ELECTROCHEMICAL DEGRADATION OF METHYL ORANGE DYE CONTAMINATED WATER

BY

ENYIA, ONYINYECHI DEBORAH

REG. NO 20204252448

A THESIS SUBMITTED TO THE DEPARTMENT OF EVIRONMENTAL MANAGEMENT, FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI

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A THESIS SUBMITTED TO THE POST GRADUATE SCHOOL,
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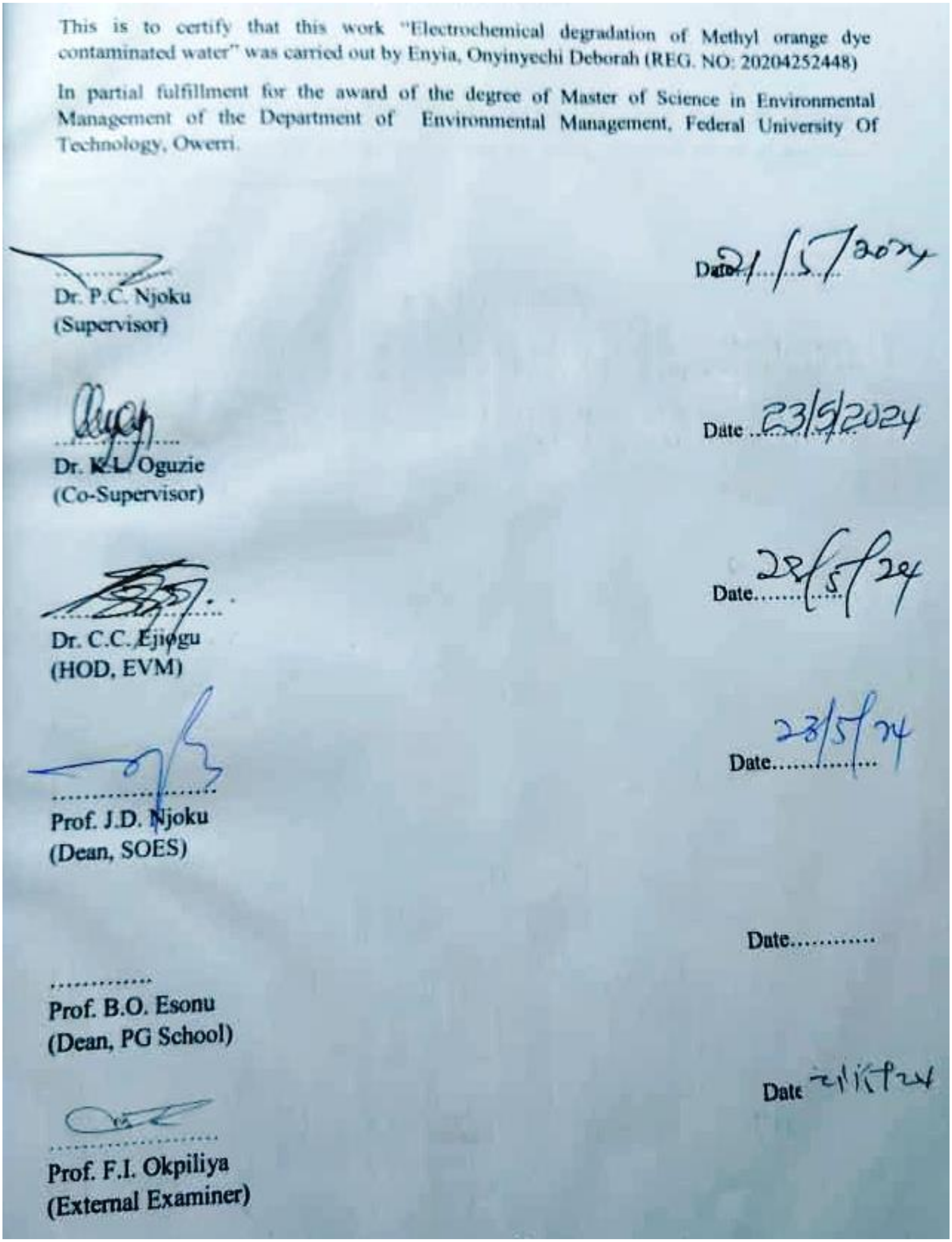
CERTIFICATION



This is to certify that this work "Electrochemical degradation of Methyl orange dye contaminated water" was carried out by Enyia, Onyinyechi Deborah (REG. NO: 20204252448)

In partial fulfillment for the award of the degree of Master of Science in Environmental Management of the Department of Environmental Management, Federal University Of Technology, Owerri.

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DEDICATION

These thesis is dedicated to God Almighty who has been my source of strength, and grace throughout the period of my course, he has been my strong pillar, my source of inspiration, wisdom, knowledge and understanding.

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ABSTRACT

In this study, the electrochemical degradation of Methyl orange, a representative of azo dye, was investigated in contaminated water using a graphite anode and copper cathode. Several key parameters were systematically explored, including time, pH, temperature, current density, and electrolyte concentration, to optimize the degradation process. An observable trend emerged, revealing intriguing insights. Increasing current density and reaction time consistently enhanced degradation efficiency. Specifically, current densities of 0.27mA/mm² and 0.53 mA/mm² exhibited rapid degradation, reaching a plateau at approximately 87%. At higher current densities of 0.8mA/mm² and 1.33mA/mm², degradation efficiency followed a more intricate pattern, culminating in remarkable removal rates of 97.88% and 97.34%, respectively. Electrolyte selection also played a pivotal role, with 1M KCl displaying the swiftest degradation efficiency of 98% within a mere 30 minutes. Conversely, 0.05 M KCl recorded the lowest degradation efficiency. Similar trends were observed with NaCl, where 1M NaCl achieved an impressive 97.2% degradation efficiency, while 0.05 M NaCl lagged significantly at 22.8%. Moreover, degradation efficiency decreased with increasing pH, with the pH 3 conditions yielding the highest efficiency at 98%. Temperature variations mirrored this trend, as a temperature of 30 ºC attained the pinnacle degradation efficiency of 99%. UV-VIS analysis further substantiated the findings, revealing a substantial reduction in absorbance peaks for Methyl orange dye, from 2.0 to 0.2 at a wavelength of 470 nm in the visible region. This signified the elimination of the azo chromophore group, an initial constituent of the dye, during electrochemical degradation. Additionally, the appearance of intermediates underscored the complexity of the degradation process. This study has significant implications for wastewater treatment plants, offering valuable insights into the optimization of cost-effective electrochemical treatment methods. The findings unraveled the intricate interplay of key parameters, paving the way for enhanced efficiency in the removal of toxic synthetic dyes and advancing the pursuit of sustainable and environmentally friendly wastewater treatment strategies.

KEYWORDS: Decolourization; Electrochemical; treatment; Electrode; Optimization; Pollution

CHAPTER ONE

INTRODUCTION

1.1 Background to the study

The wide spread use of synthetic dyes, particularly methyl orange, in various industrial processes, has led to significant environmental concerns. The imperative of wastewater treatment is underscored by the dire consequences of untreated or inadequately treated effluents on ecosystems and public health. The diverse array of pollutants that permeate wastewater includes organic and inorganic matter, pathogens, heavy metals, and nutrients. The unregulated discharge of these pollutants into natural water bodies could precipitate ecological imbalance, groundwater contamination, and the proliferation of waterborne diseases (Evelin & Chikashi, 2021). While conventional methods have their merits, certain contaminants defy easy removal. Synthetic dyes, exemplifying a group of such recalcitrant pollutants, pose challenges due to their intricate molecular structures and resistance to degradation. A paradigm shift toward advanced and innovative treatment approaches is essential to effectively address these emerging challenges. Synthetic dyes, emerges as a pressing concern.

Synthetic dyes, serving as integral components of various industries for colouration purposes, bestow vibrancy but also carry ecological and health risks. The indiscriminate release of dye-laden wastewater taints water bodies, impeding sunlight penetration and disrupting aquatic ecosystems (Maheshwari, Agrawal, & Gupta, 2021).

Even more alarming is the potential toxicity and carcinogenicity of specific synthetic dyes, posing threats to both aquatic organisms and humans along the food chain. The persistence of these dyes necessitates proactive strategies to mitigate their ecological and health impacts (Miller, Steinmaus, Golub, Castorina, Thilakartne, Bradman & Marty, 2022). Methyl orange, a member of the azo dye class, embodies vibrant properties that have rendered it a valuable tool in numerous industrial applications. Its distinctive chemical structure comprises azo (–N=N–) and sulfonic acid ($-SO_3H$) functional groups, contributing to its robust coloration and solubility characteristics. This dye finds widespread usage across industries including textiles, pharmaceuticals, and cosmetics, primarily for its ability to confer vivid shades to products (Ashok, Agrawal, Esteve-Romero, Bose, D & Dubey, 2017; Wei, Mcyotto, Chow, Nadeem, Li, & Liu,., 2021).

Despite its industrial significance, the application of methyl orange brings forth a considerable environmental burden. The discharge of wastewater laden with methyl orange not only introduces vivid coloration to water bodies but also diminishes light penetration, detrimentally affecting aquatic photosynthesis. The resulting alterations in aquatic ecosystems cascade through the food chain, with potential consequences for biodiversity and ecosystem stability. Moreover, the chemical complexity of methyl orange is coupled with the potential for toxicity. Certain derivatives of azo dyes, including methyl orange, have been implicated as potential carcinogens and mutagens, urging stringent control over their release into the environment. Regulatory bodies worldwide have recognized the necessity to restrict their concentration in wastewater, calling for effective treatment strategies (Miller *et al.*, 2022).

Historically, addressing the challenges posed by synthetic dyes like methyl orange involved traditional treatment methods. These methods include adsorption, coagulation, and biological degradation. However, the intricate chemical structure and stability of methyl orange often render these conventional methods less effective. While adsorption and coagulation can remove dye molecules to a certain extent, they fall short in providing comprehensive solutions for persistent dye removal. The quest for advanced, efficient, and sustainable treatment approaches persists.

In the face of these challenges, the realm of electrochemical methods emerges as a beacon of hope. The electrochemical degradation of methyl orange through anodic oxidation processes offers a promising avenue, characterized by the generation of reactive species that can effectively dismantle its intricate structure (Sativa, Zulfikar, & Alni 2021). This thesis delves into the exploration of these electrochemical techniques, aiming to shed light on their efficacy in addressing the recalcitrant nature of methyl orange contamination.

The removal of synthetic dyes such as methyl orange from wastewater is not only an environmental imperative but is also governed by a framework of regulatory guidelines and standards at both national and international levels. These regulations aim to ensure that the discharge of dye-containing effluents into water bodies complies with established criteria, safeguarding ecosystems and public health.

Many countries have set specific effluent standards that limit the concentration of specific pollutants, including dyes like methyl orange, in wastewater discharges. These standards define the acceptable levels of dye concentrations that can be released into the environment. For instance, limits may be expressed in terms of maximum allowable dye concentration in milligrams per liter (mg/L).

Industries discharging wastewater containing synthetic dyes are often required to obtain discharge permits. These permits outline the maximum allowable concentrations of pollutants, including methyl orange, that can be released into receiving water bodies.

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal, under the United Nations Environment Programme (UNEP), addresses the management and disposal of hazardous wastes, including certain dyes. Methyl orange and other toxic dyes are subject to strict regulations under this convention to prevent their transboundary movement and ensure their safe handling and disposal.

In the United States, the SDWA sets drinking water standards that limit the presence of specific contaminants, including organic compounds like dyes. Although it primarily pertains to drinking water quality, the Act indirectly influences the treatment of wastewater to prevent contamination of water sources.

The European Union has established the Water Framework Directive, which outlines the quality objectives for surface waters and requires member states to take measures to achieve these objectives. This directive sets standards for pollutants, including synthetic dyes like methyl orange, to protect water ecosystems.

In the United States, OSHA provides regulations and guidelines for workplace safety, including exposure limits for hazardous chemicals. Employers must adhere to these standards when handling and managing chemicals like methyl orange to protect the health and safety of workers.

The GHS, established by the United Nations, provides a globally recognized framework for classifying and labeling chemicals, including dyes. Compliance with GHS guidelines is essential to ensure the safe handling and transport of methyl orange and other hazardous dyes.

Before initiating industrial projects that involve the use of synthetic dyes, including the production and discharge of methyl orange, many countries require companies to conduct EIAs. These assessments evaluate the potential environmental impacts and propose mitigation measures, often including wastewater treatment, to comply with regulatory standards.

In addition to national and international regulations, local and regional authorities may establish specific guidelines for the removal of methyl orange and other dyes based on local environmental conditions and concerns.

Compliance with these regulatory guidelines is essential for industries and facilities handling methyl orange-containing wastewater. Effective treatment methods, such as electrochemical degradation, must be employed to meet these standards and protect the environment and human health. Failure to do so can result in legal consequences, fines, and reputational damage for non-compliant entities.

In the quest for innovative wastewater treatment strategies, electrochemical methods have emerged as promising alternatives. Harnessing the power of electrical energy to initiate chemical reactions offers advantages such as efficiency, selectivity, and the generation of reactive species that can degrade recalcitrant compounds. This shift towards electrochemical approaches marks a significant leap in the field of wastewater treatment.

Electrochemical degradation stands as a compelling approach in the treatment of organic pollutants due to its ability to initiate controlled and selective oxidation reactions. This method leverages the application of electrical energy to induce redox reactions at the electrode surface. In the context of organic pollutants, electrochemical processes facilitate the conversion of complex molecules into simpler, less harmful products. Central to this process is the generation of reactive species, primarily hydroxyl radicals (•OH), through the electrolysis of water at the electrode surface. These hydroxyl radicals exhibit potent oxidative capabilities, driving the mineralization of organic pollutants into carbon dioxide, water, and inorganic ions. The controlled and targeted nature of electrochemical oxidation makes it an attractive choice for degrading recalcitrant organic compounds(Oguzie, Oguzie, Nwanonenyi, Edoziem, & Vrsalović, 2021).

1.2 Statement of the Problem

The dyeing and finishing operations create a significant volume of effluent. Textile wastewater is notable for having a bright hue, a high concentration of suspended particles, a highly variable pH, and a high temperature and Chemical Oxygen Demand (COD) content. Methyl orange, an azo dye, its presence in the body of water and treatment has been problematic due to its high stability, resistance to biodegradation, and potential toxicity to aquatic life and humans. Conventional waste water treatment methods often fail to effectively remove these dyes, leading to the persistence of contaminated water in the environment. Additionally, this method can generate secondary pollutants and are not always cost effective or feasible for large-scale applications. Advanced oxidation processes (AOPs), including photocatalysis, ozonation, and Fentons reaction, have shown promise in degrading methyl orange but there practical application requires further optimization and understanding of operational parameters.

Electrochemical degradation has emerged as a promising alternative for the treatment of dye contaminated water. This method leverages electrochemical reactions to breakdown complex dye molecules into simpler, less harmful substances. However, the practical application of electrochemical degradation for methyl orange remover requires further investigation to optimize operational parameters, improve degradation efficiency, and ensure economic feasibility.

Addressing the challenge of methyl orange contamination through electrochemical degradation is critical to protecting aquatic environments, ensuring public health, and meeting stringent environmental regulations. However, developing an efficient scalable electrochemical degradation process can significantly contribute to sustainable water management, and meet the criteria of clean water.

1.3 Aim and Objectives

The aim of the study is to investigate the treatment of Methyl orange dye-contaminated water in an aqueous solution.

The objectives of this study are:

1. To determine of the effect of pH on percentage degradation of methyl orange dye contaminated water.
2. To determine of the effect of supporting electrolytes on percentage degradation of methyl orange dye contaminated water.
3. To determine of the effect of temperature on percentage degradation of methyl orange dye contaminated water.
4. To determine of the effect of current density on percentage degradation of methyl orange dye contaminated water.
5. To determine of degradation pathway of methyl orange dye in aqueous solution.

1.4 Justification for Study

Electrochemical oxidation emerges as a compelling solution for degrading methyl orange contaminated water owing to its efficiency, eco-friendliness, and adaptability. This method relies on electrical current to induce oxidation reactions at electrode Surfaces, swiftly breaking down organic pollutants like methyl orange into harmless by products. Notably, its environmental sustainability, versatility in scale and conditions, as well as its minimal generation of secondary pollutants, position it as promising approach.

However, electrochemical oxidation offers a cost-effective treatment alternative. While initial setup costs may exist, its efficiency in degrading contaminants reduces the necessity for extensive post-treatment processes, potentially lowering long term operational expenses. Its precise control mechanisms enable optimization of degradation efficiency, while its easy monitoring ensures consistent performance. This amalgamation of efficacy, environmental compatibility, and cost-effectiveness underscores the viability of electrochemical oxidation in addressing methyl orange contamination in water.

1.5 Scope of Study

This study focused on the electrochemical degradation of methyl orange dye in an aqueous solution using copper and graphite electrodes. The following parameters were investigated during the experiment:

1. Temperature (30°C, 45°C, 60°C)
2. Current density (0.27, 0.53, 0.8, 1.07, 1.33 mA/mm^2)
3. Electrolyte concentration (1, 0.5, 0.1, 0.05 M)
4. pH (3, 5, 7, 9, 11)

Ex-situ processes were used to contaminate the water, and the waste water does not contain as many organic components as it does in the textile sector.

CHAPTER TWO

LITERATURE REVIEW

The shortage of pure, high-quality drinking water is one of the most significant problems facing humanity today, even though more than 71 percent of the earth's surface is covered by water(Gupta *et al*., 2015; Chen *et al*., 2020; Chen *et al*., 2021). Massive amounts of treated or untreated effluent containing azo dyes and other organic pollutants are disposed of by the textile industry. However, because azo dyes degrade before or after disposal, treated effluents contain amino acids that are likely more toxic than their raw substances, whereas untreated wastewater has a wide range of negative impacts on aquatic environments and living organisms (Khalaj *et al*., 2018; Mudhoo *et al*., 2020).

Progressive advancements are being made to build innovative wastewater treatment technologies and meet the criteria of clean water (Ahmed & Haider, 2018). However, treating polluted discharged water thoroughly with current means has proven difficult (Nguyen & Juang, 2019). Several wastewater treatment strategies have been published in the literature. They generally consist of physical, chemical, and biological processes that are thought to be successful enough for water treatment in a variety of ways. Their selection is influenced by a variety of criteria such as dye concentration, sewage composition, process cost, and the presence of other contaminants in wastewater (Wawrzkiewicz *et al.,* 2019).

2.1 Physical methods for treatment

With a very high removal efficiency ranging from 85% to 99%, different physical techniques like adsorption, ion exchange, and membrane filtration are utilized to treat dye-containing wastewater based on the mass transfer mechanism(Samsami, *et al*., 2020). However, some disadvantages, such as the creation of poisonous by-products and sludge, as well as their restricted applicability, make these technologies generally unpopular(Akpomie& Conradie, 2020). Furthermore, their use in the treatment of textile wastewater is typically hampered by high temperatures, chemical oxygen demand (COD), biological oxygen demand (BOD), pH, colour, and heavy metals. Utilized.

2.1.1 Adsorption

Adsorption in wastewater treatment is the process of pollutants adhering to a solid material (adsorbent) to remove contaminants from water. It involves the physical capture and immobilization of contaminants on the adsorbent's surface, effectively purifying the wastewater.

Azam*et al* (2020) conducted a study on the development of recoverable magnetic mesoporous carbon adsorbent for the removal of methyl blue and methyl orange from wastewater. They prepared the novel magnetic mesoporous activated carbon (MMAC) from activated carbon (AC), produced from rice husk through $ZnCl_2$ chemical activation. The mesostructured was induced via Korea Advanced Institute of Science and Technology-6 (KIT-6) silica formation and magnetic behaviour were incorporated by magnetite by wetness impregnation method. KIT-6 silica enhances porosity and provides a 3D structure to improve the adsorption process. SEM, XRD, BET, and FTIR analysis techniques were employed in their characterization of the absorbent and the effect of different process parameters on the adsorption efficiency such as pH of the dye solution, initial dye concentration, and dosing of adsorbents were studied while the adsorption efficiency was evaluated by testing aliquot in UV-Visible spectroscopy. They reported that methylene blue followed the Freundlich isotherm while methyl orange was well suited to the Langmuir model. Also, magnetic mesoporous activated carbon removed 82 % methylene blue and 98.5 % methyl orange dye solution in 30 min. Their data also showed that the adsorbent was regenerated and reused for methylene blue and methyl orange for 4 cycles without a significant decrease in the adsorption efficiency. They concluded that magnetic mesoporous activated carbon is a more efficient adsorbent than mesoporous activated carbon and activated carbon because of its high surface area and high pore volume (Azam et al., 2020).

In a different study, Chatterjee *et al* (2020) experimented to understand the competitive adsorption of pollutants on a mesoporous alumina–silica nano sorbent synthesized from coal fly ash and a waste aluminium foil). They proposed a novel methodology for the synthesis of a mesoporous alumina–silica nano-sorbent from coal fly ash and waste aluminium foil. The in-depth characterizations of the nano-sorbent confirm the drastic changes in surface area, pore structure, pore volume, morphology, and crystalline structure, which facilitate its adsorption capacity. Their data showed that the nano-adsorbent successfully removed the toxic pollutants, namely lead and malachite green, from single to multi-component solutions. The as-synthesized nano-sorbent has exhibited high adsorption capacities for both lead and malachite green for single components 326.2 and 1655.2 mg/g, respectively, and for binary components 615.86 and 445.03 mg/g, respectively. More importantly, the observed adsorption capacities of the as-synthesized adsorbent for the concerned pollutants are reasonably higher than those reported in other literature. The authors also reported that the as-synthesized adsorbent showed a 15.05% and 10.07% reduction in adsorption capacity after five cycles of reuse for lead and malachite green, respectively. These observations have attested to the effective and economical nature of the adsorbent, which has a potential application in treating industrial wastewater (Chatterjee *et al*., 2020).

In another study, Slatni*et al.,* (2020) experimented with the use of Mesoporous silica synthesized from natural local kaolin as an effective adsorbent for removing Acid Red 337 and its application in the treatment of real industrial textile effluent. The authors synthesized mesoporous silica (MS) from natural clay as a silica source using Pluronic L35 (EO11PO16EO11) as a structure-directing agent. The prepared material was characterized by XRD, X-ray fluorescence, thermogravimetric analysis, SEM, TEM, and N_2 adsorption-desorption analyses. Then, mesoporous material was used for the removal of Acid Red 337 (AR337) from the aqueous solution, and the treatment of real textile effluent. They studied the effect of pH, contact time, weight of adsorbent, and initial concentration in batch adsorption and posited that the synthesized mesoporous material showed good discoloration efficiency with a 62% efficiency while experiments with real textile wastewater showed that 39%, 40%, and 31.5% of the colour, TOC, and chemical oxygen demand respectively were eliminated by using 1 g of MS per liter of wastewater(Slatni*et al*., 2020).

Adsorption is a method of dye wastewater treatment that offers several advantages and disadvantages. One of its main advantages is its effectiveness in removing a wide range of dyes and other organic contaminants. Adsorption processes are typically versatile and can be tailored to specific contaminants. Activated carbon, a commonly used adsorbent, has a well-established track record in dye removal. However, adsorption also has limitations, such as the eventual saturation of adsorbent materials, which necessitates regeneration or replacement, adding to operational costs. It may be less efficient for treating very high dye concentrations, and the disposal of spent adsorbents requires careful consideration. Despite these drawbacks, adsorption remains a valuable and widely used method for dye wastewater treatment due to its versatility and effectiveness in pollutant removal.

2.1.2 Membrane filtration

Membrane filtration is a wastewater treatment method that employs specialized membranes with tiny pores to physically separate impurities and contaminants from water. This process results in the removal of particles, microorganisms, and dissolved substances, producing treated water of higher quality. Iaich*et al* 2021 experimented on low-cost ceramic microfiltration membranes made from Moroccan clay for domestic wastewater and Congo red dye treatment. They prepared the microfiltration layers (M10/25PVA, M10, and M12) using the slip-casting technique of suspension containing the clay powder ($\phi < 63$ μm), polyvinyl alcohol, and water. Thereafter, the membranes were dried and sintered at 900°C/3 h. Chemical analysis by X-ray fluorescence, specific surface, pore size distribution, X-ray diffraction, Fourier transform infrared spectroscopy, differential thermal analysis, and thermogravimetric analysis were the techniques used for analyzing and characterizing the raw clay. The membranes were used for the microfiltration of domestic wastewater (DWW) and Congo red (CR) dye. Throughout all of the microfiltration tests, the pH remains relatively stable. The authors reported that electrical conductivity and the chemical oxygen demand decreased after 45 and 15 min, respectively for all the studied membranes. For domestic wastewater, the suspended particulate matter responsible for turbidity was almost eliminated (Re = 99%), and the CR-coloured solution was nearly totally discoloured (Rd = 99%) (Iaich *et al.*, 2021)

In a different study, Homem*et al.,* (2019) investigated the surface modification of a polyethersulfone microfiltration membrane with graphene oxide for reactive dye removal. The Polyethersulfone microfiltration membranes (mPES) were modified with polyethyleneimine (PEI) and graphene oxide (GO) by layer-by-layer self-assembly method via electrostatic interaction using a pressurized filtration system. The high positive charge of PEI allowed it to be easily assembled on the polyethersulfone substrate, and also to receive the negative layer of GO. Several techniques were applied to characterize the modified membranes (i.e., ATR-FTIR, SEM, water angle contact, and zeta potential), and proved that the modification was successfully achieved. Their results from studying the effect of PEI and GO concentrations modification showed that the best performance of all membranes was achieved with a Blue Corazol (BC) dye rejection of 97.8% and pure water permeability of 99.4 L m−2 h−1 bar−1. The membrane also presented a flux recovery ratio of > 80% after being hydraulically cleaned for 30 min. Moreover, the membrane performance was evaluated in terms of rejection of BC dye in a real dye bath wastewater, and excellent performance with a maximum rejection rate of 96% was observed. Therefore, the proposed study may provide an efficient alternative to feasible the use of microfiltration membranes, by modifying them, to improve their surface characteristics and filtration capacity, aiming to apply it in the removal of dyes from textile industries wastewater (Homem *et al.,* 2019).

In another study, Zhu *et al.*, (2020) experimented with dyes removal by a composite membrane of sepiolite-impregnated polysulfone coated by chemical deposition of tea polyphenols. The researchers used multi-amine, metformin (MTM), and polyethyleneimine (PEI) to prepare a separative layer of the composite membrane through chemical deposition with tea polyphenols (Tph). An inexpensive mixture of nature polyphenols, on a hybrid polysulfone (Psf) membrane. The supporting layer was a blend membrane of Psf, coupling agent-treated sepiolite, and cetyltrimethylammonium bromide (CTAB). They reported that both composite membranes showed dyes rejection capacity at 1 bar. PEI-Tph layer was thicker than MTM-Tph, and so did its rejection for dyes. The rejection of PT for 5 dyes was all higher than 98% and remained at 99.3% and 98.6% in 200 h for Congo red (CR) and neutral red (NR). PEI-Tph membrane displayed the potential in textile wastewater treatment (Zhu *et al.*, 2020)

Yang *et al* (2020) also studied the fabrication and characterization of a high-performance polyimide ultrafiltration membrane for dye removal. They successfully prepared a novel thermally stable polyimide (PI) polymer using 2,4,6-trimethyl-1,3-phenylenediamine, 4,4′-diaminodiphenylmethane and 1,2,4,5-benzenetetracarboxylic dianhydride components. PI was selected as a representative candidate because of its excellent thermal stability (decomposition temperature of 529 °C), as revealed by thermogravimetric analysis. This UF membrane is especially interesting as it allowed for almost complete penetration of monovalent (NaCl) and divalent (Na_2SO_4) inorganic salts because of its molecular weight cut-off of 9320 Da. The authors reported that the membrane exhibited very good surface hydrophilicity with a water contact angle of 67.6° and the PI-based UF membrane was found to be substantially effective as it showed high pure-water and dye-permeation fluxes of 345.10 and 305.58 L m^{-2} h^{-1} at 0.1 MPa, respectively. Besides, the membrane exhibited a rejection of 98.65% toward the direct red 23 dye (100 ppm) at 0.1 MPa. Thus, this PI-based UF membrane is highly beneficial and acts as a potential candidate for dye removal from wastewater produced by the textile industry (Yang *et al*., 2020)

Despite the ease and effectiveness of this method, the membranes must be periodically replaced(Samsami, *et al.*, 2020).Membrane filtration is a method of dye wastewater treatment with notable advantages and disadvantages. Its key advantage lies in its ability to provide high-quality treated water by effectively removing dyes, particles, and contaminants. It offers various membrane types and sizes to accommodate different needs. Membrane filtration is a physical process, which means no chemicals are required, reducing the environmental impact. However, it has drawbacks, including the need for frequent membrane cleaning and replacement, which can be costly. High operational pressures and energy consumption can also contribute to increased expenses. Additionally, the effectiveness of membrane filtration can be impacted by fouling and scaling, requiring careful maintenance and monitoring. Overall, it's a reliable method when considering its ability to achieve high-quality effluent but comes with associated maintenance and operational challenges.

2.1.3. Ion exchange

Ion exchange is a wastewater treatment method that utilizes ion exchange resins or materials to selectively remove ions, such as heavy metals or undesirable ions, from water by exchanging them with similarly charged ions in the resin. This process leads to the purification of water by effectively removing specific contaminants through ion swapping, improving water quality.Joseph *et al* (2020) conducted a study on the Ion-exchange mediated removal of cationic dyestuffs from water using ammonium phosphomolybdate. They studied the ability of APM particles to remove dye from dye-contaminated water to the nature of incident radiation, concentration, pH, and nature of the dye. The authors opined that APM could effectively remove cationic dyes from water as long as the pH range permitted the dye to retain its cationic behaviour. This specificity suggested that the removal of dyestuffs could be attributed to the ion exchange between ammonium ions in APM with cationic dye moieties. Their result also suggested that APM could be reused several times without affecting its efficiency and removal efficiency of 94.6% could be retained up to the 16th cycle while sensitivity to pH enabled APM to reverse the cation exchange process. The ion exchange process was not dependent on the exposure of APM particles to irradiation which confirmed that the mode of action of APM was not photocatalytic (Joseph *et al.*, 2020).

In a different study, Marin *et al* (2019) investigated the removal of the Acid Orange 10 by ion exchange and microbiological methods. The persistent pollutant azo dye, Acid Orange 10, was removed from the environment by an Amberlite IRA 400 anion exchange resin and then biodegraded by two bacterial strains. The researchers characterized The Acid Orange 10 sorption on the resin (Acid Orange 10 concentration, its contact time, and stability) based on various parameters such as pH and temperature while biodegradation and the ecotoxicity effect of Acid Orange 10 were monitored on two bacterial strains such as *Salmonella enterica* (gram-negative bacteria) and *Enterococcus faecalis* (gram-positive bacteria). Their experimental data from ion-exchange studies showed that the strongly basic anion-exchange resin Amberlite IRA 400, was removed efficiently up to 96.8% at 10^{-2} M of Acid Orange 10 concentration. Moreover, 10^{-2} M Acid Orange 10 induced in 1 h a significant 50% growth inhibition on S. enterica, but not on the

E. faecalis. The methods tested in this study can be used for the removal of Acid Orange 10 from different polluted waters (Marin *et al.*, 2019).

In another study, Bayramoglu*et al* (2020) researched on preparation and ccharacterisation of strongcationeexchangerterpolymerresin as an effectiveadsorbent for the removal of Disperse Dyes. The authors prepared (hydroxypropyl methacrylate-co-ethylene glycol dimethacrylate-co-glycidylmetharylate) terpolymer resin functionalized with sulfonic acid groups and used it as cation exchange resin for removal of two different disperse dyes (i.e., Direct Red R [DR-R] and Disperse Violet 28 [DV-28]) from aqueous solution. They reported the maximum adsorption capacity of the resin for the DR-R and DV-28 to be 86.1 and 179.6 mg/g, respectively. A desorption study was realized to evaluate the reusability of the resin and the percent desorption from the resin for DR-R and DV-28 dyes was found to be approximately 89.4% and 91.7%, respectively. The experimental data were evaluated using different kinetics and isotherm models. According to the authors, the presented resin was able to remove large amounts of organic pollutants in a short process time with a low amount of adsorbent. Thus, it was shown that the prepared resin has a high potential for use as an effective and sustainable adsorbent for the treatment of industrial wastewater *(Bayramoglu et al.*, 2020).

Huong *et al.*, (2020) also conducted a study on highly efficient dye removal and lysozyme purification using strong and weak cation-exchange nanofiber membranes. They employed Electrospinning technology in the preparation of polyacrylonitrile (PAN) nanofiber membranes. After hot pressing, alkaline hydrolysis, and neutralization treatment, a weak acid cation exchange membrane (P-COOH) was prepared. They used the ion exchange membranes were used for purifying lysozyme from chicken egg white (CEW) and their results illustrated that the recovery yield and purification factor of lysozyme were 93.43% and 29.23 times (P-COOH); 90.72% and 36.22 times (P-SO_3H), respectively. It was revealed that two types of ion exchange membranes were very suitable as an adsorber for use in dye waste treatment and lysozyme purification process. P-SO_3H strong ion-exchange membrane was more effective in either removal of TBO dye or purification of lysozyme. The ion exchange membranes not only effectively purified lysozyme from the CEW solution, but also effectively removed dye from wastewater (Huong *et al.*, 2020)

Ion exchange is a method of dye wastewater treatment that offers distinct advantages and disadvantages. Its advantages include high removal efficiency for dyes and other ions, versatility for treating various contaminants, and the ability to regenerate and reuse the ion exchange resins, reducing operational costs over time. It does not generate chemical sludge, making disposal more straightforward. However, ion exchange systems can be capital-intensive to install and maintain. The regeneration process often involves the use of chemicals, potentially negating some environmental benefits. Additionally, ion exchange may be less effective for treating very high dye concentrations. Despite these drawbacks, it remains a valuable option for specific dye wastewater treatment scenarios, particularly when high purity is required.

2.2 Biological methods for treatment

This method involves the degradation of the dye-bearing wastewater using materials such as algae, yeast, bacteria fungi for the treatment of dye wastewater(Gupta, 2019; Sidek *et al.*, 2019)Suchmaterials can breakdown and absorb various synthetic dyes (Mao et al., 2018; Wang et al., 2022). The method has been found to degrade the dyes by breaking the bond on the chromophore group releasing inorganic compounds that are less toxic. Madhuri (2020) studied eenzyme-assisted biodegradation of Direct Red 81 by Micrococcus Glutamicus NCIM 2168). The authors reported that the isolate decolorized 98.54% of the dye at pH 6 and 28°C in 9 hours. Degradation of the dye was confirmed by the change in λmax of the decolorized sample. Confirmation of the degradation was done by HPLC and GCMS studies. Degradation was brought about by Oxidoreductases. Toxicity studies revealed the non-toxic nature of the product. They concluded that the culture was able to decolorise a mixture of five dyes. Hence, the selected bacterial culture can be successfully used for the treatment of dye-containing wastewater (Madhuri, 2020).

Chen *et al*., (2008) investigated *Shewanella Sp.* biodegradation of crystal violet. They isolated the bacterial isolate, strain NTOU1, from an oil refinery's cooling system and used morphology characters, gyrase subunit beta gene, the 16S rRNA gene, biochemical test and gram staining to identify the strain as a member of *Shewanelladecolorationis* (gyrB). The scientists found that this strain needed a pH of 8 to 9 and a temperature of 30 to 40 °C in order to decolorize crystal violet under anaerobic circumstances. They discovered that Formate (20 mM) was the best electron donor and that the addition of Iron (III) citrate did not inhibit crystal violet decolorization, that the addition of thiosulphate, Iron (III) oxide, or manganese oxide slightly decreased decolorization, and that the addition of nitrite (20 mM) inhibited crystal violet decolorization. However, by supplementing the medium with formate and ferric citrate and cultivating it at optimal pH and temperature, the strain was able to remove crystal violet at a concentration of 1500 mg/L at a rate of 298 mg L^{-1} h^{-1} (the OD_{600} of the cell culture increased from 0.6 to 1.2 during decolorization). The presence of N,N-dimethylaminophenol, 4 methylaminophenol N, N,N-dimethylaminobenzaldehyde, [N, N-dimethylaminophenyl] [N-methylaminophenyl] benzophenone and N'-bis(dimethylamino) benzophenone (Michler's Ketone) was detected in their GC/MS analysis of crystal violet degradation products. These results suggest that crystal violet (CV) was biotransformed into Michler's ketone and N,N-dimethylaminophenol before being further degraded. Cytotoxicity and antimicrobial tests revealed that the decolorization process also detoxifies crystal violet.

In a separate experiment. Shedbalkar*et al*.(2008) investigated the decomposition of cotton blue dye. *Penicilliumochrochloron* decolorized cotton blue (50 mg/L) in 2.5 hours under static conditions at pH 6.5 and temperature 25 ºC. The ultimate products of cotton blue degradation, as determined by their Fourier Transform-IR spectroscopy and GC-MS analyses, were sulphonamide and triphenylmethane. They identified pH, temperature, and biomass maturity as factors influencing the rate of decolorization. Shedbalkar et al. (2008) also found that a rise in lignin peroxidase extracellular activity and the presence of aminopyrine N-demethylase, tyrosinase and lignin peroxidase activities in the cell homogenate indicate that these enzymes are involved in the decolorization process. Studies on the phytotoxicity and microbiological toxicity of extracted metabolites show that they are less harmful.

Khehra *et al.,* (2005) conducted another study to enrich and isolate bacterial strains capable of decolorizing azo dyes present in soil/sludge samples collected from waste disposal sites of local textile industries. They isolated *Bacillus cereus* (BN-7), *Pseudomonas putida* (BN-4), *Pseudomonas fluorescence* (BN-5), and *Stenotrophomonasacidaminiphila* (BN-3) capable of completely decolorizing C.I. Acid Red 88 (AR-88), and used them to form the HM-4 consortium. The scientists also noted that whereas individual cultures took more than 60 hours to completely decolorize the additional dye, the combined metabolic activity of the isolates allowed AR-88 (20 mg/L) to be completely decolored in just 24 hours. They also tested the consortium for its ability to decolorize different concentrations of other commonly used azo dyes, in addition to AR-88, and discovered that it could decolorize 82% of C.I. Reactive Red 120; 99% of C.I. Acid Red 119, 97; 99% of C.I. Acid Blue, 113; 94% of C.I. Acid Red, and 78% of C.I. Acid Red 88 dyes in 24 hours at an initial concentration of 60 mg/L of the mineral salt medium.

Employing thirty-nine strains of ligninolytic micro-organisms (fungi), Novotny et al. (2004) examined the degradability of Cu-phthalocyanine, anthraquinone, and azo dye structures and discovered that 60% of the dyes were susceptible to attack whereas 80–90% of the other dyes were. They reported that Irpexlacteus could decolorize a variety of phthalocyanine, thiazine, anthraquinone, triphenylmethane and azo dyes in stationary liquid culture at a concentration of 200 mg/L. After two weeks, their decolorization levels ranged from 60 to 100 %. Novotny *et al* discovered that sodium azide and n-propyl gallate selectively inhibited manganese-dependent peroxidase (MnP) and laccase, indicating that MnP is involved in the decolorization of anthraquinone- and azo dyes. I. lacteus decolorized 100% of Remazol Brilliant Blue R (150 mg/L) immobilized on pinewood cubes in six days. They also found that *I. lacteus* effectively removed color from textile industry effluent including Acid Black (AB), Drimarene Red (DR), Remazol Green (RG), and Drimarene Blue (DB), with corresponding decolorization rates of 35 %, 80%, 45%, and 100 % in 3-5 days.

In a different study, Haque *et al.,* (2021) experimented on a Novel bacterial biofilm consortium that degrade and detoxify the carcinogenic diazo dye Congo red. They prepared four biofilm consortia (C1=Vitreoscilla sp. ENSG301, Acinetobacterlwofi ENSG302, Klebsiellapneumoniae ENSG303 and Pseudomonas fuorescens ENSG304, C2=Escherichia coli ENSD101, Enterobacterasburiae ENSD102 and E. ludwigii ENSH201, C3=E. asburiae ENSD102, Vitreoscilla sp. ENSG301 and Bacillus thuringiensis ENSW401, and C4=E. coli ENSD101, E. ludwigii ENSH201 and B. thuringiensis ENSW401) and assessed for bioremediation of CR. The authors observed that all the biofilm consortia remarkably decolorized (96.9 to 99.5%) the CR (100 mg/L) in static condition within 72 h incubation at 28 °C. These consortia also synthesized significantly more intracellular azoreductase and laccase enzymes than extracellular of these enzymes. UV–Vis spectral analysis revealed that the major peak at 478 nm wavelength of CR completely disappeared. FTIR analysis showed several major peaks along with azo bonds are completely or partly disappeared, deformed, or widened. Chemical oxygen demand was reduced by 86.4, 85.5, 87.0 and 86.2% by C1, C2, C3, and C4, respectively. Accordingly, biodegraded metabolites of CR by different biofilm consortia did not inhibit the germination of wheat seeds and bacterial growth. Thus, these biofilm consortia can be applied in the bioremediation of wastewater containing CR for safe disposal into the environment. To our knowledge, this is the first report on the degradation and detoxification of aqueous solution containing CR by bacterial biofilm consortia (Haque *et al*., 2021).

In another study, Ameen *et al.*, (2021) experimented with decolourisation of acid blue 29, disperse red 1, and CR by different indigenous fungal strains. They assessed the ability of different indigenous Aspergillus strains (i.e., *A. flavus*, *A. fumigatus*, *A. niger*, and *A. terreus*) to degrade the azo dyes Acid Blue 29 (AB29), Disperse red 1 (DR1) and Congo red (CR). The authors observed that the optimal conditions for dye decolorization by the above-mentioned strains appeared to be as follows: temperature range 30-35° C, pH 7, glucose as the carbon source (10 g/ L), ammonium sulphate as the nitrogen source (1.5 g/L) and 100 mg/L initial dye concentration. The Aspergillus strains decolorized all azo dyes by more than 86%. The HPLC and GC-MS analyses confirmed that aniline (retention time 9.0 min), 3-nitroaniline (retention time 15.92 min), 4-nitroanline (retention time 17.81 min), N, N' diethyl-1,4-phenylendiamine (retention time 18.184 min), and benzidine (retention time 15.07 min) were formed as the intermediate metabolites of dye degradation. All Aspergillus strains decolorized 85% of the dyes in synthetic wastewater (Ameen *et al.,* 2021).

Victor *et al* (2020) also examined Metabolite Identification from the Biodegradation of Congo Red by Pichia sp. Their result of absorbance spectra from UV-V is spectrophotometer showed there were two absorbance peaks of CR, the slightly lower one at 335 nm and the higher one at 485 nm. The observed maximum absorbance wavelength of CR was known to be at 497-498 nm, different from the result observed. Since decolorisation was tested in sodium acetate buffer, the content of the buffer increases the ionic strength of the solution and causes the peak wavelength of Congo red absorbance to shift toward a shorter wavelength. Both peaks at 335 nm and 485 nm existed before and after decolorization by a crude enzyme from Pichia sp., however, there was a decrease in overall absorbance. After one hour, there was a 51.7% decrease in absorbance at 485 nm which is equivalent to a decrease in Congo red concentration from 0.005% to 0.0026%. They separated the biodegradation from the enzyme by ethyl acetate and then Gas Chromatography-Mass Spectroscopy (GC-MS) method was employed to identify the biodegradation product. Chromatogram results of GC-MS showed that Congo red was degraded into various products such as biphenyl, naphthalene, and smaller molecules with 94 m/z and 51 m/z. These results suggest the involvement of azo reductase and laccase-like enzymes which cleaves azo bonds and oxidize the dye molecules to smaller molecules. This study implies the use of Pichia sp. as a bioremediation agent for the removal of azo dyes (Victor *et al*., 2020).

Biological treatment offers both advantages and disadvantages for dye wastewater treatment. One of its key advantages is its environmental friendliness, as it relies on natural microorganisms to break down dyes, generating minimal chemical waste and reducing the carbon footprint. Additionally, it can effectively treat a wide range of dye types. However, it has some limitations, including longer treatment times compared to some chemical methods, sensitivity to fluctuations in wastewater characteristics, and the potential for incomplete dye removal. Biological treatment may also require careful monitoring and control to maintain optimal conditions for microbial activity. Despite these challenges, it represents a sustainable and promising option for dye wastewater treatment in certain applications.

2.3 Chemical methods for treatment

Chemical approaches such as coagulation-flocculation, electrochemical, and advanced oxidation processes are used to treat dye-containing wastewater.

2.3.1 Coagulation-flocculation

Impurities and poisons are generally present in high concentrations in wastewater. It can be treated with coagulants before disposal. Metal salts and/or polymers can be employed in this treatment method as coagulants, whereas flocculants are polymers that make flocs more aggregative to foster easy separation(Ã, 2006). Garvasis*et al* (2020) conducted a study on the efficient removal of Congo red from aqueous solutions using a phytogenic aluminium sulfate nano coagulant. They synthesized Aluminium sulfate nanoparticles (ASNPs) using Hemigraphiscolorata leaf extract with minimal use of corrosive solvents. The coagulation efficiency of ASNPs for Congo red dye solution was explored under various constraints like coagulant dosage, initial concentration, pH, temperature, presence of inorganic ions and settling time. The authors reported that One-hundred and forty (140) mg/L of ASNPs removed 99.5% of Congo red dye (100 mgL/1) from the solution. The variation in pH of the solution in the range 3–9 and the increase in temperature from 30℃ to 70℃ did not affect the efficiency of the nano coagulant. They also observed that the generated sludge settled within 30 min and SVI was found to be 31 mL/g. The nano coagulant can be reused up to five cycles of coagulation (Garvasis *et al*., 2020). Low dosage, consistent efficiency, easy sludge management, reusability along with cost-effectiveness makes phytogenic ASNPs a potential coagulant for the removal of CR.

In another study, Wei *et al.,* (2020) examined the Eco-friendly decolorization of cationic dyes by coagulation using natural coagulant Bentonite and biodegradable flocculant Sodium Alginate. Four basic dyes Rhodamine B (RB), Malachite Green (MG), Methylene Blue (MB), and Basic Violet 14 (BV) were used to cover a range of variations in the experiments. They reported that the removal of the dyes increased with the addition of SA as the flocculant/coagulant aid. Bentonite as a natural coagulant aided by the biodegradable flocculant, SA, is an effective combination for the removal of basic dyes (colour removal). The effect of coagulant dosage on the overall dye removal efficiency/decolorization rate was explored and followed by the investigation of the mechanism of dye removal by the coagulation process. Optimum dye removal efficiencies for RB, MG, MB, and BV by using both Bentonite and Sodium Alginate combined were, 91.5%, 98.2%, 98.5%, and 98.8%, respectively with pH set at 9.0. FTIR was used to characterize the sludge to determine the functional groups (Wei *et al.*, 2020). The resultant outcome in this study indicates that using Bentonite as a natural coagulant, aided by a biodegradable flocculant, Sodium Alginate, provides an effective and environmentally friendly coagulation option for removing colour from basic dyes.

Coagulation-flocculation is a widely used method for treating dye wastewater, offering both advantages and disadvantages. Its advantages include effectiveness in removing a variety of dyes and colloidal particles, ease of operation, and adaptability to different wastewater characteristics. It often doesn't require a high energy input, making it cost-effective. However, it has limitations such as the production of chemical sludge, which necessitates proper disposal, and the potential need for pH adjustment or additional chemicals. Coagulation-flocculation may also be less efficient for treating certain dyes or wastewater with fluctuating compositions. Despite these drawbacks, it remains a practical and commonly employed method for dye wastewater treatment.

2.4. Electrochemical Method

Electrochemical methods have emerged as effective techniques for the degradation of wastewater contaminants. These processes harness the power of electricity to facilitate chemical reactions that break down harmful pollutants. Several types of electrochemical methods are employed in wastewater treatment, including electrocoagulation, electrooxidation, and electro-Fenton processes.

2.4.1 Electro-coagulation

Electro-coagulation is a rapidly growing area of wastewater treatment due to its ability to remove contaminants that are generally more difficult to remove by filtration or chemical treatment systems, such as total petroleum hydrocarbons, suspended solids, emulsified oil, heavy metals, and refractory organics. Donneys*et al.,* (2019) studied the removal of indigo carmine dye by electro-coagulation using magnesium anodes with polarity change. They investigated the effect of the main parameters such as temperature, anodic material, current density, initial dye concentration, and agitation speed on the diminishing of indigo carmine concentration and non-purgeable organic carbon. Image analysis was used in conjunction with zeta potential measurements to understand the mechanism of flocs formation. The authors reported the best results as 80% and 96% removal for non-purgeable organic carbon and dye content respectively at room temperature, by using a turbulent regime, initial dye concentration of 100 mg $L^{-1,}$ and 50 A m^{-2} as current density with AZ31 alloy as electrodes. They also observed that high-purity magnesium reached 75% in non-purgeable organic carbon removal and 86% in dye removal at the conditions. An additional improvement of 43% in the diminishing of the organic carbon content was observed when polarity change was used, a phenomenon that was attributed to the distribution of the oxidation reaction between electrodes, avoiding the saturation of the surface with oxide and hydroxide layers (Donneys-Victoria et al., 2019).

In another study, Hashim *et al.*, (2019) investigated the effect of initial pH value on the removal of reactive black dye from water by electro-coagulation. Their results showed that the removal efficiency increased gradually as the initial pH increased from 4 to 6 to reach its maximum level (96%) at the neutral range of pH, then it decreased to 74% as the initial pH increased to 8. This change in the removal efficiency with the initial pH could be attributed to the predominant species of aluminum coagulants, where in alkaline and acidic conditions; the prevailing species have low adsorption capacity for pollutants. While, in the neutral range of pH, the predominant species have a high adsorption capacity for pollutants (Hashim *et al*., 2019).

In a similar study, Moneer *et al.,* (2022) investigated the effect of a novel electrode on the removal of Reactive Yellow 17 dye by electro-coagulation technique. The anode is a PVC tube with an iron net wrapped around the tube with a surface area of 95.88 cm^2, while the cathode is a stainless-steel tube with a surface area of 118.2 cm^2 for each cathode. Under optimum conditions, they reported a removal efficiency of 99.8%. Their thermodynamic parameters showed the spontaneity of the mechanism of removal with energy consumption and cost of operation reported as 21.7 kWh/kg dye and 1.115 US$/m^3, respectively (Moneer *et al*., 2022).

In a study conducted by Phalakornkule *et al*., (2008), an investigation was presented concerning electrochemical variables within the operation of a continuous upflow electrocoagulation process for the treatment of textile wastewater. As part of their experiments, they utilized Reactive Blue 140, a dye based on porphyrin, as a representative dye. Through a batch mode approach, the study identified optimal values for design and operational parameters. These included the use of an iron anode, maintaining an 8 mm distance between electrodes, ensuring a current density of at least 30 A/m^2, and allowing for a minimum contact time of 5 minutes. These optimized parameters were subsequently applied in the design of a continuous upflow electrocoagulation reactor. To assess the flow behavior within the upflow reactor, the researchers employed a computational fluid dynamics (CFD) program that employed the finite volume method for simulating flow patterns. Under these ideal parameter values, it was observed that water passing the electrode plates exhibited a uniform distribution. Consequently, the reactor demonstrated satisfactory performance, achieving a 90% color removal rate with an associated energy consumption of approximately 1.4 kWh/m^3(Phalakornkule *et al*., 2008)$^.$

In another study conducted by Phalarkornkule *et al.,* (2010), they introduced a method for recovering hydrogen from an electrocoagulation process employed in the treatment of dye-containing wastewater. The electrocoagulation system utilized in their research comprised a continuous-mode electro coagulator connected to a gas separation tank and two sedimenters. Their findings demonstrated the substantial harvest of hydrogen using the gas separation tank, designed in alignment with a traditional upflow anaerobic sludge bed configuration. The actual hydrogen yields observed in experiments closely matched theoretical calculations. For the electro coagulation treatment of Reactive Blue 140 and Direct Red 23, the electrical energy demand was 1.42 and 0.69 kWh m^{-3}, respectively. Conversely, the energy yield from the harvested hydrogen amounted to 0.2 kWh m^{-3}. The electro coagulation system effectively treated water, achieving a high level of satisfaction, with color removal at 99%, COD (Chemical Oxygen Demand) removal at 93%, and TS (Total Suspended Solids) removal at 89% (Phalakornkule *et al*., 2010).

Electro coagulation is an efficient method for removing dyes from wastewater, offering advantages like versatility and minimal chemical use. However, it has drawbacks, including energy consumption, electrode fouling, and potential pH adjustment needs. Initial setup costs can be high, and its effectiveness varies with wastewater characteristics. Proper disposal of generated sludge remains a concern. Careful consideration is necessary to determine if electro coagulation is the right choice for dye treatment in a specific context.

2.4.2 Electro-Fenton

The Electro-Fenton method is an electrochemical advanced oxidation process based on the electro catalytic production of hydroxyl radicals (•OH) in situ. Unlike the chemical Fenton process, which occurs with additional reagents, electrochemistry generates (H_2O_2) or regenerates (Fe^{2+} as a catalyst) the reagents required to make •OH. Keleyin *et al* (2021) experimented with the treatment of textile industry wastewater by electro-Fenton process using graphite electrodes in batch and continuous modes. According to the authors, the use of the electro-Fenton process as a post-treatment technology for biologically treated textile wastewater led to a significant reduction in the colour, COD, and TOC content of textile wastewater. In a continuous system, 89 % colour, 93 % COD, and 58 % TOC removal efficiencies were attained at pH 3, current intensity 1.65 A, Fe^{2+} of 2 mM, and flow rate 25 mL.min^{-1}. They also reported corresponding average energy consumption, electrical energy efficiency, and current efficiency to be 16 kWhm^{-3}, 17 kWhm^{-3} order− 1, and 0.300 (Kuleyin *et al.*, 2021). The results showed that the EF process with graphite anode and cathode is a promising technology improving the wastewater quality for potential reuse

In other to understand the degradation and mineralization of Malachite Green in an electro-Fenton process. Yazdani (2018) studied the influence of several important parameters including solution pH (2–11), current density (0–20 mA/cm^2), H_2O_2 concentration (0–200 mg/L), and MG concentrations (200, 600, 1000, 1500, 2000, 3000 mg/L) at different reaction time (2.5–30 min). The intermediates produced during the degradation were determined by GC–MS. The optimum pH, current density, and H_2O_2 concentration were found to be approximately 3, 10 mA/cm^{2,} and 50 mg/L, respectively. He concluded that acidic pH was required to increase the efficiency of the electro-Fenton process. At optimum conditions and a reaction time of 15 min, Malachite green was completely removed without any significant variation in the corresponding maximum wavelengths or new absorption bands. Due to the formation of intermediates, almost all the organic compounds were completely mineralized (95.3%) to CO_2 and water at a reaction time of 30 min. Results indicated the effect of hydroxyl radical (·OH) on MG degradation is greater than that of superoxide radical scavenger ($O^{\cdot -\ 2}$). The results showed that the degradation process of MG followed the pseudo-first-order kinetic model and the treatment time required in the electro-Fenton process was 4.6 times lower than in the electro-coagulation process (Yazdani, 2018). Furthermore, the results showed that EFP was an extremely efficient process for the degradation and mineralization of a high concentration of MG (1000 mg/L) at a short reaction time.

In a different study, Fayazi and Ghanei (2020) conducted an experiment on the electrochemical mineralization of methylene blue dye using electro-Fenton oxidation catalyzed by a novel sepiolite/pyrite nanocomposite. The morphology and structure properties of the prepared catalyst were thoroughly studied by field emission scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, energy-dispersive X-ray spectroscopy, and elemental mapping analysis. The electro-Fenton studies were carried out in an undivided electrochemical cell equipped with a platinum (Pt) sheet as an anode and a graphite plate as a cathode. The researchers examined the effects of initial pH, applied current intensity, catalyst dose, and initial dye concentration on the mineralization of Methylene blue, and their values were determined as 3.0, 1.0 g L^{-1}, 50 mg $L^{-1,}$ and 150 mA, respectively. They reported almost total mineralization for a 50 mg L^{-1} Methylene blue solution in 75 min reaction time. (Fayazi & Ghanei-Motlagh, 2020).

The electro-Fenton method for dye degradation offers several advantages. It is highly effective in breaking down various dye types, thanks to its high oxidation potential. Additionally, it operates under mild conditions, reducing energy consumption. This method doesn't rely on extensive chemical additions, which can lower operating costs and make it more environmentally friendly. It generates minimal sludge and can be adapted for the treatment of various wastewater contaminants.

However, there are some disadvantages to consider. The electro-Fenton process requires a constant supply of electricity, resulting in energy costs. Catalysts, such as iron ions, may be necessary, adding complexity and expense to the treatment. Proper pH control is essential for optimal performance. Scaling up the process can be challenging, and its effectiveness depends on the specific characteristics of the dye and wastewater being treated.

2.4.3 Electrochemical Oxidation

The introduction of an electric current or a potential difference between two electrodes (anode and cathode) generates hydroxyl radicals or other oxidizing species, depending on the anode material employed and the kind of electrolyte of support utilized. In this way, electrooxidation can be either direct or indirect; in the first case, the pollutant is degraded at the anode via a charge transfer reaction, whereas in the second case, the pollutant is eliminated via the action of species formed during the oxidation of the water or electrolytes present in the solution. Xia *et al* (2020) studied the electrochemical oxidation of Acid Orange 7 azo dye using a PbO_2 electrode. They reported the removals of AO7, chemical oxygen demand (COD), and total organic carbon (TOC) as 87.15%, 49.88%, and 44.94% after 60 min of electrolysis at the optimal conditions (Na_2SO_4 concentration 0.1 M, initial pH 5, initial AO 7 concentration 100 mg L^{-1} 14 and applied current density 20 mA cm $^{-2}$), respectively. And the corresponding degradation rate constant was 0.035 min^{-1}(First-order kinetics). The intermediates formed during the electrochemical process were identified, and a possible degradation pathway was proposed, which was initiated by the oxidation of the azo bond (-N=N-), hydroxylation, and substitution reaction of $-NH_2$ and $-SO_3H$ under the attack of •OH and ended with the formation of mineralization products such as NH_4^+, NO_3^-, SO_4^{2-} , CO_2 and H_2O. The toxicity of treated AO 7 solution towards Vibrio fischeri increased slightly at first and then rapidly reduced to non-toxicity with prolonging time (Xia *et al*., 2020).

In a similar study, Tang *et al* (2020) conducted an experiment on the electrochemical oxidative degradation of X-6G dye by boron-doped diamond anodes. The oxidative process was analyzed by color removal rate, and the degree of mineralization was evaluated by TOC. The optimal experimental parameters of their study were determined as 100 mA cm^2, 0.05 M Na_2SO_4 electrolyte, pH 3.03, 60℃, and an initial X-6G concentration of 100 mg/ L. As a result, color completely disappeared after 0.75 h of electrolysis, and TOC was removed by 72.8% after 2 h of electrolysis (Tang *et al*., 2020). The EO of a BDD electrode as an anode can be a potent treatment method for X-6G synthetic wastewater.

Studying the electrochemical decolorization of dispersed blue-1 dye in an aqueous solution. Oguzie *et al.*, (2021) employed the use of graphite electrodes in decolorizing Disperse Blue—1 dye in an aqueous solution, with NaCl as a supporting electrolyte. They reported that the decolorization efficiency increased steadily with electrolysis time, current density, and electrolyte concentration, but decreased with increasing dye concentration, while showing a nonlinear trend with pH, with maximum efficiency of 90% obtained at pH 7. Increasing the system temperature from 28 to 50℃ caused decolorization efficiency to increase, especially at low dye concentrations, reaching 96% at 25 mg/L. Decolorization efficiency was subdued at high dye concentrations, even with high current densities. This effect was however overcome by increasing the supporting electrolyte concentration. Their results from DFT computations showed that the amine functions in the p-phenylenediamine moieties are the reactive sites for oxidative decolorization of dispersed blue 1 dye (Oguzie *et al.*, 2021).

In a similar study, Yang *et al.*, (2016) investigated the effects of supporting electrolytes, degradation temperature, current density, and pH value on the decolourisation efficiency of Methyl orange. Results revealed that at initial pH=6.0, 45^{o}C temperature, 50 mA·cm^{-2} current density, 0.08 mol·L^{-1} electrolyte (Na_2SO_4) concentration, and 30 min electrolysis time, the colour removal efficiency and COD removal reached 99.6% and 72.6%, respectively. They reported that the reaction mechanism of electrocatalytic Methyl orange degradation by Nb/PbO_2 electrode mainly involved the OH radical attack of parent molecules, and the degradation followed pseudo-first-order kinetics (H. Yang *et al*., 2016)

Each treatment method's unique characteristics might be advantageous in one manner but restricting in another. Treatment procedures that have high installation and operating costs, longer processing times, poor output, and emit harmful byproducts after treatment are frequently less suitable for industrial applications (Wong *et al.*, 2019). As a result, it is critical to developing an alternate treatment method capable of entirely degrading or removing pollutants (Yahya *et al.*, 2018).

Electrochemical methods, particularly electro-oxidation, offer several advantages for the degradation of dyes in wastewater treatment. They are highly efficient, effectively removing a wide range of dye types without the need for additional chemicals, reducing operational costs and environmental impact. This method allows for selective targeting of contaminants, generates minimal sludge, and provides operators with control over process parameters for optimization. It's versatile, applicable to various dyes, and environmentally friendly, minimizing hazardous byproducts. Additionally, electro-oxidation is relatively energy-efficient compared to some other treatment processes, making it a promising and sustainable option for dye removal in wastewater.

The efficiency and effectiveness of electrochemical degradation are influenced by a multitude of factors, each playing a pivotal role in determining the extent of pollutant removal. Among these factors, pH, significantly affects the electrochemical degradation process as it dictates the nature of chemical reactions occurring at the electrode surface. Varying pH levels can influence the generation of reactive species and subsequent degradation pathways. Current density, representing the flow of electrical current per unit area of electrode, affects the rate of pollutant degradation. The choice of electrode material is critical, as different materials possess varying catalytic properties that impact the generation of reactive species and overall process efficiency. The composition of the electrolyte solution also plays a role in modulating reaction kinetics and the availability of reactants. Current density, electrode material, and electrolyte composition are of paramount importance(Bensalah *et al.*, 2009).

In the context of methyl orange, the electrochemical degradation process holds the potential to address the compound's complex structure and resistance to conventional treatment methods. The oxidative power of generated hydroxyl radicals can break down the intricate azo bond and sulfonic acid groups present in methyl orange, leading to its eventual mineralization into simpler and less toxic byproducts.

The significance of this electrochemical approach extends beyond the mere degradation of methyl orange; it provides an innovative strategy for addressing a broader class of recalcitrant organic pollutants. This is particularly relevant in the current era where the emergence of diverse synthetic compounds necessitates advanced and versatile treatment methods.

As we progress through the upcoming chapters, we will delve deeper into the intricacies of electrochemical degradation mechanisms, dissect the interplay of influencing factors, and translate this knowledge into the effective treatment of methyl orange-containing wastewater. This study seeks to unravel the potential of electrochemical processes in revolutionizing the landscape of wastewater treatment, offering an avenue towards sustainable and efficient degradation of challenging organic pollutants.

2.4.3.1 Anode materials for Electrochemical Oxidation of organic pollutants

It is important to take into account the chemical makeup of potential anodic materials, suitable operating conditions, and anodic oxidation methods to design improved and more cost-efficient anodic oxidation technology. electrocatalysts for degrading halogenated organic contaminants (Martin *et al*., 2016; Chen *et al*., 2019;) or electrochemical oxidation methods for wastewater treatment (Moradi *et al*., 2020). Goren *et al* (2022) investigated the electrochemical removal of methylene blue (MB) from water using commercially available and low-cost flexible graphite. They employed BoxBehnken experimental design (BBD) to optimize the system's performance with the minimum number of tests possible, as well as to examine the independent variables' impact on removal efficiency, energy consumption, operating cost, and effluent Methyl blue concentration. The electrical potential and electrolyte dosage both improved the Methyl blue removal efficiency since increased electrical potential facilitated the production of oxidizing agents and an increase in electrolyte dosage translated into an increase in electrical current transfer. As expected, Methyl blue removal efficiency increased with longer operational periods. The combined effects of operating time−electrical potential and electrical potential−electrolyte concentration improved the Methyl blue removal efficiency. The maximum removal efficiency (99.9%) and lowest operating cost (0.012 $/m3) were obtained for initial pH 4, initial MB concentration 26.5 mg/L, electrolyte concentration 0.6 g/L, electrical potential 3 V, and operating time 30 min. The reaction kinetics was maximum for pH 5, and as the pH increased the reaction rates decreased (Goren *et al*., 2022). The consequent techno-economic assessment showed that electrochemical removal of MB using low-cost and versatile flexible graphite had a competitive advantage**.**

In a different study, Hamous *et al.*, (2020) investigated the electrochemical degradation of an azo dye, Orange G performed using a platinum electrode. They studied the influence of the dye concentration (50-150 mg/L), the pH of the medium, and the density of the electric current on the rate of discoloration, the rate of mineralization, the efficiency of the electric current, and the energy consumption. The UV-visible spectra of OG plotted against the degradation time showed a decrease in the intensity of the characteristic dye peaks. In an environment rich in chlorides, all peaks disappear after 15 min of degradation. However, the peaks at wavelengths of 200 and 290 nm appeared after one hour of treatment. In K_2SO_4, the eliminated percentages are respectively 46, 54, and 61% for wavelengths of 245, 330, and 480 nm. This suggests that the degradation mechanisms in K_2SO_4 and KCl environments are not the same. In the middle rich in chlorides, the eliminated percentage of OG did not seem to be affected by the increase in the concentration. These results confirm the hypothesis that the electrochemical oxidation process is very favorable for concentrated pollutants discharge (Hamous *et al.*, 2020).

In another study, Belal *et al* (2021) experimented on advanced electrochemical degradation of basic yellow 28 textile dye using IrO_2/Ti meshed electrodes in different supporting electrolytes. Their results showed that the optimum conditions were a current density of 0.03A cm^{-2} initial dye concentration of 2×10^{-5} M, pH of 2.5 or 6.5 for Na_2SO_4 or NaCl, and a supporting electrolyte concentration of 0.08 or 0.03 M for Na_2SO_4 or NaCl, respectively. The degradation efficiency was followed using Ultraviolet-visible (UV–Vis) spectrophotometry, cyclic voltammetry, and chemical oxygen demand (COD). Cyclic voltammetry was carried out in the potential window from +1.0 V to −1.0 V. After 15 min, the color removal of the BY28 dye was 92.9% and 93.3% and the COD removal was 26.8% and 46.2% in the presence of Na_2SO_4 and NaCl, respectively. Besides, the corresponding current efficiency and energy consumption was estimated to validate the proposed electrochemical method. The results revealed that NaCl was more powerful than Na_2SO_4 as a supporting electrolyte (Belal *et al.,* 2021)

Tang *et al.,* (2020) also studied the electrochemical oxidative degradation of X-6G dye by boron-doped diamond anodes. To balance the degradative effects and power consumption in the electrolysis process, the effects of a series of operating parameters, including current density, supporting electrolyte, initial pH, reaction temperature and initial dye concentration, were systematically studied. The oxidative process was analyzed by color removal rate, and the degree of mineralization was evaluated by TOC. The optimal experimental parameters were finally determined: 100 mA cm^2, 0.05 M Na_2SO_4 electrolyte, pH 3.03, 60℃, and an initial X-6G concentration of 100 mg/L. As a result, color completely disappeared after 0.75 h of electrolysis, and TOC was removed by 72.8% after 2 h of electrolysis. (Tang *et al*., 2020). In conclusion, the EO of a BDD electrode as an anode can be a potent treatment method for X-6G synthetic wastewater.

In a similar study, Samarghandi *et al.,* (2020) investigated the electrochemical degradation of methylene blue dye using graphite-doped PbO_2 anode. An anodic oxidation process with a graphite anode coated with lead dioxide (G/b-PbO_2) was optimized for the degradation of methylene blue (MB) and the treatment of real textile wastewater. The G/b-PbO_2 anode was prepared by the electrochemical precipitation method. The scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) analyses confirmed the successful coating of graphite substrate with the b-PbO_2 film. The effect of four independent variables including pH, reaction time, current density, and electrolyte concentration of Na_2SO_4 on the performance of the electrochemical oxidation system was modeled by using a complete central composite design and was then optimized by genetic algorithm method. The accuracy of the proposed quadratic model by CCD was confirmed with a p-value of 0.9. The optimum conditions for solution pH, reaction time, current density, and Na_2SO_4 electrolyte concentration were obtained to be 5.75, 50 min, 10 mA/cm^2, and 78.8 mg/L, respectively. In these conditions, they reported that the experimental removal efficiencies of MB using G/b-PbO_2 and graphite anodes were 96.2% and 68.3%, respectively. The electrochemical removal of MB using both G/ b-PbO_2 and graphite anodes well followed the pseudo-first-order reaction (R2 > 0.9). Cyclohexane, cyclohexa-2,5-dien-1-ylium, and N-(sec-butyl) aniline were the most abundant intermediates identified by LC-MS analysis. However, the complete mineralization of MB was achieved in 60 min. The optimized anodic oxidation process successfully improved the biodegradability of real textile wastewater (BOD=COD > 0:4) (Samarghandi *et al.*, 2020)

The graphite is attacked by the oxygen generated at the anode. Part of it reacts to make carbon dioxide, and the rest disintegrates into a fine powder that turns the water black. It takes some hours for the degradation to become noticeable, so it will work for a while, but the graphite anode is a consumable item. Due to their good electrocatalytic activity and great chemical stability, active anodes such as Pt, RuO_2, IrO_2, and graphite have been used as anodes lately(Kaur & Kaur, 2016). However, due to their low capacity for oxygen evolution, they only permit incomplete oxidation of organic contaminants (OEP). Anodes' existing effectiveness for the breakdown of organic contaminants is significantly influenced by their limited oxygen evolution potential (Li *et al.*, 2005).

To completely oxidize organic contaminants to CO_2, dimensionally stable anodes like PbO_2, SnO_2, and boron-doped diamond (BDD) are appropriate anode materials for wastewater treatment(Radjenovic& Sedlak, 2015). BDD anodes have also been the subject of extensive research in recent years; because of their characteristics, such as the high O_2overpotential, they are better suited than metal oxide anodes for the direct oxidation of contaminants. Although several substrates like Si, Nb, and Ti have been used to increase BDD anode efficiency, they are expensive(Nidheesh *et al.*, 2018). PbO_2 provides a more affordable alternative to the pricey BDD anode for the electrochemical oxidation of organic contaminants (Hu *et al.*, 2021).

According to Chaplin (2019), the most effective and promising methods for eliminating stubborn organic pollutants from water and different wastes are electrochemical ones (Chaplin, 2019). Presently, this technique offers prospective solutions for reducing pollution produced by industrial effluents because it was created for alternate use in wastewater treatment decades ago (Brillas & Martínez-Huitle, 2015).

CHAPTER THREE

MATERIALS AND METHOD

3.0 INTRODUCTION

This chapter covers materials and experimental approaches for this research work. It includes materials preparation (section 3.1), experimental method (section 3.2), and analytical procedure (section 3.3).

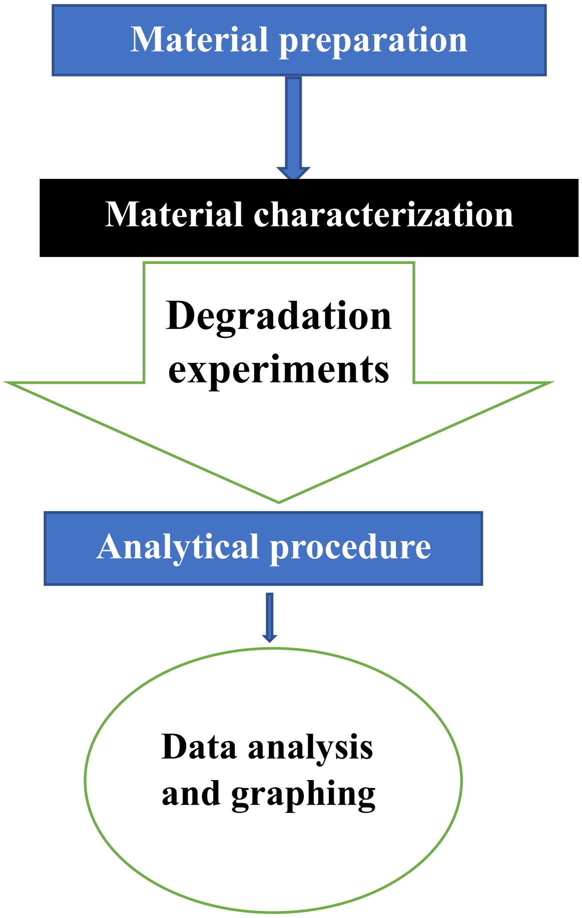

Figure 3.1: Experimental Flow Chart

3.1 Material Preparation

3.1.1 Chemicals and reagents

Methyl orange obtained from Kentin ltd were used to prepare the wastewater effluent. Sodium chloride and potassium chloride (Chemiscience ltd) were used as supporting electrolyte. Hydrochloric acid and sodium hydroxide also obtained from Chemiscience ltd were used for pH adjustment. All the other chemicals were analytical reagent grade and used without further purification**.**

3.1.2 Preparation of Methyl orange Dye

The stock solution of 1000ppm of Methyl Orange solution was prepared by dissolving 1g of methyl orange powder in 1L of distilled water. The solution was stirred continuously using a magnetic stirrer to ensure homogeneity.

3.2 Experimental Procedure

All electrochemical degradation experiments were performed in a 500 mL-batch reactor. Copper anodes and a graphite cathode were placed inside the sample solution parallel to each other at a distance of 2 cm from each other. About 10 ml of KCl / NaCl was used as the supporting electrolyte at different concentrations. H_2SO_4 and NaOH were used to adjust the pH of the sample solution (pH meter; SensION, HACH). The reactor contents were mixed by a magnetic stirrer at a constant speed of 250 rpm. After adjusting the pH of the solutions containing Methyl orange and supporting electrolytes, experiments were conducted galvanostatically with a DC power supply (DAZHENG PS-305D, China). Finally, after the end of the electrochemical degradation reaction, an appropriate aliquot of the reaction solution was taken for analysis.

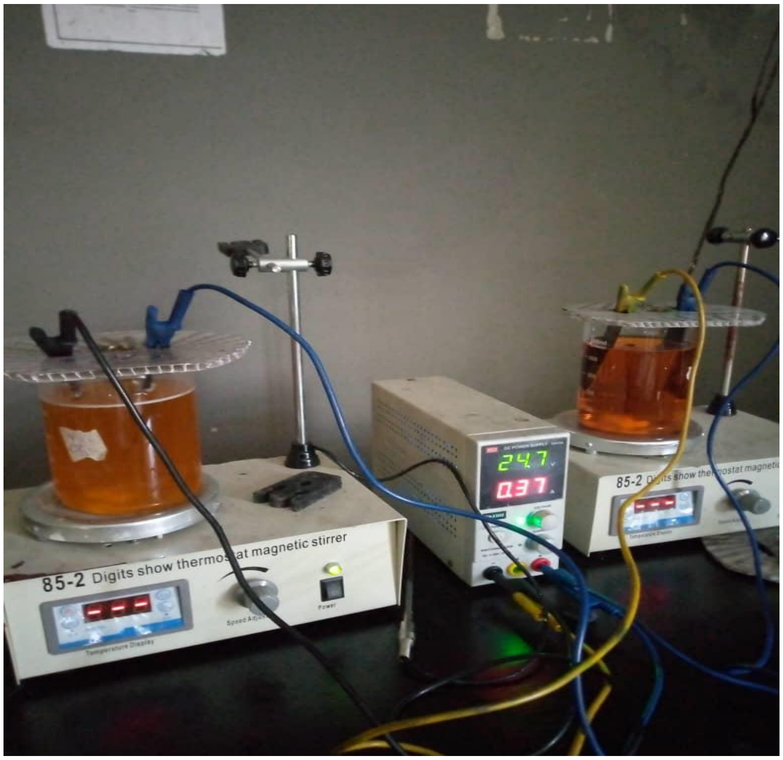

Figure 3.2: Electrochemical Degradation set-up

Table 3.1: Experimental Parameters

Variable	Values
Ph	3-11
Current density	0.27 – 1.33 mA/mm^2
Temperature	30-60^{0}C
Type of Supporting Electrolyte	KCl, NaCl
The concentration of Supporting Electrolyte	0.005-1 M

3.2.1 Effect of pH on Electrochemical Degradation

By altering the solution's starting pH (3, 5, and 9) the impact of pH on the rate of degradation was investigated. Depending on the situation, either 0.1 M HCl or 0.1 M NaOH was used to modify the pH. With constant stirring and dropwise addition of the acid/base, the pH was measured.

3.2.2 Effect of Temperature on Electrochemical Degradation

The effect of temperature on the degradation rate was studied by varying the initial temperature of the solution using a thermostat. The temperature was also monitored manually by a mercury bulb thermometer.

3.2.3 Effect of Supporting Electrolyte on Electrochemical Degradation

The effect of supporting electrolytes on degradation rate was studied by varying the type of electrolyte NaCl and the varying concentration 0.005, 0.1, 0.5, and 1 M. The same procedure is repeated for KCl.

3.2.5 Effect of Current Density on Electrochemical Degradation

The effect of current density on degradation rate was studied by varying the amount of current passing through the electrode for 1, 2, 3, 4, and 5A.

3.3 Analytical Procedure

UV-3600i (Shimadzu) was used to test the ultraviolet spectrum of Methyl orange solution under different degradation times. The samples were taken every 10 min, and then, the samples were scanned by ultraviolet with a wavelength range of 200–800 nm. The Methyl orange removal efficiency (DE) followed the equation:

$$\boldsymbol{DE = \frac{A_{0-}\,A_t}{A_0} \times 100(1)}$$

where A_0 is the absorbance of Methyl orange at the initial and A_t is the absorbance of Methyl orange at the given time t.

$$\boldsymbol{EC\left(\frac{kWh}{dm3}\right) = \frac{I(A)\times V(V)\times t(hr)}{Q(dm3)}} \qquad (2)$$

Where *I* is the current in ampere *(A)*, *V* is the cell voltage in volts *(V)*, *t* is the time in hours *(hr)*, and *Q* is the quantity/volume (dm^3) of the dye-contaminated wastewaters present in the electrolytic cell. The applied voltage was constant at 25 V over a period of 1.17 hr., and the volume of the dye solution in the electrolytic cell is 0.5 dm^3

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 INTRODUCTION

This study aims to investigate the electrochemical degradation of methyl orange-contaminated water. An electrochemical cell consisting of a graphite anode and a copper cathode connected to a DC supply was used in this study. Figures 4.1–4.5 show the various degradation profiles.

4.4 Effect of Changing Current Density

In electrochemical degradation, the current density is responsible for initiating electron flow into the electrochemical cell. The effect of current density on the degradation of Methyl orange dye-contaminated wastewater was examined in this study. The initial concentration of Methyl orange was 30 mg/L with 10 ml of conducting electrolyte – 1 M NaCl.

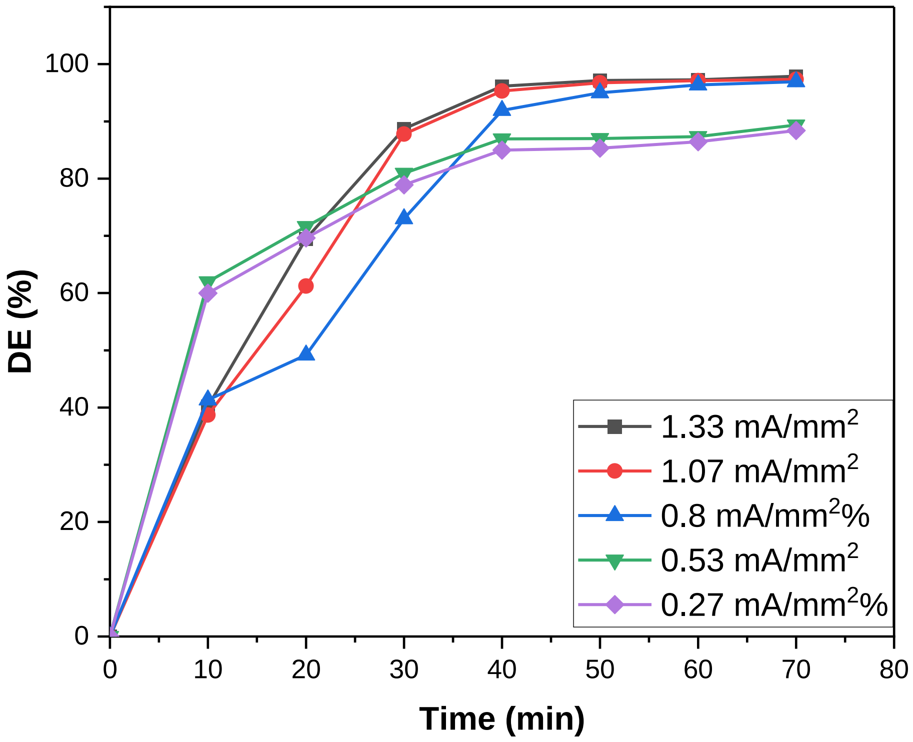

Figure 4.1: Effect of current density on decolorization efficiency of Methyl orange *(Dye concentration = 30mg/L, Temperature (T) = 28^{o}C, Voltage = 25V, Electrolyte = 1 M NaCl)*

In fig 4.1 there is an observable trend of increase in degradation efficiency as current density and time increase. Current densities 0.27 mA/mm^2 and 0.53 mA/mm^2 achieved a degradation efficiency in the first 10 mins before slowing down and stabilizing around 87%. Current density 0.8 mA/mm^2 showed an irregular pattern of progression while 1.33 mA/mm^2 achieved the highest form of degradation (97.88%) and was closely followed by 1.07 mA/mm^2 (97.34%).

It has been observed from the experimental outcome that as current densities increase, there is a resultant increase in the percentage decolorization of Methyl orange dye-contaminated wastewater. Increasing current density reduces the charge loading for dye degradation, due to the increased production of chlorine/hypochlorite at higher current densities(Rajkumar *et al.*, 2007) Higher current densities aided the electro-generation of more of the oxidizing agents like the hydroxyl radicals – OH, H_2O_2, and OCl^-, which oxidizes and attacks the dye compound resulting in degradation of the dyes into CO_2 and H_2O (Gui *et al*., 2019).

4.2 Effect of Supporting Electrolyte Concentration

Electrolytes are electrically conductive chemicals that can aid in the indirect oxidation of dye compounds in an electrolytic cell. The influence of sodium chloride (NaCl) and potassium chloride (KCl) concentration on the decolorization rate of wastewater was investigated in this experiment. Separately, 10 ml of NaCl and KCl supporting electrolytes with concentrations of 1 M, 0.5 M, 0.1 M, and 0.05 M were added to 500 ml batches of Methyl orange with a concentration of 30 ppm.

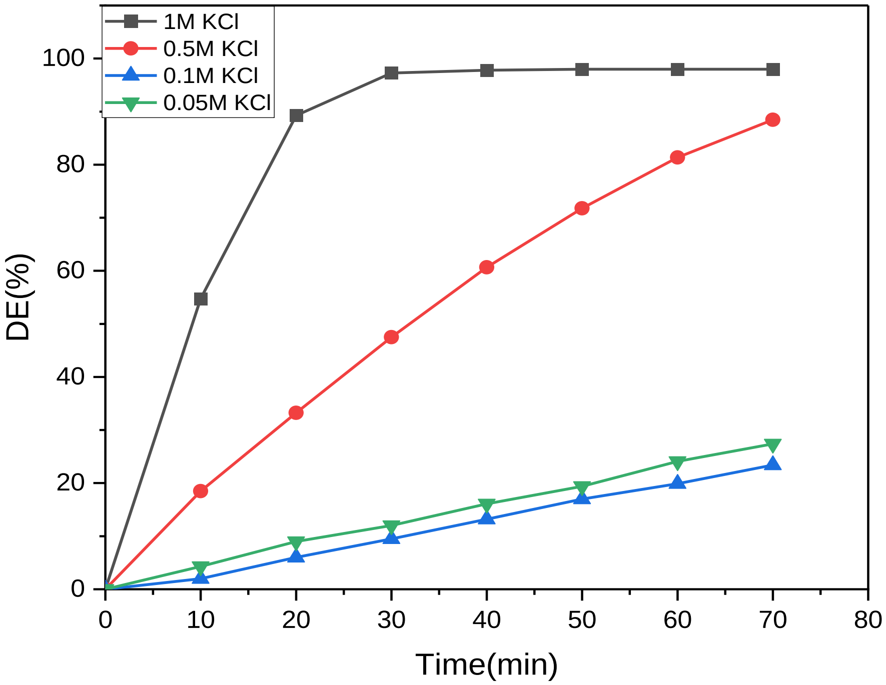

Figure 4.2: Effect of supporting electrolyte on decolorization efficiency of Methyl orange using KCl

(Dye concentration = 30mg/L, Temperature (T) = 30°C, Voltage = 25 V, Electrolyte = 1 M KCl, Current density = 1.33mA/mm^2)

It can be seen from fig 4.2 that 0.1-0.5 M showed linear progression with time while 1M possessed a non-linear relationship with time. 1M KCl achieved the highest degradation efficiency of 98% at the quickest time of 30 min while 0.05 M recorded the lowest degradation efficiency.

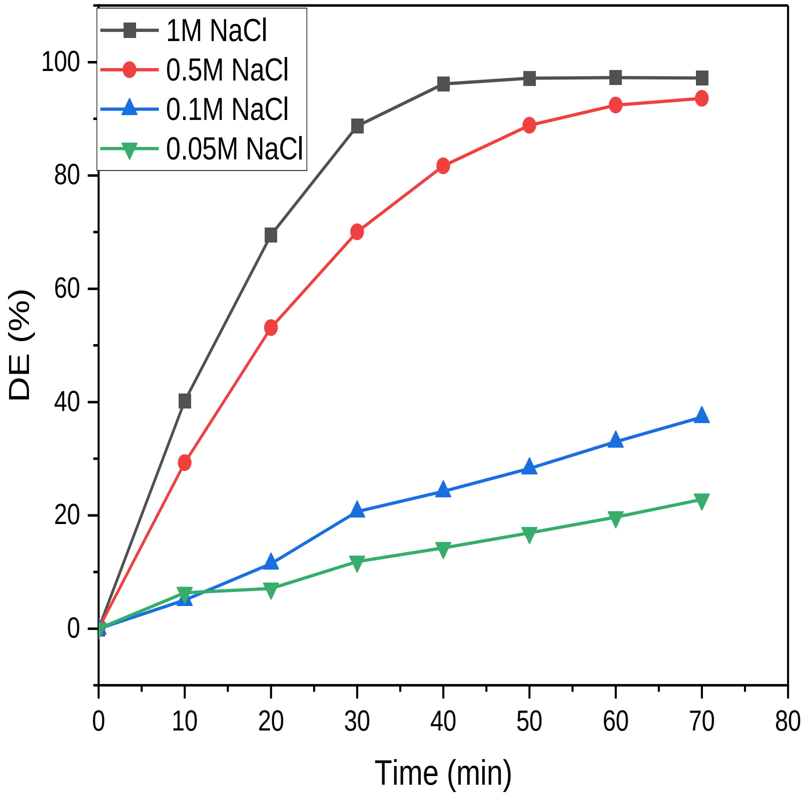

Figure 4.3: Effect of supporting electrolyte on decolorization efficiency of Methyl orange using NaCl

(Dye concentration = 30 ppm, Temperature (T) = 30°C, Voltage = 25 V, Electrolyte = 1 M NaCl, Current density = 1.33mA/mm^2)

The plot in figure 4.3 can be divided into two sections. The first section consists of a straight-line graph of 0.1 M and 0.05 M NaCl while the second section consists of a curved line graph of 1M and 0.5 M NaCl. 1M achieved the highest degradation efficiency of 97.2% while 0.05 M achieved the lowest degradation efficiency of 22.8%.

Methyl Orange decolonization happened when the concentration of the supporting electrolytes changed. For both NaCl and KCl as supporting electrolytes, the rate of decolonization increased with concentration. This phenomenon is caused by the concentration and mobility of primary oxidizing species (Oguzie *et al.*, 2021). When Cl- acquired from the electrolyte is changed according to the reaction mechanism, hypochlorite (OCl) is created as oxidizing specie.

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Anodic reaction: $2Cl^- \longrightarrow Cl_2 + 2e^-$ (i)

Cathodic reaction: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$(ii)

Bulk solution reaction: $Cl_2 + H_2O \longrightarrow HOCl + HCl$ (iii)

$HOCl \longrightarrow H^+ + OCl$ (iv)

While the supporting electrolytes Na^+ and K^+ ion functions as electrical conductors in the wastewater. OCl ion acts as an oxidant, affecting the active sites of dye complexes such as the chromophore group and causing dye degradation. A similar outcome has been observed by Yang *et al.*, (2016).

4.1 Effect of pH on Methyl orange Degradation

This session looked at the influence of pH on the breakdown of Methyl orange. To test a suitable pH and the effect of different pH environments (acidic, neutral, and basic) on the oxidative degradation of dye-contaminated wastewater, the solution pH was varied to 3, 5, 7, 9, and 11 by introducing 1 M of aqueous NaOH or H_2SO_4. The analytical result obtained for Methyl orange for all the pH range at 70 minutes of electrolysis is represented in Fig 4.4

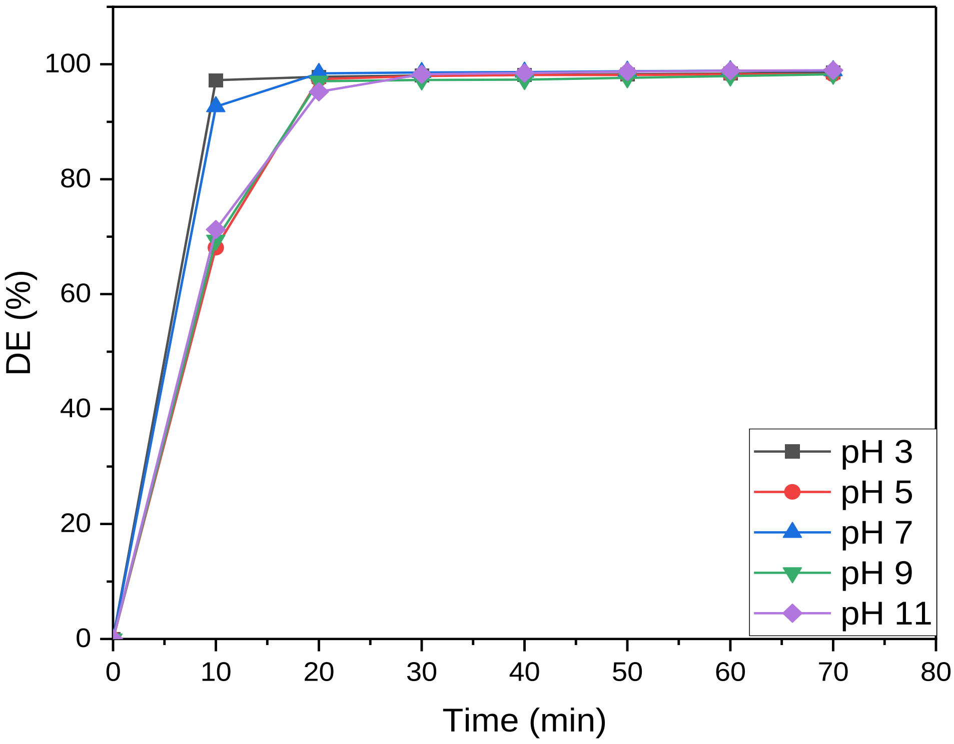

Figure 4.4.: Effect of initial pH decolorization efficiency of Methyl orange

(Current density = 1.33mA /mm^2, Temperature (T) = 30^{o}C, Voltage = 25 V, Electrolyte = 1 M KCl)

Figure 4.4 shows the impact of several pH ranges on the electrochemical degradation of Methyl orange. The plot showed a rapid increase in degradation efficiency for all the pH values before steadying out their highest points. It can be seen that pH 3 achieved a very high decolorization efficiency in 10 min when compared to other values.

pH impacts various aspects, including the chemical states of solution species and solvent molecules, electrostatic interactions at the electrode/solution interphase, the kind of active oxidizing species generated during the reaction, and so on (Oguzie *et al.*, 2021).From the results we can infer that the change in pH had little or no effect on the degradation efficiency of Methyl orange. This is observation is supported by the work done by (Harsini *et al.*, 2016) on the electrochemical degradation of malachite green using nanoporous carbon paste. It is therefore suggestive that both pH range supports high degradation efficiency.

4.3 **Effect of Temperature on Degradation of Methyl orange**

Experiments were undertaken at 30, 45, and 60°C using 30 mg/L of the dye-contaminated water to determine the optimal temperature for the degradation of Methyl orange solutions. The resultant effect of temperature on electrochemical degradation is shown in Fig. 4.5.

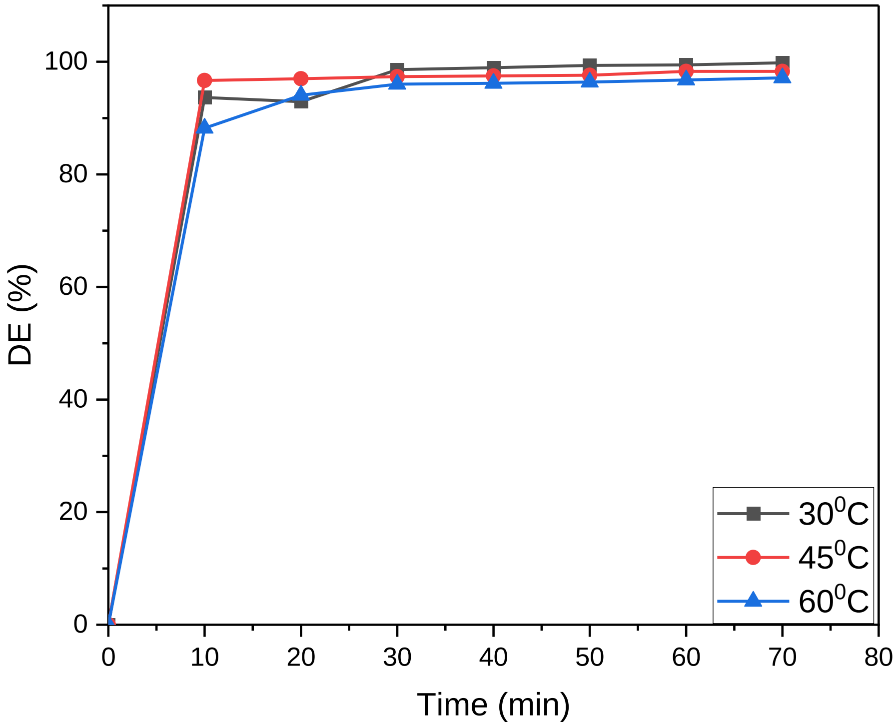

Figure 4.5: Effect of temperature on decolorization efficiency of Methyl orange

(Dye concentration = 30mg/L,Voltage = 25 V, Electrolyte = 1 M KCl, Current density = 1.33mA/mm^2*)*

The degradation profile in Fig. 4.5 shows a very fast degradation result, with over 90% achieved under 20 mins for each initial temperature before stabilizing.

Indeed, the influence of temperature on the electro-oxidation of organics is neither consistent nor certain but varies according to the nature of the organic compound and the environment. Although temperature increase is ordinarily expected to lead to enhanced reaction rates, it has been observed in some cases to decrease electro-oxidation and decolorization rates. For instance, (Kaouthar *et al.,* 2107) reported that increasing temperature beyond 25^{o}C decreased the rates of electro-catalytic oxidation and de-colorization of methyl orange in water containing NaCl as a supporting electrolyte. Increased temperature leads to a decrease in removal efficiency, this behavior was attributed to a decrease in the rate of generation of chlorine/hypochlorite at high temperatures. Another reason may be the less solubility of Cl_2 gas while increasing the temperature of the solution (Oguzie *et al.*, 2021). Although this study showed little to no difference in variation of initial temperature with time.

4.5 Ultraviolet-Visible Studies of Methyl Orange contaminated water

Ultraviolet-Visible (UV-Vis) studies is a technique that is deployed for detecting the presence of chromophore groups or conjugate bonds based on their light absorbing properties. Full wavelengths scan using an UV-Vis serve an important role of visualizing and displaying peaks and valleys corresponding to the chromophores present in the dyes compound.

As observed, in the case of Methyl orange (MO), the peaks reduced in height as electrolysis proceeds from time zero (0) minutes, until they are completely reduced at seventy (70) minutes. The absorption band moved from the visible region (500 – 400 nm) to the ultraviolet region (400 – 200 nm) indicated a bathochromic shift in absorption maxima of the chromophore.

The large azo dye structure consisting of the N=N bonds and aromatic rings molecules fragmented during the electrochemical oxidation process, forming smaller compounds. This resulted in a reduced absorbance peak of MO from 2.0 to 0.2 at wavelength of 470 nm for the visible region. The decrease in absorbance peak at the visible region is indicative of the absence of the azo chromophore group that was initially present in the dye compound before electrochemical degradation commenced**.** (Guenfoud *et al*., 2014)reported that it could be linked to intermediate degradation as well as aromatic ring degradation. Conversely, in the UV region, there was an increase in absorbance for MO suggestive of newly formed intermediates. Between 200 and 220 nm, a new absorption band arises that is most likely caused by the presence of short chain carboxylic acids, which are oxidation byproducts (Mora-Gomez *et al*., 2019).

Table 4.1: Absorbance peak before and after dye degradation

	Visible Region	**Ultraviolet region**
	Methyl Orange	Methyl Orange
Absorbance peak before degradation (0 minutes)	2.0 (470 nm)	0.9 (210 nm)
Absorbance peak after degradation (70 minutes)	0.2 (470 nm)	1.5 (210 nm)

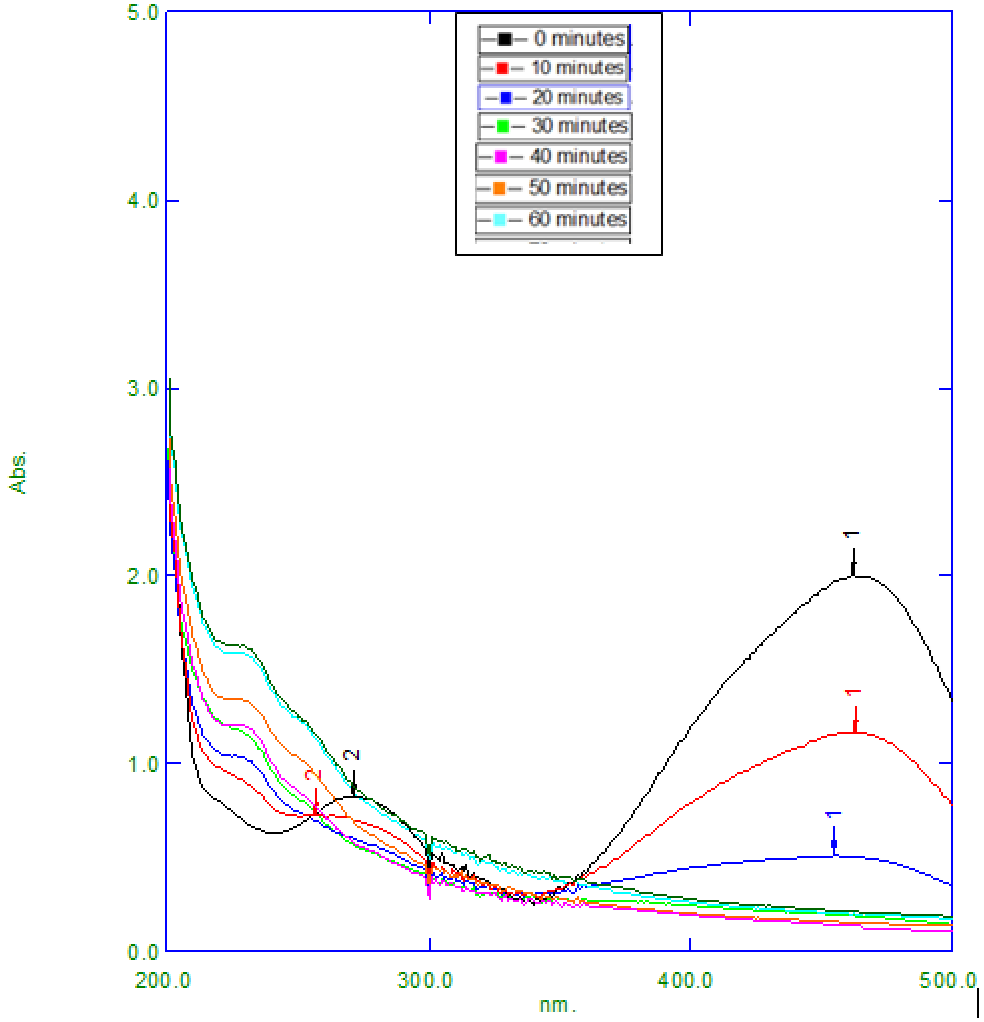

Figure 4.6: Ultraviolet visible spectrum studies of methyl orange dye degradation

Figure 4.7: Typical Color change after 70 min of treatment

4.6 FTIR Results

Fourier-transform infrared spectroscopy (FTIR) serves as a potent analytical tool for studying chemical compounds' structural characteristics and molecular composition. In this investigation, we employed FTIR to examine Methyl Orange (MO), a widely used azo dye, and its oxidized derivative. By scrutinizing the FTIR spectra, we gained critical insights into the chemical alterations that transpired during the oxidation of MO.

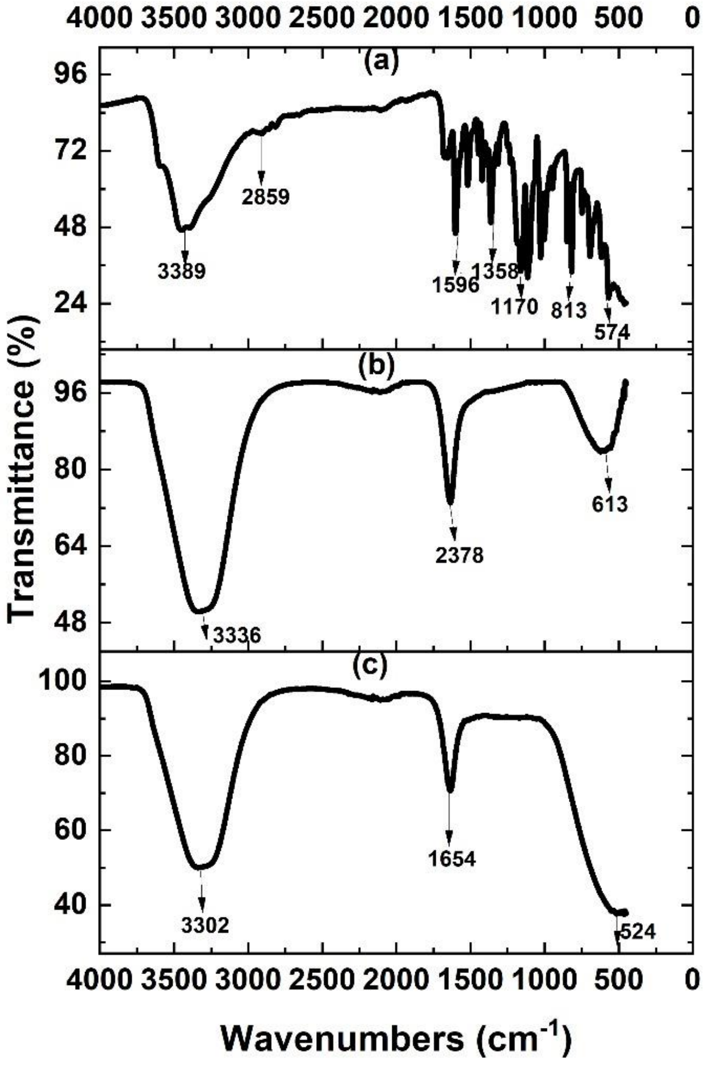

Figure 4.8: FTIR spectrum of (a) Methyl orange powder (b) Methyl orange solution (c) Degradation solution of Methyl orange dye

The FTIR spectrum of MO unveiled key peaks that shed light on its chemical nature. These included peaks at 2920 cm^{-1} (asymmetric $–CH_3$ stretching vibrations), 1676 cm^{-1} and 1646 cm^{-1} (–C–H bending within aromatic rings), and 1031 cm-1, 939 cm^{-1}, and 690 cm^{-1} (–C–H stretching vibrations of the benzene ring). Additionally, peaks at 1600 cm-1 and 1516 cm^{-1} (–N=N– stretching vibrations) and 1361 cm^{-1} and 1184 cm^{-1} (–C–N stretching) confirmed MO's azo nature, while a peak at 1111 cm^{-1} verified its sulfonic nature. Upon oxidation, the FTIR spectrum of the modified MO product exhibited notable changes, including the appearance of peaks associated with –N–H stretching vibrations of the amine. The absence of peaks related to –N=N– stretching vibrations further substantiated the reduction of the azo group. Overall, the FTIR analysis elucidated the chemical transformations within MO during reduction and provided valuable insights into its molecular structure.

4.7 Energy Consumption

The main operational expense deployed for the electrochemical oxidation of MO and CR dyes is related to the use of electrical energy. To be able to integrate an energy source for the degradation of the dyes, a direct current power source was connected to the electrolytic cell. Using equation 2, the precise energy consumption (kWh/dm^3) dissipated from the direct current power supply to the electrolytic cell.

As shown in table 4.2, the highest electrical energy consumption was 292.5 kWh/dm^3 when a current density of 3.3 mA/mm^2 was applied, while the lowest electrical energy consumption was 58.5 kWh/m^3 at current density of 0.7 mA/mm^2. Applying higher current density result in higher hydrogen and oxygen evolution reaction (Kariyajjanavar *et al.*, 2010), Current density of 3.3 mA/mm^2 reached more than 90% dye decolorization rate using electrolyte concentration of 0.5 molar. Hence, to achieve more than 90% decolorization efficiency of 500 ml of dye in a period less than or equal to 70 minutes, electricity supply of 292.5 kWh will be required.

Table 4.2: Electrical energy input for degradation of Methyl orange dye

Current density (mA/mm^2)	**Current (A)**	**Energy consumption (kWh/dm^3)**
3.3	5	292.5
2.7	4	234
2	3	175.5
1.3	2	117
0.7	1	58.5

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

The electrochemical degradation of methyl orange dye involves using electrodes to facilitate the breakdown of dye molecule into simpler, less harmful substances through oxidation processes. Key parameters such as, electrode materials, electrolyte solution, pH, current density, and monitoring techniques plays critical roles in optimizing the efficiency and effectiveness of the degradation process.

5.2 Conclusion

Based on the findings of this study, it can be concluded that contaminated Methyl orange dye can be degraded with high efficiency using the electrochemical method. Operating factors such as temperature, and pH had little effect on degrading efficiency; however, differences in supporting electrolyte concentration and current density indicated a more pronounced shift. The maximum degradation efficiency was recorded in acidic environments, high current density, high electrolyte concentration, and at a low temperature of 30^0C.

5.3 Recommendation

1. Wastewater treatment facilities should consider implementing electrochemical degradation processes with optimized pH, current density, and temperature control to enhance the removal of dye contaminants.
2. Further research should focus on scaling up the process and exploring its application under varying environmental conditions to assess broader feasibility and efficiency
3. Regulatory bodies should promote research and development in electrochemical treatment methods as part of broader environmental protection strategies
4. Further studies should explore the impact of varying temperatures beyond the scope of the research and investigate the long- term stability of different electrode materials under continuous operation
5. More studies should be carried out with other types of supporting electrolytes to evaluate their impact on the electrochemical degradation efficiency of methyl orange dye

3) More analytical studies should be carried out for detailed analysis of water treatment parameters e.g. Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), etc

5.4 Contribution to knowledge

This research has contributed significantly to the data on the recent usage of copper-graphite electrodes in the electrochemical treatment of dye wastewater. This study has also shown that just a little amount of current is required to achieve high degradation, which is advantageous for Nigeria given the country's energy scarcity. Furthermore, the study enhances understanding of the relationship between operational parameters and degradation efficiency in electrochemical processes.

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