants to its surface. In this investigation, the examination of the effects of various dosages on the removal rate of pollutants was done. It was found that when a dosage of 15 g was administered, the removal rate increased markedly. Specifically, the removal rate rose from 79% when lower doses of 3 g and 9 g were used, to an impressive 87% with the higher dosage of 15 g. This significant improvement in pollutant removal was observed across nearly all evaluated parameters, highlighting the effectiveness of the higher dosage in enhancing the removal of pollutants from the system.

The effectiveness of the biosorbent during the removal procedures was significantly increased when 15 g of the adsorbent was used, and the response time was 90 minutes. Specifically, the COD removal rate surged from 37% to an impressive 88.2% (see Figure 4-12-a). Additionally, the colour removal efficiency increased from 76% to 87.5% (see Figure 4-12b), demonstrating a significant reduction in colour-related pollutants. Furthermore, the removal of phenolic compounds also saw remarkable progress, with the removal rate increasing from 83% to 89% (see Figure 4-12c). Table 4-3 illustrates that the duration of the treatment process was crucial in improving the removal of contaminants. For example, even with a 3 g dosage, the concentration decreased, and the removal rate increased to 75% across all parameters when the reaction time reached 90 minutes. These findings highlight the effectiveness of increased adsorbent dosage and extension of reaction times in enhancing the removal of various contaminants, making it a promising approach for improving water treatment processes.

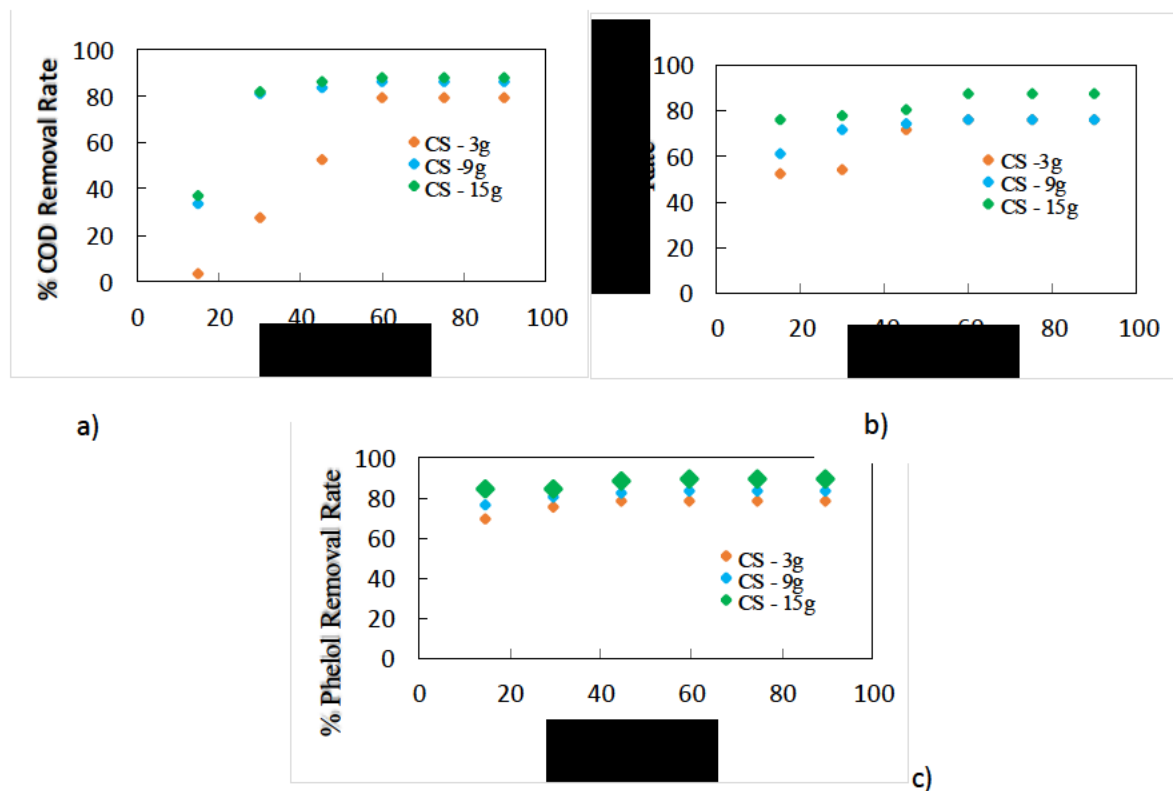


Figure 4- 12. The effect of time and dosage on a) COD, b) colour, and c) phenol removal rate using chitosan

Table 4-3. Chitosan performance at the maximum time (90 minutes)

Dosage (g)	COD initial concentration 2029 mg/L		Colour initial concentration 1955 mg/L		Phenol initial concentration 1948 mg/L	
	Final concentration	Removal Rate (%)	Final concentration	Removal Rate (%)	Final concentration	Removal Rate (%)
3	420 mg/L	79.3	48 mg/L	75.4	422.6 mg/L	78.3
9	277 mg/L	86.3	473 mg/L	75.8	326.1 mg/L	83.3
15	241 mg/L	88	168.3 mg/L	90	201.6 mg/L	88.9

The findings of this study suggest that chitosan is not only a promising technique for the treatment of COD, colour, and phenol in oily wastewater but also has the potential to substantially improve overall water quality. By specifically targeting and reducing waterborne pollutants, chitosan offers a practical solution for the treatment of oil-contaminated wastewater, contributing to efforts aimed at environmental protection and sustainable water resource management.

4.5. Adsorption Kinetics

The adsorption kinetics were studied in COD and phenol using pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. Figures 4-13 and 4-14 depict the PFO linear graphs for COD and phenol, while Figures 4-15 and 4-16 depict the PSO linear graphs for COD and phenol. The correlation coefficient R^2 was higher for the PSO kinetic model compared to the PFO model, indicating that the PSO model is a better fit for this study's adsorption. The linear expressions of PSO are commonly used in adsorption, and this study's results are consistent with the findings of other researchers (Huang, Lee and Shih 2018; Stanly, Jelmy and John 2020; Tran 2023).

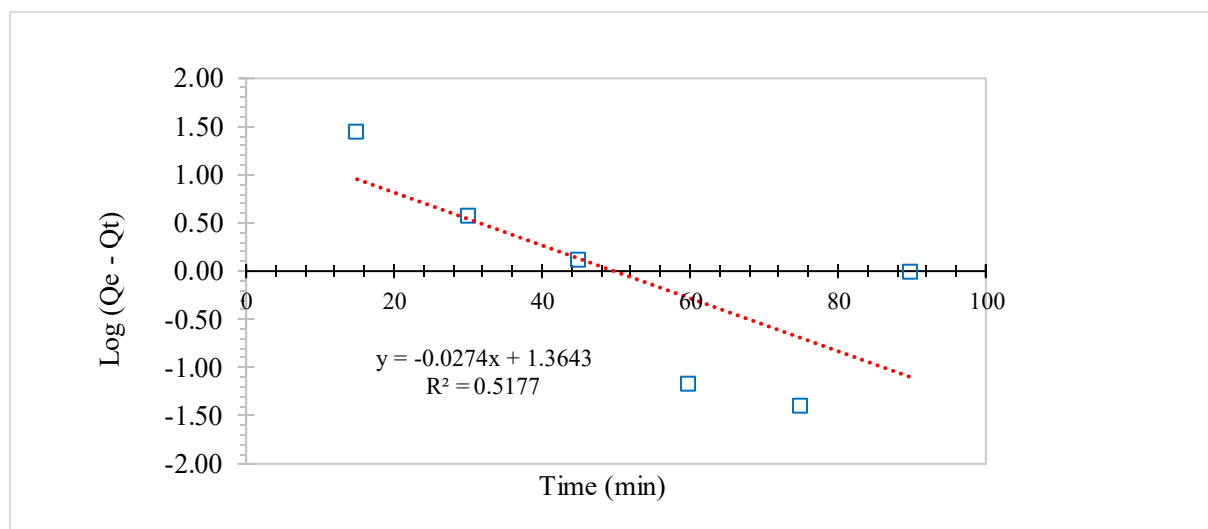


Figure 4- 13. Plot for chitosan PFO kinetic model – COD.

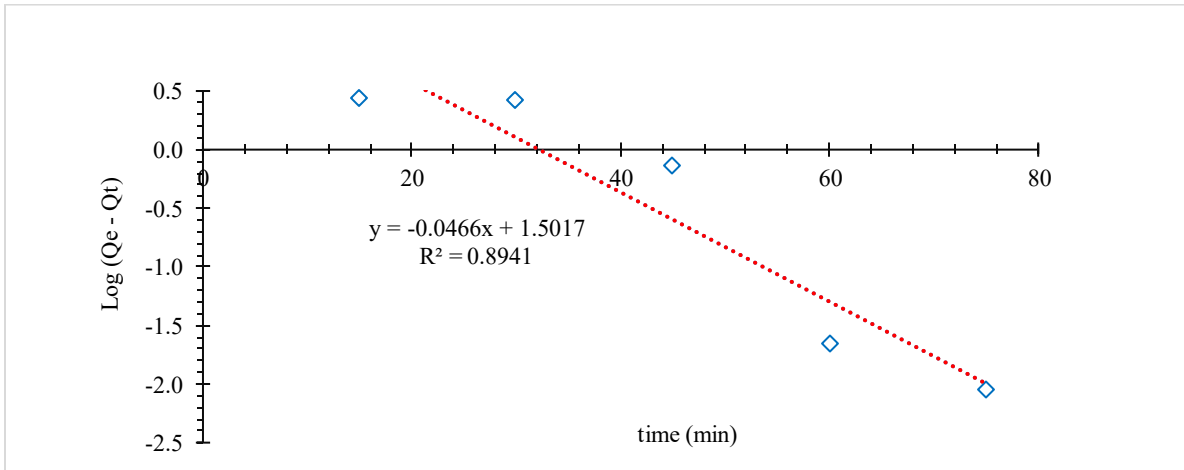


Figure 4- 14. Plot for chitosan PFO kinetic model –phenol.

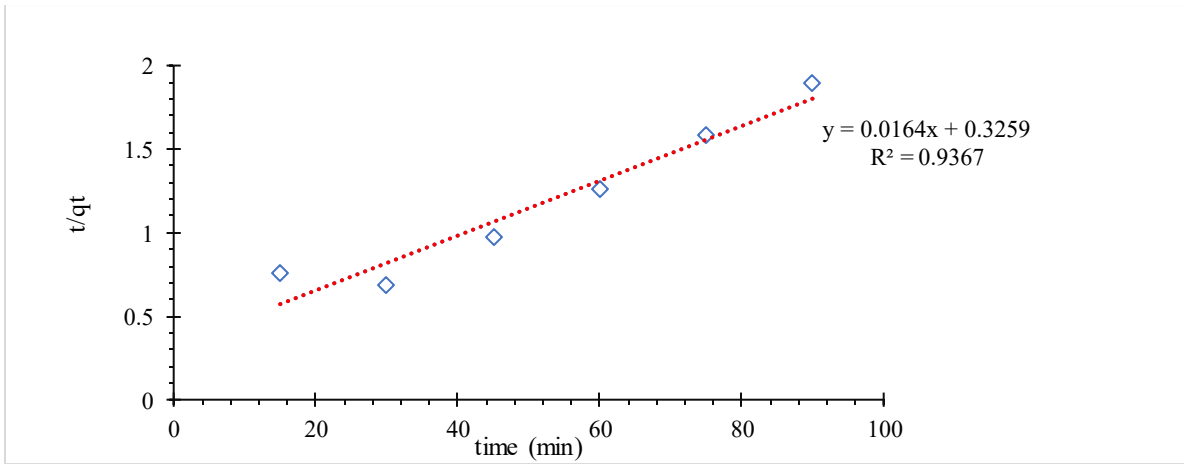


Figure 4- 15. Plot for chitosan PSO kinetic model – COD.

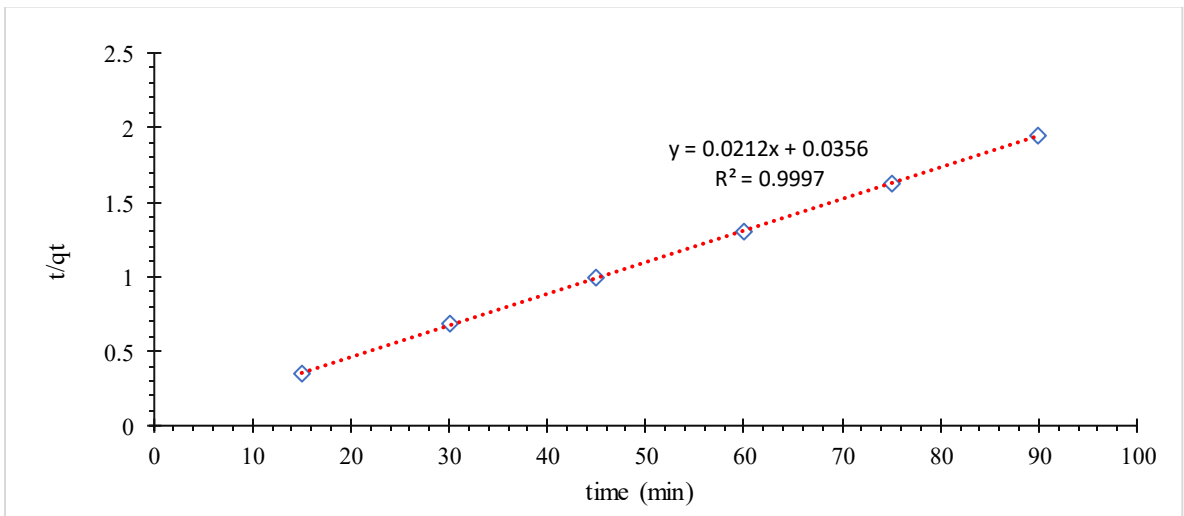


Figure 4- 16. Plot for chitosan PSO kinetic model – phenol.

With the PSO, the values of q_e and k_2 were found to be 47.17 mg.g⁻¹ and 0.013 g.mg.min⁻¹, for the phenol and 60.98 mg.g⁻¹ and 0.000825 g.mg.min⁻¹ for q_e and k_2 when CODs were removed using chitosan.

4.6. Adsorption Isotherms

Equilibrium adsorption isotherms are commonly used to estimate an adsorbent's capacity, surface characteristics, and affinity in the adsorption process. The Langmuir and Freundlich equilibrium models, the most extensively used sorption isotherms, were chosen among all theoretical models for estimating the adsorption capacity of the chitosan bio adsorbent in this investigation. This work employed isotherm models to examine the correlation between the amount of COD and phenol adsorbed on biosorbent chitosan and the equilibrium concentrations of these pollutants in raw oily wastewater. The initial illustrations showing the reduction of pollutants overtime before applying adsorption models are found in Figures A1 and A2 in the Appendix.

4.6.1. Langmuir isotherm

The term isotherm refers to the equilibrium between the adsorbent and adsorbate systems at constant temperature. The Langmuir model implies that just one layer of adsorbate occurs (monolayer postulate) and that the energy traits of the adsorption sites are equivalent (Wang *et al.* 2022). The Langmuir model offers an arranged region due to the generation of a monolayer, allowing the maximum adsorption capacity q_{max} to be computed (Galardini *et al.* 2020).

The Langmuir isotherm was verified by applying the linear equation in Figures 4-17 and 4-18, where the C_e/q_e graphs for COD and phenol adsorption as a function of C_e are presented as the linear regression equation for the Langmuir isotherm for the process of sorption. The correlation coefficients (R^2) for phenols and COD were 0.999 and 0.995, respectively, which are both close to 1. This might indicate that the adsorption method used in this investigation favours Langmuir adsorption. The values of monolayer capacity (q_{max}) and Langmuir constant (K_L) were derived from the experimental data, and the results from the linear plots are presented in Table 4-4.

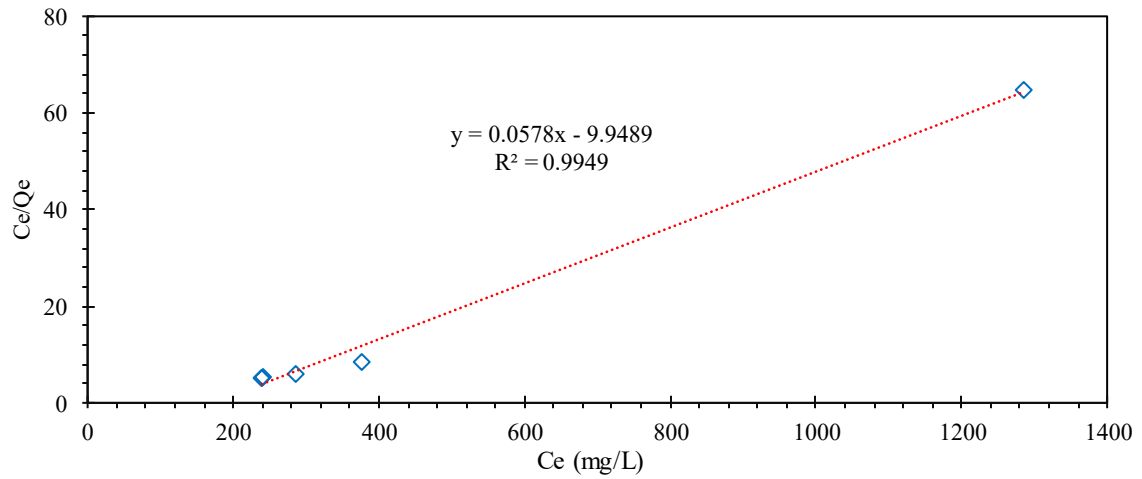


Figure 4- 17. Chitosan- Langmuir plot for COD

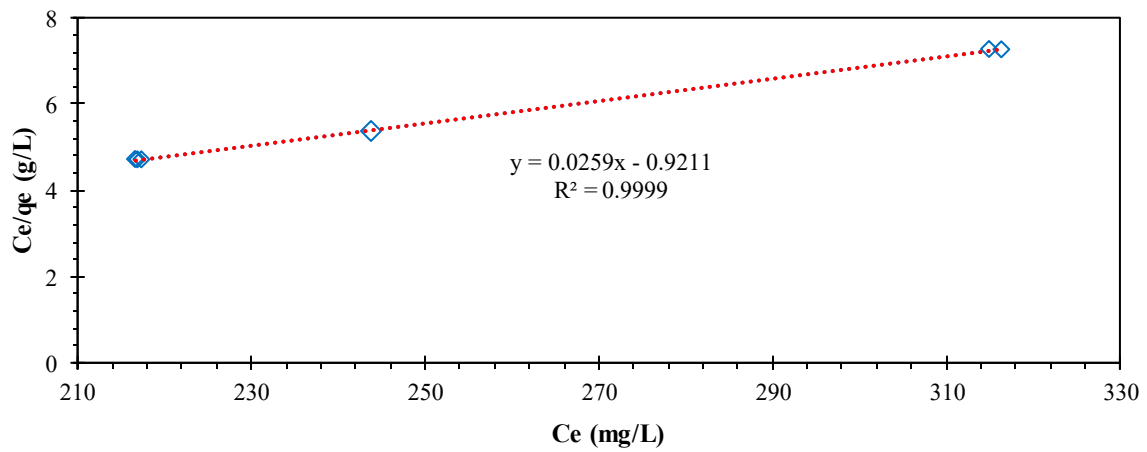


Figure 4- 18. Chitosan- Langmuir plot for phenol.

4.6.2. Freundlich isotherm

The Freundlich isotherm is an empirical model that can be used to explain the equilibrium relation between the sorbent and the sorbate for heterogeneous surfaces and in the case of multilayer adsorption (Vigdorowitsch *et al.* 2021). The sorption data was tested using the Freundlich's linearized adsorption isotherm model. The intercepts and slopes (shown in Figures 4-19 and 4-20) of the Freundlich plots were used to calculate q , $1/n$, and n values, which are presented in Table 4-2. The Freundlich plot resulted in R^2 values of 0.967 and 0.999 for the COD and phenol, respectively, which is also good as it is close to 1.

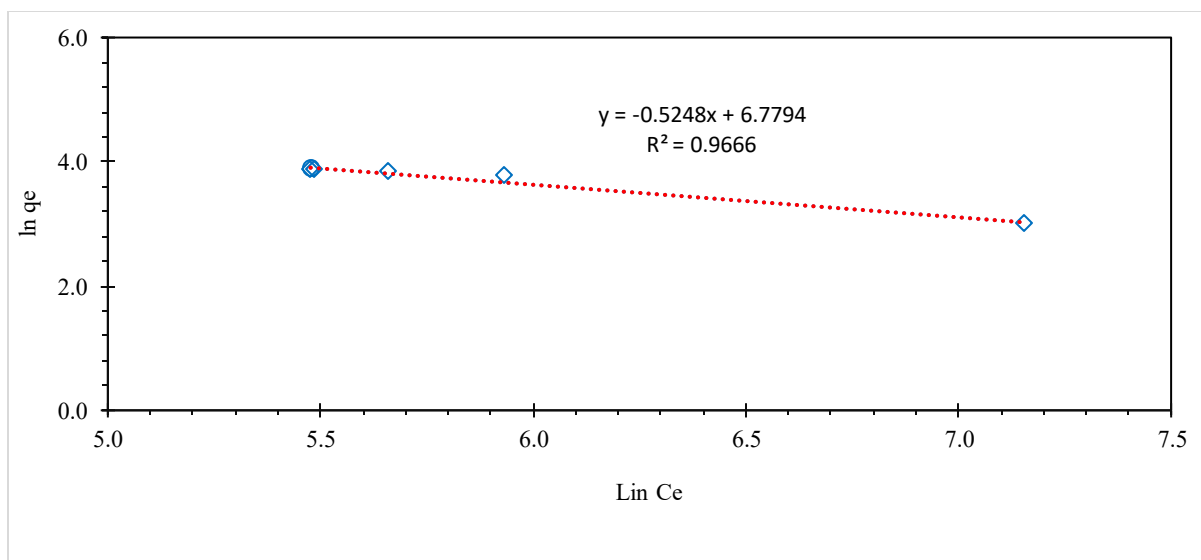


Figure 4- 19. Chitosan- Freundlich plot for COD

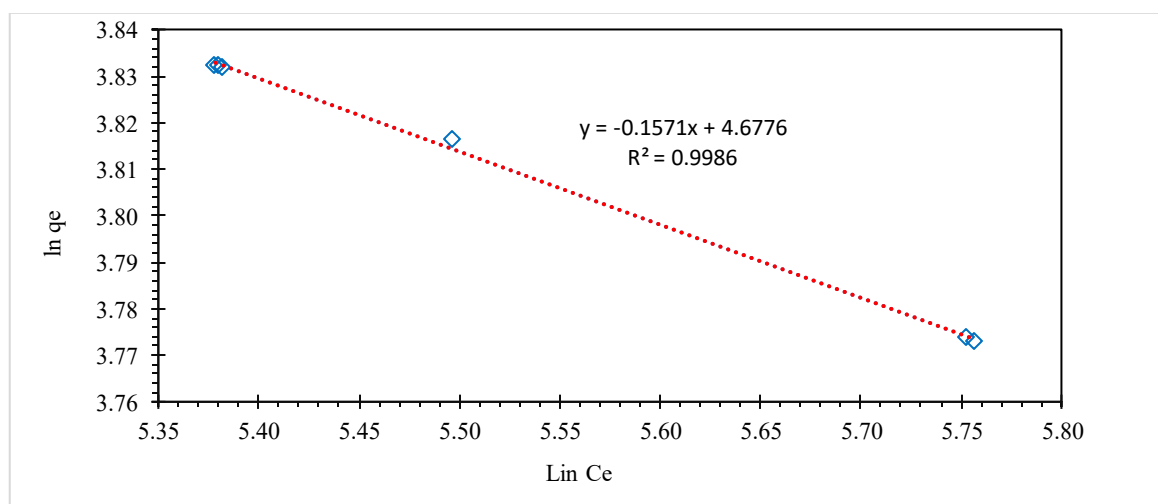


Figure 4- 20. Chitosan Freundlich plot for phenol

A brief comparison of the isotherm parameters for the Langmuir and Freundlich models is presented in Table 4-4. The linear plots illustrated in Figures 4-17 to 4-20 suggested a reasonable model and the value of the coefficient of determination, R^2 suggested a reasonable model. From the R^2 values in Figure 4-17 to 4-20 and Table 4-4, it can be seen that the adsorption of COD and phenol by chitosan flakes is more likely to favour both the Langmuir and Freundlich models. However, since $0 < R_L < 1$, the adsorption process is favourable with the Langmuir model, as opposed to $n < 0$ which represents unfavourable adsorption by the Freundlich model. The findings and the linear plots are congruent with the studies conducted by (Edet and Ifelebuegu 2020; Khan *et al.* 2020).

Table 4-4. Chitosan adsorption isotherms constants for COD and phenol adsorption.

Model	Parameters	COD value	Phenol value
Langmuir	q_{\max} (mg/g)	17.3	38.6
	K_L (L/mg)	-0.575	-0.0239
	R_L	0.0012	0.000053
	R^2	0.9949	0.999
Freundlich	Q (mg/g)	879.5	107.5
	$1/n$	-0.5248	-0.157
	n	-1.905	-6.369
	R^2	0.9666	0.99986

4.7. Optimization of electrocoagulation (EC) and chitosan (CS) adsorption

4.7.1. Optimisation using completed experiments

The response surface methodology (RSM) used the imported data from completed experiments and they were custom-designed for optimization and validation purposes. The results of the completed experiments are displayed in Tables 4-5 and 4-6 below. The study utilized this data as an optimization tool for factorial variables. The design used numerical factors: electrolysis time and the number of blades for the EC, and the reaction time and biosorbent dosage for the chitosan adsorption to evaluate the optimum conditions of the efficiency of parameters (responses) in percentages (%).

Table 4-5. Experimental results for the EC treatment runs

Run	Factor 1 A: time (min)	Factor 2 B: No. of blades	Response 1 COD (%)	Response 2 Colour (%)	Response 3 Phenol (%)
1	10	1	28	72.5	62.5
2	10	2	36.5	75.1	81
3	20	1	36.6	81.2	86.2
4	20	2	45.5	87.2	87.3
5	30	1	80.8	86.5	86.9
6	30	2	84.1	87.8	90
7	40	1	87.9	86.8	87.2
8	40	2	88.7	89.9	90.7
9	50	1	88.9	91.1	88.4
10	50	2	89.1	91.7	93.5
11	60	1	90.5	91.2	89.2
12	60	2	90.6	96.7	94
13	70	1	90.7	91.2	89.5
14	70	2	91.4	96.7	94.2
15	80	1	90.9	91.4	89.6
16	80	2	91.8	96.8	94.5

Table 4-6. Experimental results for the chitosan treatment runs

Run	Factor 1 A: Dosage (g)	Factor 2 B: Time (min)	Response 1 COD (%)	Response 2 Colour (%)	Response 3 Phenol (%)
1	3	15	3.5	52.3	68.6
2	3	30	27.8	54	75.1
3	3	45	52.7	71.5	77.8
4	3	60	79.2	75.5	78.3
5	3	75	79.3	75.4	78.3
6	3	90	79.3	75.4	78.3
7	9	15	33.9	60.7	75.7
8	9	30	81.1	71.8	80.3
9	9	45	83.3	74.1	81.9
10	9	60	86.2	75.8	83.2
11	9	75	86.3	75.8	83.2
12	9	90	86.3	75.8	83.3
13	15	15	36.7	76.1	83.8
14	15	30	81.4	77.7	83.8
15	15	45	85.9	80.2	87.5
16	15	60	88.1	87.5	88.8
17	15	75	88.1	87.5	88.9
18	15	90	88.2	87.5	88.9

4.7.2. ANOVA statistical analysis for the EC and chitosan

The results were analyzed using the analysis of variance (ANOVA) approach. Based on the obtained results, it was discovered that not all the experimental data fit on quadratic and linear equations, but they are described better with the reduced cubic model and reduced quadratic model. Since ANOVA is a statistical method used to compare the differences between means, it is often employed to begin with a complex model and then seek simpler models that still fit the data well (Stat-Ease 2024).

4.7.2.1. Optimisation model equations.

Equations 4-1 to 4-6 display the effects of coefficients, where these coefficients predict the degree of COD, colour, and phenol removal. To improve the predictability of the response variables, model reduction was required. The favourable and adverse coefficients of the terms are connected with the extent to which the terms of the models can affect the response. Coefficients with a plus (+) sign indicate synergistic effect factors, while coefficients with a negative (-) sign indicate antagonistic effect factors. Positive coefficients show that a factor or combination of variables contribute favourably to contaminant removal. In contrast, negative coefficients show that a factor or combination of factors contribute unfavourably to contaminant removal. The magnitudes of the coefficients, once again,

coincide with the degree to which the response variable is influenced (Mohammed and Al-Zuheri 2018; Kweiyor Tetteh and Rathilal 2020).

4.7.2.2. EC and chitosan equations

Identifying key variables and their interactions is crucial when evaluating how different response factors influence the rates of pollutant removal from oily wastewater. In this study, the optimization tool Response Surface Methodology (RSM) was utilized to validate and correlate experimental findings. Although the individual performances of the parameters were strong, RSM indicated that the combination of parameters X_1 (reaction time) and X_2 (number of blades) had no significant effect on the EC-COD (Y_1) decrease rate. However, this combination did perform well in terms of color removal rate (Y_2) and phenol removal rate (Y_3). Additionally, it was found that the individual parameters significantly influenced the chitosan removal rates in Y_4 – Y_6 . The empirical equations were then provided as follows:

EC equations

$$Y_1 = 88.51 + 28.7X_1 + 1.46X_2 - 2.17X_1X_2 - 29.76X_1^2 \quad \text{Equation 4.1}$$

$$Y_2 = 91.13 + 8.93X_1 + 1.87X_2 + 0.5667X_1X_2 - 6.46X_1^2 \quad \text{Equation 4.2}$$

$$Y_3 = 91.37 + 0.2210X_1 + 2.86X_2 - 8.35X_1^2 + 9.59X_1^3 \quad \text{Equation 4.3}$$

Chitosan equations

$$Y_4 = 88.46 + 12.21X_1 + 13.83X_2 - 9.98X_1X_2 - 5.48X_2X_3 - 0.34X_1^2 - 26.29X_2^2 + 15.9X_2^3 \quad \text{Equation 4.4}$$

$$Y_5 = 75.13 + 7.71X_1 + 8.73X_2 - 3.21X_1X_2 + 2.72X_1^2 - 5.99X_2^2 \quad \text{Equation 4.5}$$

$$Y_6 = 82.75 + 5.44X_1 + 3.54X_2 - 0.5936X_1X_2 + 0.2528X_1^2 - 3.23X_2^2 \quad \text{Equation 4.6}$$

4.7.2.3. Correlation matrix

A correlation matrix, as depicted in Tables 4-7 and 4-8, serves as an analytical tool that visually represents the relationships among a set of variables or factors. Each cell within the matrix contains a coefficient that quantifies the strength and direction of the correlation between two variables. These coefficients can take on values ranging from -1 to +1. A coefficient of -1 indicates a perfect negative correlation, meaning that as one variable increases, the other decreases in a perfectly predictable manner. Conversely, a coefficient of +1 indicates a perfect positive correlation, suggesting that both variables move together in the same direction. A value of 0, on the other hand, denotes a weak or non-existent relationship, implying that changes in one variable do not predict changes in the other.

It is important to note that the main diagonal of the correlation matrix consists entirely of ones. This reflects that each variable is perfectly correlated with itself—hence, the correlation value is always 1.

In the specific context of this study, the findings suggest that there are no significant interrelationships among the factors analyzed. This independence indicates that each factor operates effectively and is influential in its own right, without being affected by or affecting the others.

Table 4-7. Electrocoagulation matrix table

Intercept	-0.000	0.000	0.000	-0.753
A-Rn time	1.000	0.000	-0.000	0.000
B-No. of blades	0.000	1.000	-0.000	-0.000
AB	-0.000	-0.000	1.000	-0.000
A ²	0.000	-0.000	-0.000	1.000

Table 4-8. Chitosan matrix table

Intercept	-0.000	-0.000	0.000	-0.677	-0.560
A-Dosage	1.000	-0.000	0.000	0.000	0.000
B-Rxn Time	-0.000	1.000	0.000	0.000	0.000
AB	0.000	0.000	1.000	-0.000	-0.000
A ²	0.000	0.000	-0.000	1.000	-0.000
B ²	0.000	0.000	-0.000	-0.000	1.000

4.7.3 Model responses

The analysis uses the F value, the variation between the samples (Gamage and Weerahandi 1998), and the p-value describes how likely you are to have found a particular set of observations if the null hypothesis were true (Bevans 2021). The F value, often referred to as the F ratio or F statistic, measures the ratio of variance among group averages (the signal) to variance within each group (the noise).

The ANOVA F value can indicate whether there is a significant difference between the levels of the independent variable. A higher F value suggests that the treatment variables are significant (Kissell and Poserina 2017). The EC responses illustrated in Tables 4-9 to 4-11, display that the model F values for the experiments were 29.12, 43.36, and 14.16 for the COD, colour, and phenol, respectively, and it was found to be indicating that the model is significant. A p-value less than 0.05 indicates that the model terms are significant (Bevans 2021), and all p-values for the study's parameters were less than 0.0001. In this case, A, B, A², B² and AB² are significant model terms.

The predicted correlation coefficient, R² and adjusted correlation coefficient, adj R² help one to determine the number of independent variables to be included in the regression model. A model with few variables can produce biased results, also an overspecified model can reduce the model's precision.

Predicted R^2 indicates the likelihood of the model being accurate for future data, whereas modified R^2 can provide an accurate model for current data. The predicted and adjusted R^2 must be in close agreement, i.e., within 0.2 (Stat-Ease 2024). Higher R^2 indicates that the model predictions are very close to the experimental data, and the scatter plot must further illustrate it. For the EC, the predicted R^2 values of 0.8328, 0.8565, and 0.4724 for COD, colour, and phenol, respectively, where only COD and colour were in reasonable agreement with the respective adjusted R^2 of 0.8823, 0.9187, phenol predicted value was above 0.2, According to Stat-Ease (2024), if the predicted R^2 is significantly higher than the adjusted R^2 (more than 0.2), it may indicate overfitting. This occurs when a model learns specific patterns or noise from the training data, leading to poor performance on new data which might be due to large block effect, the adjusted value for the phenol was found to be 0.7783. The R^2 values for this study were found to be 0.9137, 0.9404, and 0.8374 for the COD, colour, and phenol, respectively. Table 4-12 to 4-14 is the illustration of Chitosan responses, The statistical analysis yielded R^2 of 0.9404, 0.9196, and 0.9757 for the COD, colour, and phenol, respectively for the chitosan and Predicted R^2 of 0.8345, 0.8315 and 0.9193 for COD, color, and phenol, which proves that the statistical model was appropriate.

Table 4-9. EC- ANOVA for the reduced cubic model. Response 1- COD

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	7696.84	4	1924.21	29.12	< 0.0001 significant
A-Reaction time	5646.52	1	5646.52	85.45	< 0.0001
B-No. of blades	34.22	1	34.22	0.5179	0.4868
AB	32.44	1	32.44	0.4909	0.4981
A ²	1983.66	1	1983.66	30.02	0.0002
B ²	0.0000	0			
AB ²	0.0000	0			
Residual	726.90	11	66.08		
Cor Total	8423.74	15			

R^2 = 0.9137, *Df= Degree of freedom

Table 4-10. EC- ANOVA for the reduced cubic model, Response 2- colour

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	698.62	4	174.66	43.36	< 0.0001 significant
A-Rn time	546.72	1	546.72	135.1	< 0.0001
B-No. of blades	56.25	1	56.25	13.96	0.0033
AB	2.20	1	2.20	0.5466	0.4752
A ²	93.45	1	93.45	23.20	0.0005
B ²	0.0000	0			
AB ²	0.0000	0			
Residual	44.31	11	4.03		
Cor Total	742.94	15			

R^2 = 0.9404

Table 4-11. EC- ANOVA for the reduced cubic model. Response 3- phenol

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	727.52	4	181.88	14.16	0.0003 significant
A-Rn time	.0475	1	0.0475	0.0037	0.9526
B-No. of blades	130.53	1	130.53	10.16	0.0086
A ²	155.94	1	155.94	12.14	0.0051
A ³	59.40	1	59.40	4.63	0.0546
Residual	141.26	11	12.84		
Cor Total	868.79	15			

R²=0.8374

Table 4-12. Chitosan- ANOVA for reduced cubic model. Response 1 – COD

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	10937.20	6	1822.87	28.94	< 0.0001 significant
A-Dosage	1790.35	1	1790.35	28.42	0.0002
B-Reaction Time	203.73	1	203.73	323	0.0996
AB	557.99	1	557.99	8.86	0.0126
A ²	427.80	1	427.80	6.79	0.0244
B ²	1981.03	1	1981.03	31.45	0.0002
A ³	0.0000	0			
B ³	201.32	1	201.32	3.20	0.1014
Residual	692.85	11	62.99		
Cor Total	11630.05	17			

R²=0.9404, *Df= Degree of Freedom

Table 4-13. Chitosan - ANOVA for Quadratic model. Response 2- colour

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1544.63	5	308.93	27.44	< 0.0001 significant
A-Dosage	713.57	1	713.57	63.39	< 0.0001
B-Reaction Time	640.74	1	640.74	56.92	< 0.0001
AB	57.63	1	57.63	5.12	0.0430
A ²	29.65	1	29.65	2.63	0.1306
B ²	103.04	1	103.04	9.15	0.0106
Residual	135.08	12	11.26		
Cor Total	1679.71	17			

R²=0.9196

Table 4-14. Chitosan - ANOVA for Reduce Quadratic model. Response 3- phenol

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	492.71	5	98.54	96.19	< 0.0001
A-Dosage	355.24	1	355.24	346.75	< 0.0001
B-Reaction Time	105.37	1	105.37	102.86	< 0.0001
AB	1.97	1	1.97	1.93	0.1904
A ²	0.2557	1	0.2557	0.2496	0.6264
B ²	29.87	1	29.87	29.16	0.0002
Residual	12.29	12	1.02		
Cor Total	505.01	17			

R² = 0.9757

4.7.4. The fit statistics

The fit statistic is simply the ratio of two variances which measures dispersion, or the degree to which the data deviates from the mean. The Adeq Precision metric evaluates the signal-to-noise ratio. A ratio greater than four is preferred (Stat-Ease 2024). With the EC the ratios of 15.29, 19.67, and 12.64 for the COD, color and phenol, respectively, suggested a valid signal (see Tables 4-15 to 4-17). With the chitosan (CS), the Adeq Precision metric evaluates the signal-to-noise ratios of 18.59, 17.82, and 32.26 demonstrated in Tables 4-18 to 4-20, suggest a valid signal.

Table 4-15. EC ANOVA fit statics for COD

Std. Dev.	8.13	R²	0.9137
Mean	75.75	Adjusted R²	0.8823
C.V. %	10.73	Predicted R²	0.8328
		Adeq Precision	15.2850

Table 4-16. EC ANOVA fit statics for colour

Std. Dev.	2.01	R²	0.9404
Mean	88.36	Adjusted R²	0.9187
C.V. %	2.27	Predicted R²	0.8565
		Adeq Precision	19.6607

Adeq- *Adequate

Table 4-17. EC ANOVA fit statics for phenol

Std. Dev.	3.58	R²	0.8374
Mean	87.79	Adjusted R²	0.7783
C.V. %	4.08	Predicted R²	0.4724
		Adeq Precision	12.6437

Table 4-18. CS- ANOVA fit statics for COD

Std. Dev.	7.94	R²	0.9404
Mean	69.30	Adjusted R²	0.9079
C.V. %	11.45	Predicted R²	0.8345
		Adeq Precision	18.5891

Table 4-19. CS- ANOVA fit statics for colour

Std. Dev.	3.36	R²	0.9196
Mean	74.15	Adjusted R²	0.8861
C.V. %	4.52	Predicted R²	0.8315
		Adeq Precision	17.8191

Table 4-20. CS- ANOVA fit statics for phenol

Std. Dev.	1.01	R²	0.9757
Mean	81.41	Adjusted R²	0.9655
C.V. %	1.24	Predicted R²	0.9193
		Adeq Precision	32.2600

4.7.5. Numerical optimization of process variables

A numerical optimization goal is a mathematical term that measures the quality of a solution. The ramp display combines individual graphs to make them easier to read. The dot on each ramp indicates the factor setting or response prediction for that solution (Stat-Ease 2024). All optimization factors for this study were set to be in a range, and responses were maximized. The ramp plot for the electrocoagulation and chitosan process variables under optimal conditions is shown in Figures 4-21 and 4-22, respectively.

Ramp function graphs with blue and red dots in Figure 4-21 and Figure 4-22 represent two key factors: reaction time and the number of blades and their three responses in EC they also represent the reaction time and biosorbent dosage as well as the responses COD, colour, and phenol removal rates for the chitosan.

The height of the dot represents its desirability, and values of desirability functions range from 0 to 1. The value 0 is assigned when the components offer an unacceptable reaction, whereas the value 1 corresponds to the optimal performance for the investigated factors (Stat-Ease 2024). A positive slope of the ramp represents the maximization of the numerical value. Ramp graphs conclude the desirability of 98.6% and 96.8% for EC and chitosan, respectively. The selected solutions are the formulation that best achieved the projected variable, which is illustrated in Table 4-21 for the EC and in Table 4-22 for the chitosan.

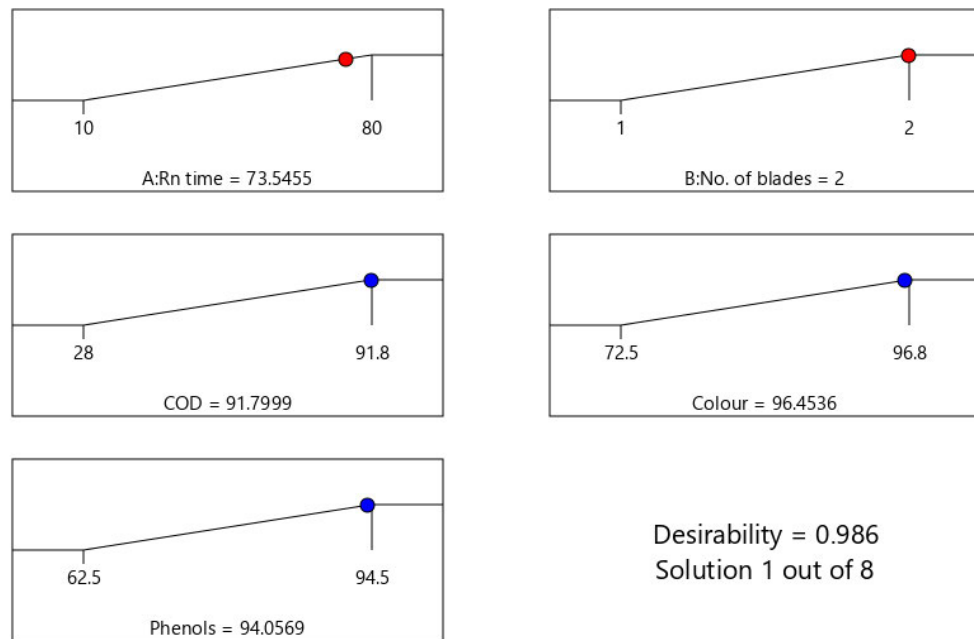


Figure 4- 21. Ramp plot for the electrocoagulation process variables at optimized conditions.

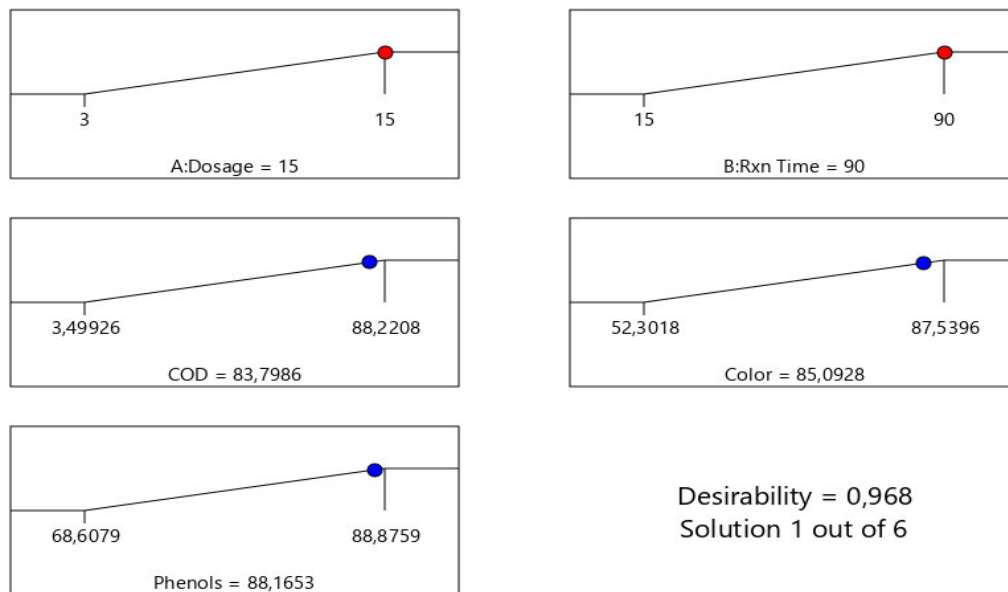


Figure 4- 22. Ramp plot for the chitosan process variables at optimized conditions

Table 4-21. Electrocoagulation optimization solutions.

Number	Rn time	No. of blades	COD	Colour	Phenol	Desirability	
1	73.547	2.000	91.799	96.454	94.057	0.986	Selected
2	74.002	2.000	91.508	96.439	94.134	0.986	
3	74.264	2.000	91.335	96.429	94.181	0.986	
4	74.853	2.000	90.935	96.406	94.293	0.986	
5	75.213	2.000	90.683	96.389	94.366	0.986	
6	75.640	2.000	90.375	96.368	94.457	0.985	
7	69.223	2.000	94.067	96.484	93.560	0.977	

Table 4-22. Chitosan optimization solutions.

Number	Dosage	Reaction Time	COD	Colour	Phenol	Desirability	
1	15	90.000	83.799	85.093	88.165	0.968	Selected
2	15	89.651	83.810	85.152	88.198	0.968	
3	15	87.700	83.938	85.467	88.368	0.967	
4	15	85.083	84.265	85.837	88.570	0.965	
5	15	83.039	84.624	86.086	88.705	0.962	
6	15	82.500	84.732	86.146	88.738	0.962	

4.7.6. Verification of results

Additional experiments were conducted to validate the theoretical optimal conditions predicted by the model's solutions. Confirmation tests are an essential component of the response surface methodology (RSM) optimization process, according to Stat-Ease (2024), they are employed to validate that the outcomes of the confirmation experiment and the original experiment are identical. This is crucial because, even when two studies are conducted using the identical procedure, there may be drift over time. If the initial experiments were conducted in a lab or using prototypes, confirmation experiments can also help confirm that the outcomes of the two processes are consistent. Stevens and Anderson-Cook (2019) also highlighted the importance of confirmation runs.

4.7.6.1. Electrocoagulation results verification.

Using input factors selected by the model: a running time of 74 minutes and double aluminium blade electrodes. The actual experimental removal rate and the model prediction data were in very close agreement with an error of less than 0.5 in all parameters (see Table 4-23). The outcome of this verification was congruent with the study conducted by Darvishmotevalli *et al.* (2019).

Table 4-23. Verification of electrocoagulation results at optimum conditions selected by RSM.

Optimal conditions	COD removal rate	Colour removal rate	Phenol removal rate
Model response	91.799	96.454	94.057
Experimental results	91.56	96.054	93.8
Error	0.239	0.4	0.257

4.7.6.2. Chitosan results verification

The selected inputs for the models were carefully calibrated to optimize the biosorption process, featuring a biosorbent dosage of 15 g and a reaction time of 90 minutes. The actual experimental removal efficiencies and the model prediction data, exhibiting an error margin of less than 5% across all tested parameters (see Table 4-24). This close correlation underscores the reliability of the model and the effectiveness of the chosen biosorbent in achieving high levels of pollutant removal. The biosorbent findings in this study are harmonious with those discovered by sebagai Penjerap-Bio (2017).

Table 4-24. Verification of chitosan results at optimum conditions selected by RSM

Optimal conditions	COD removal rate	Colour removal rate	Phenol removal rate
Model response	83.799%	85.793%	88.165%
Experimental (Verification results)	88.0%	86.8%	88.7%
Error	4.2	1.01	0.535

4.8. A comparison between EC's and chitosan's prospective capabilities.

The effectiveness of electrocoagulation (EC) and chitosan (CS) approaches for removing oil recycling refinery wastewater has been investigated, as well as the optimal settings, working mechanism, and rate capacity of these techniques in refinery wastewater treatment. Figure 4-23 compares the two techniques, with the findings demonstrating that both EC and Chitosan (CS) are excellent techniques for treating oil-contaminated wastewater; nevertheless, this figure shows that EC outperforms CS in terms of oily wastewater contamination removal rate.

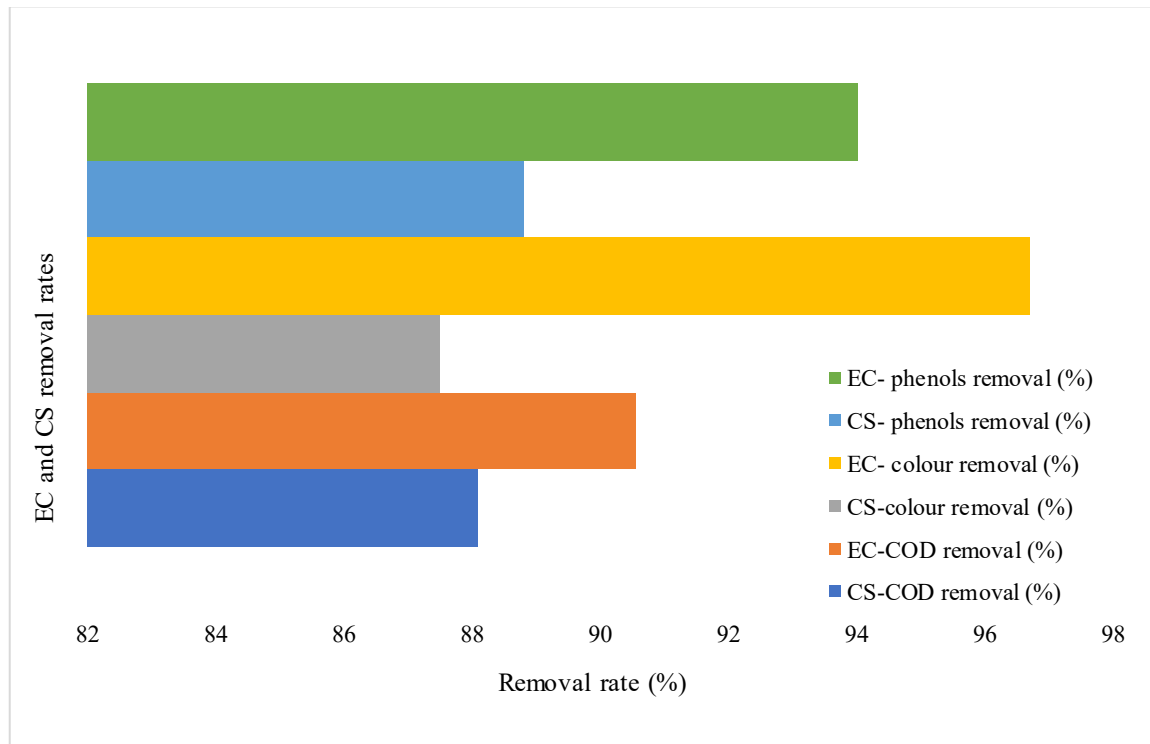


Figure 4- 23. COD, colour, and phenol comparing electrocoagulation (EC) and chitosan (CS) removal rate at optimal conditions.

4.9. Summary

The trials were carried out to determine the best approach for treating oily wastewater. These methods' capacity to remove COD, colour, and phenol was studied. When electrocoagulation was investigated, it yielded favourable findings when a double sheet of aluminium produced up to 91.45%, 96.7%, and 94.45% reductions in COD, colour, and phenol, respectively, at an electrolysis time of 80 minutes and a current of 0.1 Amps.

Laboratory investigations revealed that chitosan biosorbent is one of the most powerful adsorbents obtained from crustaceans; its characterization was assessed using SEM, EDX, and FTIR. Adsorption isotherms (Langmuir and Freundlich) were used to validate the absorbance capacity of ions. The R^2 values for the Langmuir isotherms were 0.9949 and 0.9999, respectively, when COD and phenol were investigated. The R^2 values for the Freundlich isotherm were 0.9666 and 0.9986, respectively, when COD and phenol concentrations were investigated. The rate of adsorption was also investigated through

the application of PFO and PSO adsorption kinetics, where the value of R^2 for phenol yielded 0.2999 and 0.9997 for the 1st-order and second-order kinetics, respectively. The R^2 values for the CODs were 0.5177 and 0.9367 for the 1st and second order, respectively. When the biosorbent chitosan dosage range was 3-15g and the reaction time was 15 to 90 minutes, it demonstrated its maximum potential to remove up to 88%, 87.53, and 88.50% of the COD, colour, and phenol, respectively, at 90-minute operating time and 15 g adsorbent dosage.

The use of the RSM design expert tool, which used completed experiments greatly aided in verifying the optimum operating conditions for oily wastewater utilizing chitosan and electrocoagulation.

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1 Introduction

This study provides a comprehensive examination of methods for the treatment of oily effluent generated from an oil recycling refinery. Specifically, it investigates two techniques: electrocoagulation and the application of the biosorbent chitosan. The effectiveness of these methods was rigorously evaluated through a series of experiments that measured their removal efficiencies for various pollutants, including Chemical Oxygen Demand (COD), colour, and phenol.

A detailed analysis of the success criteria was established based on the results obtained during the study. Each method's performance was assessed not only on its ability to reduce pollutant concentrations but also in terms of operational efficiency and feasibility for implementation in industrial settings. The findings included a breakdown of how each technique responded to different pollutant types, allowing for a comparison of their efficacy. Moreover, the limitations and challenges encountered throughout the study were discussed, such as variations in pollutant concentrations and the influence of environmental factors on treatment efficiency. Based on these observations, there is a need to offer thoughtful recommendations for future research, which may include investigations into optimizing treatment conditions, exploring the scalability of these methods, and assessing the long-term sustainability of using biosorbents like chitosan in industrial applications.

5.2. Conclusion regarding the specific objectives

5.2.1. To evaluate the efficacy of electrocoagulation in the treatment of oil refinery wastewater by measuring COD, colour, and phenol reduction rates.

- The study investigated electrocoagulation processes using single and double aluminium blades as electrodes. While both configurations proved effective, the double-blade arrangement demonstrated superior results.
- This study effectively highlights the potential of the BP-P arrangement of aluminium electrodes in enhancing water treatment processes.
- The optimal conditions for the EC process were found at double blades, 80 minutes of electrolysis time, a constant current of 0.1 Amps, a voltage of 30 volts, and a pH of 7. Under these conditions, the EC process removed 91.41%, 96.7%, and 94.5% of COD, colour, and phenol, respectively.

5.2.2. To synthesize and evaluate chitosan utilizing adsorption kinetics and isotherms, then assess its efficacy in treating oily wastewater by evaluating COD, colour, and phenol reduction rates.

- The Fourier Transform Infrared (FTIR) analysis demonstrated the presence of three distinct amine groups within oyster chitosan. In contrast, mussel-based chitosan exhibited only a single amine group. This significant difference indicates that oyster-based chitosan yields a higher concentration of amine groups compared to mussel-based chitosan, which may influence its functional properties. Furthermore, scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX) provided valuable insights into the surface morphology of the chitosan samples. The SEM images revealed the detailed texture and structural features of the oyster chitosan, while the EDX analysis confirmed the elemental composition, showing the presence of key components such as calcium (Ca), oxygen (O), and carbon (C) within the chitosan matrix. Additionally, the degree of deacetylation of the chitosan derived from oysters was measured and found to be 80.46%.
- A comprehensive series of laboratory tests were performed to investigate the effectiveness of chitosan in treating wastewater, using dosages of 3 g, 9 g, and 15 g. The results indicated that under optimal conditions—specifically, a 15 g dosage combined with a 90-minute reaction time—chitosan proved to be highly effective in removing contaminants from the water. It achieved impressive removal rates of 88% for chemical oxygen demand (COD), 87% for colour, and 89% for phenolic compounds. These findings highlight chitosan's potential as an effective biodegradable material for environmental remediation.
- In this study, the pseudo-second-order (PSO) model emerged as the most appropriate adsorption kinetic model, as it effectively mirrored the equilibrium conditions of the system. Additionally, the Langmuir isotherm demonstrated the best compatibility with the chitosan adsorption process. This was evidenced by its impressive R^2 values of 0.9666 for chemical oxygen demand (COD) and 0.9999 for phenol, indicating a strong correlation and suggesting that the adsorption mechanism operates under a monolayer coverage scenario.

5.2.3. Optimization of the operating parameters of the electrocoagulation and chitosan biosorbent treatment options.

- To evaluate and compare the effectiveness of two treatment methods for purifying oily wastewater—electrocoagulation (EC) and the biosorbent chitosan—an experimental approach known as one-factor-at-a-time (OFAT) was utilized in the laboratory setting. This method allowed for the systematic examination of individual variables while keeping others constant to identify optimal conditions for each technique. In contrast, the application of the biosorbent

chitosan involved using 15 g of the material and a processing duration of 90 minutes. The effectiveness of chitosan as a biosorbent was assessed based on its ability to absorb and remove oil pollutants from the wastewater. The findings suggest that while EC is faster, the use of chitosan as a biosorbent provides an environmentally friendly alternative for wastewater treatment, showcasing distinct advantages in resource efficiency.

- During the experiments, the electrocoagulation process was conducted using a double-blade electrode, which facilitated the efficient removal of contaminants. It was determined that this method required a processing time of 80 minutes to achieve satisfactory purification results.
- For both EC and chitosan adsorption, a set of imported data from previous OFAT was employed. The results showed R^2 values greater than 0.9 in all parameters in both approaches; nevertheless, a significant difference was observed when EC outperformed chitosan, with a ramp plot attractiveness of 98.6% versus 96.8% for chitosan. Furthermore, the EC verification results yielded an error of less than 0.5 where the RSM model predicted the removal efficiencies of 91.8, 96.5, and 94.1% for COD, colour, and phenols, respectively. Laboratory verification yielded 91.6, 96.1, and 93.8% for the COD, colour, and phenols, respectively. The chitosan on the other hand predicted 83.8%, 85.8%, and 88.2% for the COD, colour, and phenol, respectively when RSM was utilized. The confirmation results were found to be 88%, 86.8, and 88.7% for the COD, colour and phenol, respectively.

5.2.4. To compare electrocoagulation and chitosan techniques using the removal rates of the COD, colour, and phenol.

- The efficacy of two methods in eliminating pollutants from oil refinery wastewater was carefully assessed, specifically focusing on chemical oxygen demand (COD), color, and phenol. The methods under consideration were electrocoagulation (EC) and the use of the biosorbent chitosan. The electrocoagulation method showcased remarkable removal efficiencies, achieving an impressive 91.41% reduction in COD, 96.7% in color removal, and 94.5% in phenol concentration. The chitosan method demonstrated comparatively lower removal rates, with reductions of 88% for COD, 87% for color, and 89% for phenol.
- These findings clearly indicate that electrocoagulation outperforms chitosan when it comes to the removal of COD, color, and phenol from wastewater produced by oil recycling refineries. Such insights are critical for wastewater treatment applications, as they suggest that electrocoagulation may serve as a more effective solution for achieving regulatory compliance standards and promoting environmental sustainability in oil refinery operations.

Overall conclusion of EC and CS

The experimental condition (EC) showed better performance than the control condition (CS) in many crucial areas. The EC showed a lot of benefits when it came to electricity bills, lowering expenditures while keeping effectiveness. Also, electricity use went down a lot under the EC, which means that resources were used more efficiently. The results show that the EC is better than the EC VS CS framework in terms of cost-effectiveness and performance efficiency.

5.3. Future recommendations

- For highly concentrated oily wastewater, it is important to have efficient filtration and preliminary treatment. This helps to remove most pollutants and reduces scum formation in EC treatment and sludge in chitosan treatment, which in turn can cut down reaction time. Post-treatment is also necessary to maintain the proper conditions of the wastewater.
- Modified chitosan could be more effective than pure chitosan treatment. It has been proven to exploit its biological activity and improve its adsorption capacity (Hastuti, Masykur and Hadi 2016; Chen et al. 2022).
- The coupling of EC and chitosan (Hybrid) is still an open research that might produce even higher efficiency.
- It is necessary to investigate electrocoagulation using renewable energy sources. Although this study and the literature indicate that electrocoagulation is effective in removing contaminants,, it still links to a non-renewable energy source, hence alternative renewable energy sources are required.
- When used exclusively for optimization, the RSM model produced remarkable results in this study. It would have been a great option for successfully planning the experiment, thus researchers are encouraged to use it.

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APPENDICES

A1 Running Conditions

Electrocoagulation running conditions.

Temperature: 25°C

Voltage: 30v

Current: 0.1Amps

Speed: 250 rpm

Chitosan running conditions.

Temperature: 25°C

Dosages 3-15g/L

Speed: 250 rpm

Table A-1. Experimental results for the COD, colour, and phenol runs using electrocoagulation

		COD initial concentration 2029mg/L	Colour initial concentration 1955 mg/L	Phenol initial concentration 1948 mg/L
Number of Blades	Reaction Time (min)	Reduction in concentration (mg/L)	Reduction in concentration (mg/L)	Reduction in concentration (mg/L)
Single	10	1460	538	731.02
	20	1287	367	267.95
	30	390	263	255.23
	40	244.5	259	249.81
	50	225.5	173.5	226.38
	60	192	171.5	209.55
	70	189	172	203.7
	80	184.1	168.3	201.7
Double	10	1288	486.5	370.7
	20	1105	250	247.7
	30	322.5	238	195.1
	40	229	197	180.4
	50	221	161.5	126.8
	60	175	65.33	116.1
	70	175	64.33	113.33
	80	174.3	63	106.46

Table A-2. Experimental results for the COD, colour, and phenol runs using chitosan.

		COD initial concentration 2029mg/L	Colour initial concentration 1955 mg/L	Phenol initial concentration 1948 mg/L
Dosage (g)	Reaction Time (min)	Reduction in concentration (mg/L)	Reduction in concentration (mg/L)	Reduction in concentration (mg/L)
3	15	1958	932.5	611.5
	30	1464	899.5	485.4
	45	959	558	433.2
	60	422	481	422.9
	75	421	480.33	422.76
	90	420	479.5	422.6
9	15	1342	768	473.7
	30	382.5	551	384.4
	45	338.5	507	353.1
	60	279	473	327.7
	75	278.5	473.3	326.87
	90	277.5	473.3	326.1
15	15	1285	467.5	316.4
	30	377	435.5	315
	45	287	387	243.9
	60	241.5	244.5	217.5
	75	240.5	243.67	217.02
	90	239	243.6	216.68

A2. Calculations and plots

Sample calculations

EC Energy Consumption on Electrocoagulation

$$E = UIt$$

Equation 4.1

$$(30 \times 0.1 \times 1.33 = 4 \text{ Wh})$$

$$= 0.004 \text{ kWh}$$

Aluminium consumption

$$\text{Mass (of electrode)} = \frac{M I t}{n F}$$

Equation 3.3

$$= \frac{26.98 \times 0.1 \times 4800}{3 \times 96485}$$

$$= 44.7 \text{ mg}$$

$$= \mathbf{0.0447 \text{ g}}$$

$$\begin{aligned} \text{Moles of } e^- &= \frac{Q}{F} = \frac{I t}{F} \\ &= \frac{0.1A \times 4800s}{96485} \end{aligned}$$

$$= 0.00167 \text{ moles of aluminium}$$

Mass of Aluminium consumed = n M

$$= 0.00167 \times 26.98$$

$$= \mathbf{0.09 \text{ g aluminium consumed}}$$

Removal efficiency for the COD and colour, and phenol were calculated using:

$$\frac{C_0 - C}{C_0} \times 100$$

Where: C_0 is the initial(sample) concentration

C is the final concentration after treatment.

Degree of Deacetylation of Chitosan

Mussel chitosan

$$\alpha = \frac{Na \times Va - Nb \times Vb}{1000}$$

$$\alpha = \frac{0.1M \times 10\text{cm}^3 - 0.01M \times 5\text{cm}^3}{1000}$$

$$\alpha = 0.0009$$

$$\text{DD [\%]} = \frac{\alpha}{\frac{w - 161 \times \alpha}{204} + \alpha} \times 100$$

$$\text{DD [\%]} = \frac{0.0009}{\frac{0.2 - 161 \times 0.0009}{204} + 0.0009} \times 100$$

$$\mathbf{DD\% = 76, 92\%}$$

Oyster chitosan

$$\alpha = \frac{Na \times Va - Nb \times Vb}{1000}$$

$$\alpha = \frac{0.2M \times 5\text{cm}^3 - 0.01M \times 5\text{cm}^3}{1000}$$

$$\alpha = 0.00095$$

$$\text{DD [\%]} = \frac{\alpha}{\frac{w - 161 \times \alpha}{204} + \alpha} \times 100$$

$$\text{DD [\%]} = \frac{0.00095}{\frac{0.2 - 161 \times 0.00095}{204} + 0.00095} \times 100$$

$$\mathbf{DD\% = 80, 46\%}$$

Oyster chitosam Molar Mass

$M = \text{DD} \times M(\text{D-glucosamine}) + ((100 - \text{DD}) \times (\text{Acetylglucosamine}))$

$$= (0.846 \times 161 \text{ g/mol}) + (0.154 \times 203 \text{ g/mol})$$

$$= 136.2 + 31.26$$

$$= \mathbf{167.46 \text{ g/mol}}$$

Table A-3. EC and CS energy and cost calculations

ENERGY AND COST CALCULATIONS

	ELECTROCOAGULATION	BIOSORPTION
Working conditions	<ul style="list-style-type: none"> Oil refinery wastewater volume: 250 ml Electrode material: Aluminium Number of blades: 2 Current: 0.1 Amps Voltage: 30 volts Time: 80 minutes (1.33 hrs) pH. Neutral Instrument: DC Power supply pH. Neutralizing reagents: HCl and NaOH 	<ul style="list-style-type: none"> Oil refinery wastewater volume: 400ml Biosorption material: chitosan Mass of biosorbent: 15g Time: 90 minutes (1.5 hrs) pH. Neutral Instrument: Jar tester pH. Neutralizing reagents: HCl and NaOH Power (jar tester): 0.2 KW ESKOM standard connection:3.5kw (Allal <i>et al.</i> 2024).
Energy consumption	$E = U I t$ $= 30 \times 0.1 \times 1.33$ $= \mathbf{0.004 \text{ KWh}}$	$E = P t$ $= 0.2 \times 1.5$ $= \mathbf{0.3 \text{ kWh}}$
Electricity cost	$E_{\text{cost}} = 0.004 \times 3.5$ $= \text{R}0.014$	$E_{\text{cost}} = 0.3 \times 3.5$ $= \text{R}1.05$
Consumables and Overheads	Cost of aluminium blades: $10 \times \text{R}25 = \text{R}250$ and courier fee: $\text{R}60$ Subtotal: R310 Reagents (pH. Adjusters): HCl (pure): $\text{R}450/\text{L}$, NaOH (pure) $\text{R}76/\text{L}$, 30ml of concentrates were used $V_1 = \frac{0.1M \times 30ml}{12M (HCl)} = 0.25ml (0.00025m^3)$ Cost of HCl used = $0.00025m^3 \times \text{R}450 = \text{R}0.11$ $V_1 = \frac{0.1M \times 30ml}{19M (NaOH)} = 0.16ml (0.00016 m^3)$ Cost of NaOH used: $0.00016 m^3 \times \text{R}76 = \text{R}0,012$ Total cost of consumables: 0.122 Labour: 2 students earning $\text{R}25/\text{hr}$ (experimental time = 4hrs Cost of labour = R200	Transport to seafood restaurant: $\text{R}40 \times 2 = \text{R}80$ Production cost (heating and drying) $\pm \text{R}100$ Reagents used > Industrial grade used in the production $\pm \text{R}50$ Subtotal: R230 Reagents (pH. Adjusters): HCl (pure): $\text{R}450/\text{L}$, NaOH (pure) $\text{R}76/\text{L}$ 30ml of concentrates were used $V_1 = \frac{0.1M \times 30ml}{12M (HCl)} = 0.25ml (0.00025m^3)$ Cost of HCl used = $0.00025m^3 \times \text{R}450 = \text{R}0.11$ $V_1 = \frac{0.1M \times 30ml}{19M (NaOH)} = 0.16ml (0.00016 m^3)$ Cost of NaOH used: $0.00016 m^3 \times \text{R}76 = \text{R}0,012$ Total cost of consumables: 0.122 Labour: 2 students earning $\text{R}25/\text{hr}$ (experimental time = 4hrs Cost of labour = R200
TOTAL COST	Total cost = +Electricity cost + consumables + overheads $= \text{R}0.014 + 0.122 + (\text{R}200 + 310.)$ $= \mathbf{\text{R}510.136}$	Total cost = +Electricity cost + consumables + overheads $= \text{R}1.05 + 0.122 + (\text{R}200 + 230)$ $= \mathbf{\text{R}431.172}$

MASS BALANCE

Table A-4. Mass balance for EC and CS

	ELECTROCOAGULATION	CHITOSAN
Pollutants mass balance	COD $\frac{C_i - C_o}{1000} v$ $\frac{2029\frac{\text{mg}}{\text{l}} - 174.3\frac{\text{mg}}{\text{l}}}{1000} \cdot 0.25\text{l}$ = 0.464g was removed	COD $\frac{C_i - C_o}{1000} v$ $\frac{2029\frac{\text{mg}}{\text{l}} - 239\frac{\text{mg}}{\text{l}}}{1000} \cdot 0.4\text{l}$ = 0.716g was removed
	Colour $\frac{C_i - C_o}{1000} v$ $\frac{2029\frac{\text{mg}}{\text{l}} - 63\frac{\text{mg}}{\text{l}}}{1000} \cdot 0.25\text{l}$ = 0.473 g was removed	colour $\frac{C_i - C_o}{1000} v$ $\frac{2029\frac{\text{mg}}{\text{l}} - 243.6\frac{\text{mg}}{\text{l}}}{1000} \cdot 0.25\text{l}$ = 0.68 g was removed
	Phenol $\frac{C_i - C_o}{1000} v$ $\frac{2029\frac{\text{mg}}{\text{l}} - 94.5\frac{\text{mg}}{\text{l}}}{1000} \cdot 0.25\text{l}$ = 0.463 g was removed	Phenol $\frac{C_i - C_o}{1000} v$ $\frac{2029\frac{\text{mg}}{\text{l}} - 216.7\frac{\text{mg}}{\text{l}}}{1000} \cdot 0.25\text{l}$ = 0.69 g was removed

Adsorption isotherms plots and calculations.

Langmuir Adsorption Isotherm Langmuir Adsorption Isotherm for COD

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} KL + \frac{C_e}{q_{max}} \quad \text{Equation 2.9}$$

A linear plot(trendline) was selected.

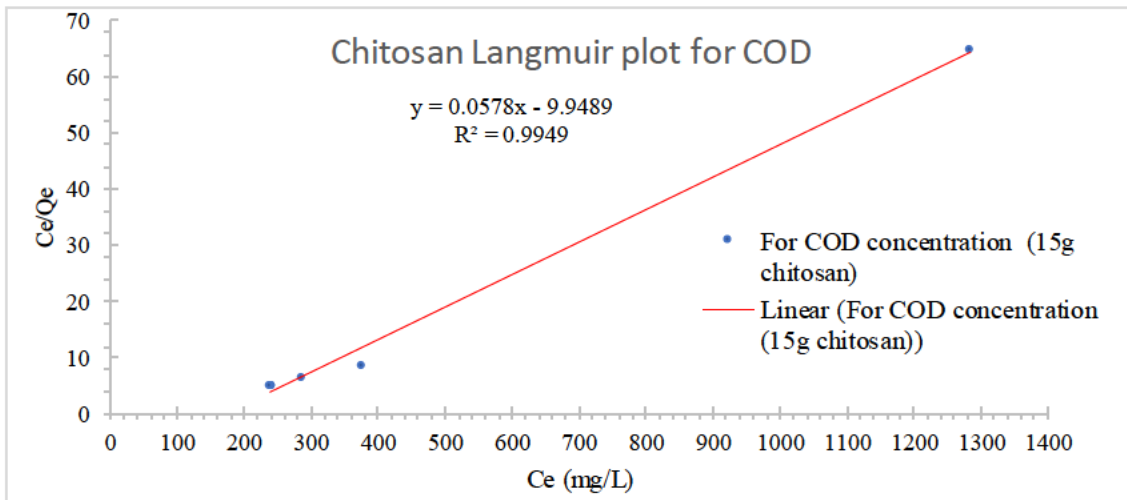


Figure 4-15. Chitosan Langmuir Isotherm plot for the COD

q_e (equilibrium adsorption capacity) calculated from the equation:

$$q_e = \frac{[C_o - C_e] \cdot V}{W}$$

Where C_o is the initial concentration,

C_e is the concentration at equilibrium,

W is the weight of the adsorbent

V is the volume of wastewater.

From the linear equation $y = 0.0578x - 9.9489$

$$\frac{1}{q_{max}} = 0.0578$$

$$q_{max} = 17.3$$

$$K_L = \frac{1}{q_{max}} \cdot -9.9489$$

$$= \frac{1}{17.3} \times -9.9489$$

$$= -0.575$$

$$R_L = \frac{1}{1 + K_L \cdot C_o}$$

$$= \frac{1}{1 - 0.575 \times 2029}$$

$$= \underline{\underline{0.0012}}$$

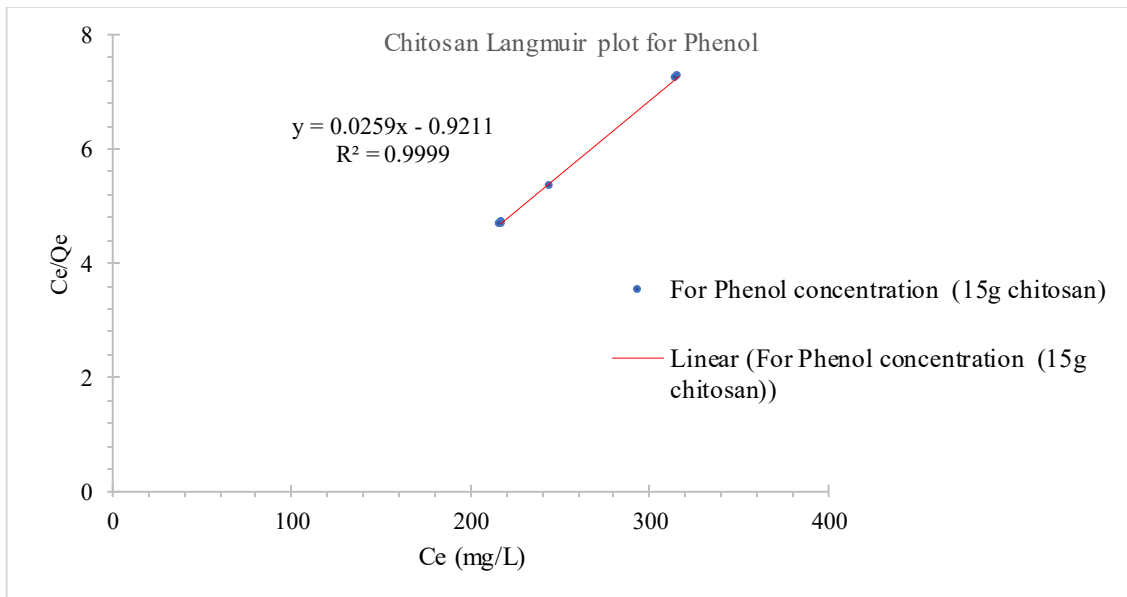


Figure 4-16. Chitosan Langmuir plot for the phenol.

From the linear equation $y = 0.0259x - 0.9211$

$$\frac{1}{q_{max}} = 0.0259$$

$$q_{max} = 38.6$$

$$K_L = \frac{1}{q_{max}} \cdot -0.9211$$

$$= \frac{1}{38.6} \cdot -0.9211$$

$$= -0.0239$$

$$R_L = \frac{1}{1 + K_L X C_0}$$

$$= \frac{1}{1 - 0.0239 \times 1948}$$

$$= \underline{0.00053}$$

Freundlich adsorption isotherm

$$\ln q = \ln K_f + \frac{1}{n} \cdot \ln C_e.$$

Equation 2.10

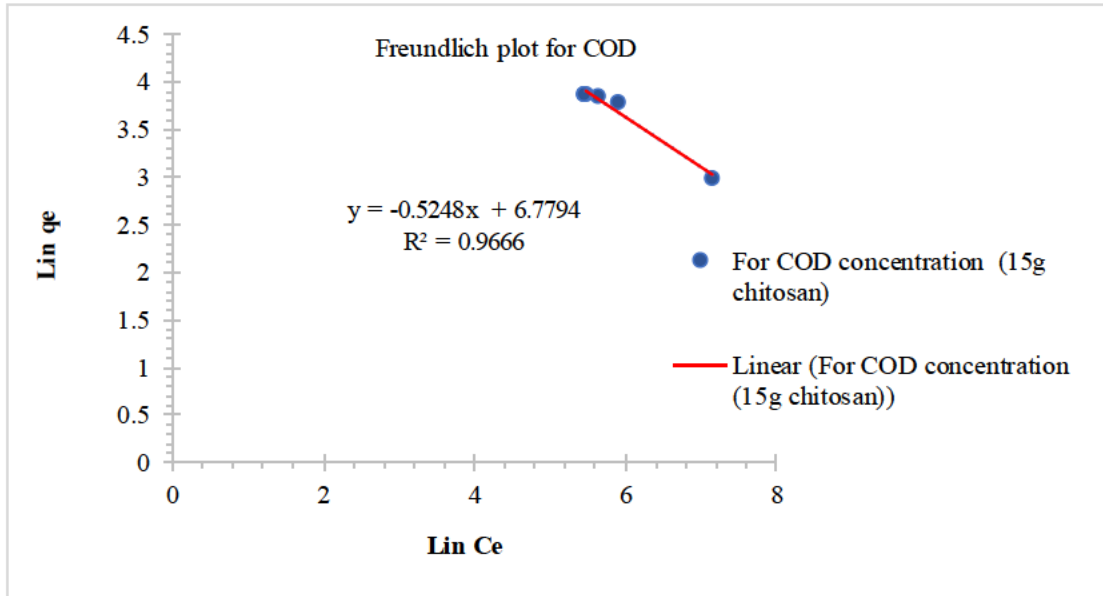


Figure 4-17. Chitosan Freundlich Isotherm plot for the COD

From the linear equation $y = -0.5248x + 6.7794$

$$\frac{1}{n} = -0.5248$$

$$n = \frac{1}{-0.5248}$$

$$= -1.905$$

$$\ln q = 6.7794$$

$$q = e^{6.7794}$$

$$= \underline{879.5}$$

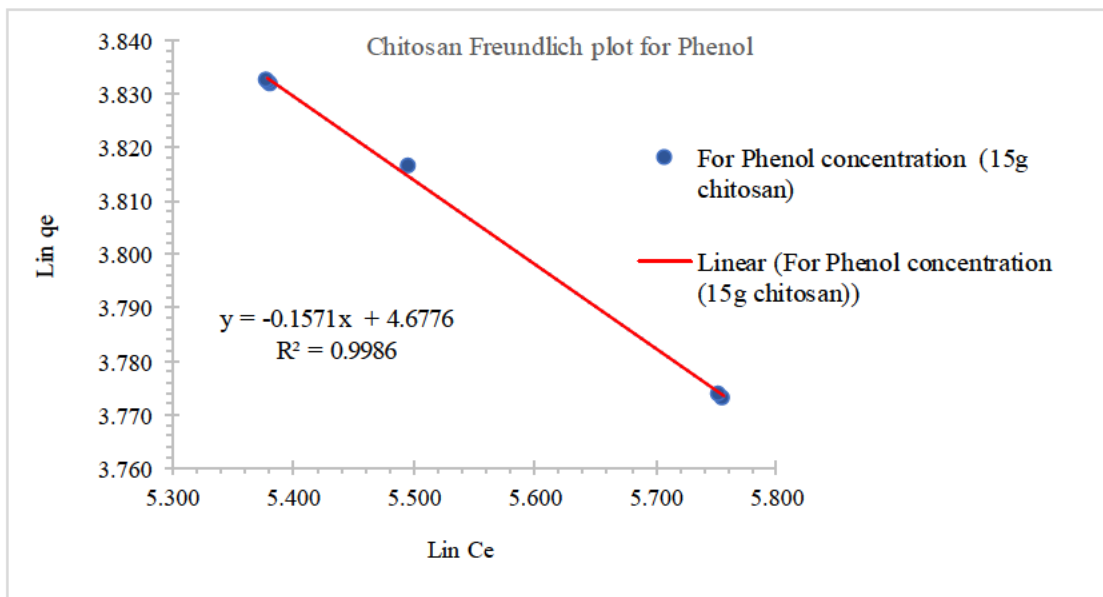


Figure 4-18. Chitosan Freundlich Isotherm plot for the phenol

From the linear equation $y = -0.157x + 4.6776$

$$\frac{1}{n} = -0.157$$

$$n = \frac{1}{-0.157}$$

$$= -6.369$$

$$\ln q = 4.6776$$

$$q = e^{4.6776}$$

$$= \underline{107.5}$$

A3- Response Surface Methodology Tables and Plots

Electrocoagulation ANOVA- coded factors coefficients

EC Coefficients in Terms of Coded Factors - COD

Table A-5. EC Coefficients in Terms of Coded Factors- COD

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	88,51	1	3,09	81,70	95,31	
A-Rn time	28,70	1	3,10	21,86	35,53	1,0000
B-No. of sheet	1,46	1	2,03	-3,01	5,94	1,0000
AB	-2,17	1	3,10	-9,01	4,66	1,0000
A ²	-29,76	1	5,43	-41,72	-17,81	1,0000
B ²	ALIASED					
AB ²	ALIASED					

EC Coefficients in Terms of Coded Factors -Colour

Table A-6. EC ANOVA Coefficients in Terms of Coded Factors- Colour

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	91,13	1	0,7630	89,45	92,81	
A-Rn time	8,93	1	0,7665	7,24	10,62	1,0000
B-No. of sheet	1,87	1	0,5018	0,7706	2,98	1,0000
AB	0,5667	1	0,7665	-1,12	2,25	1,0000
A ²	-6,46	1	1,34	-9,41	-3,51	1,0000
B ²	ALIASED					
AB ²	ALIASED					

EC Coefficients in Terms of Coded Factors – Phenol

Table A-7. EC ANOVA Coefficients in Terms of Coded Factors -Phenol

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	91,37	1	1,36	88,37	94,37	
A-Rn time	0,2210	1	3,63	-7,78	8,22	7,05
B-No. of sheet	2,86	1	0,8959	0,8844	4,83	1,0000
A ²	-8,35	1	2,39	-13,62	-3,07	1,0000
A ³	9,59	1	4,46	-0,2241	19,40	7,05

EC ANOVA plots

Design-Expert® Software
Factor Coding: Actual

All Responses

0  1

X1 = A: Rn time

X2 = B: No. of blades

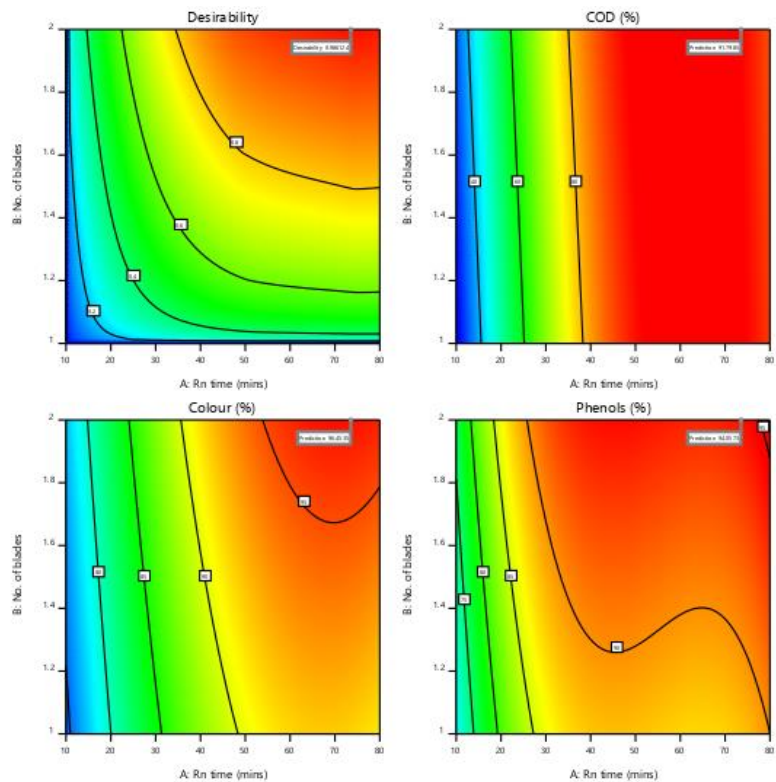


Figure A-1. Contour plots for the Electrocoagulation

Design-Expert® Software
Factor Coding: Actual

All Responses

X1 = A: Rn time

Actual Factor
B: No. of blades = 2

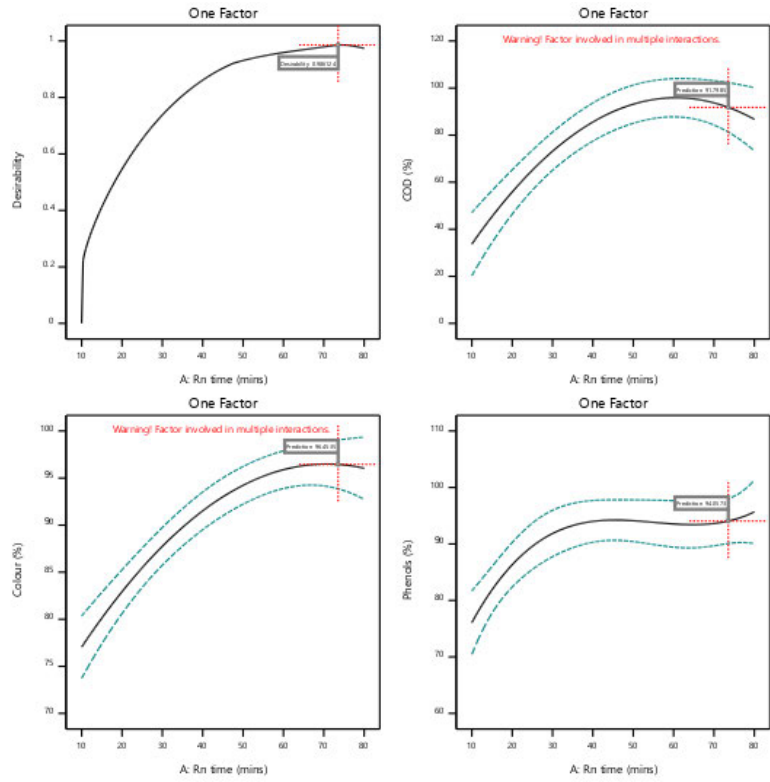


Figure A-2. One factor plots for the Electrocoagulation.

Design-Expert® Software
Factor Coding: Actual

All Responses

X1 = A: Rn time

X2 = B: No. of blades

B- 1
B+ 2

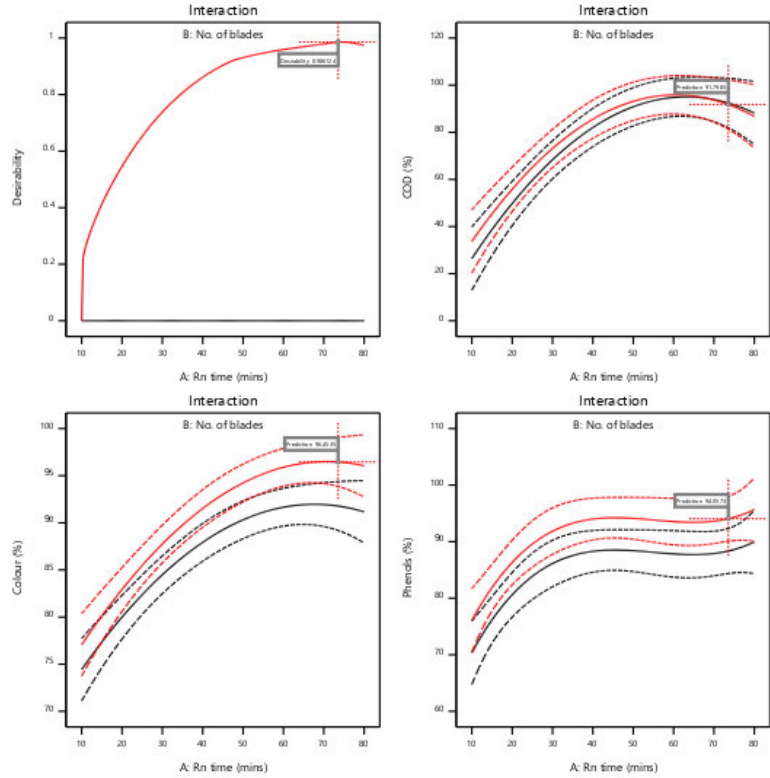


Figure A-3. EC – optimization interaction

Chitosan ANOVA coded factors coefficients

Chitosan Coefficients in Terms of Coded Factors -Response 1 - COD

Table A-8. Chitosan Coefficients in Terms of Coded Factors COD

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	88,46	1	3,91	79,86	97,07	
A-Dosage	12,21	1	2,29	7,17	17,26	1,0000
B-Rxn Time	13,83	1	7,69	-3,10	30,76	7,89
AB	-9,98	1	3,35	-17,36	-2,60	1,0000
A ²	-10,34	1	3,97	-19,08	-1,61	1,0000
B ²	-26,29	1	4,69	-36,60	-15,97	1,0000
A ³	ALIASED					
B ³	15,90	1	8,89	-3,67	35,48	7,89

Chitosan Coefficients in Terms of Coded Factors, response 2- Colour

Table A-9. Chitosan ANOVA Coefficients in Terms of Coded Factors- Colour

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	75,13	1	1,65	71,53	78,73	
A-Dosage	7,71	1	0,9685	5,60	9,82	1,0000
B-Rxn Time	8,73	1	1,16	6,21	11,26	1,0000
AB	-3,21	1	1,42	-6,30	-0,1188	1,0000
A ²	2,72	1	1,68	-0,9324	6,38	1,0000
B ²	-5,99	1	1,98	-10,31	-1,68	1,0000

Coefficients in Terms of Coded Factors – response 3-Phenol)

Table A-10. Chitosan ANOVA Coefficients in Terms of Coded Factors -Phenol

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	82,75	1	0,4986	81,66	83,84	
A-Dosage	5,44	1	0,2922	4,80	6,08	1,0000
B-Rxn Time	3,54	1	0,3492	2,78	4,30	1,0000
AB	-0,5936	1	0,4277	-1,53	0,3383	1,0000
A ²	0,2528	1	0,5061	-0,8498	1,36	1,0000
B ²	-3,23	1	0,5978	-4,53	-1,93	1,0000

Chitosan ANOVA plots

Design-Expert® Software
Factor Coding: Actual

All Responses
● Design Points
0 1

X1 = A: Dosage
X2 = B: Rxn Time

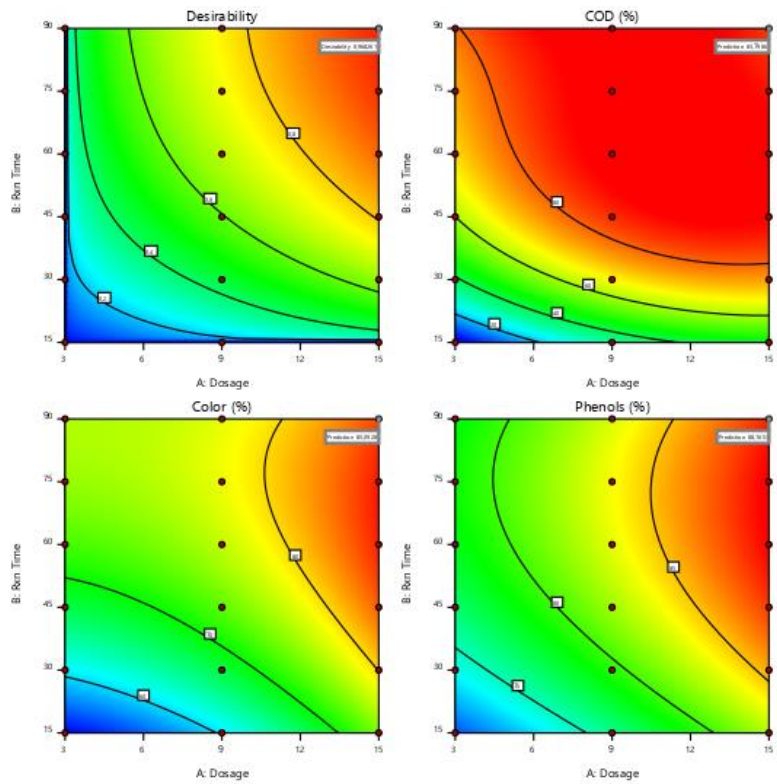


Figure A-4. Contour plots for Chitosan

Design-Expert® Software
Factor Coding: Actual

All Responses
● Design Points

X1 = A: Dosage

Actual Factor
B: Rxn Time = 90

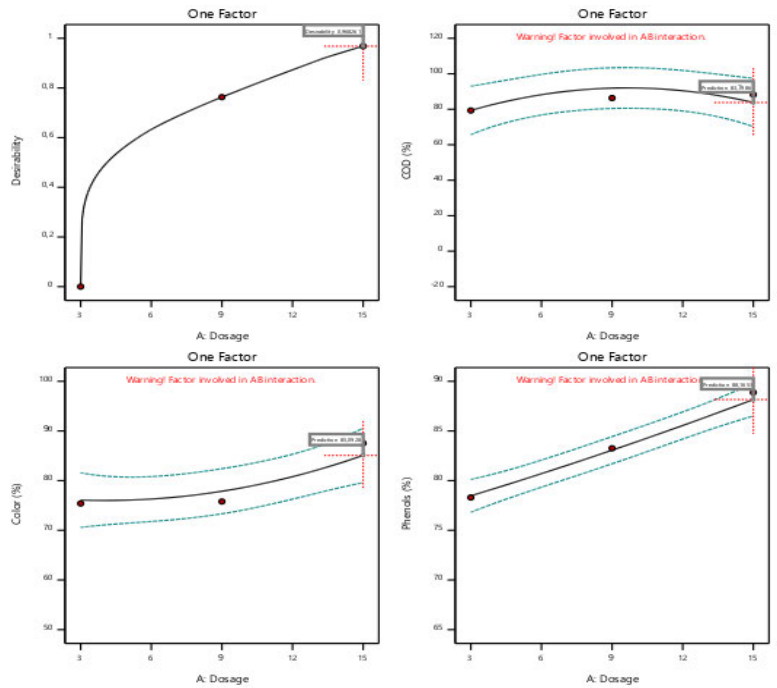


Figure A-5 One factor plot for Chitosan

Design-Expert® Software
Factor Coding: Actual

All Responses
● Design Points

X1 = A: Dosage
X2 = B: Rxn Time

B- 15
B+ 90

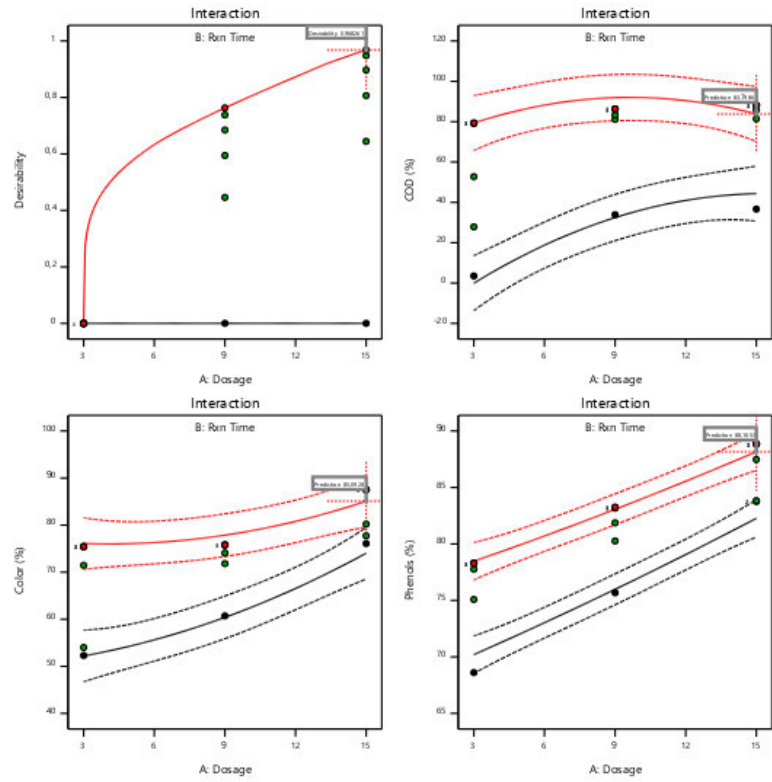


Figure A-6 Chitosan interaction plot.