

**PHOTODEGRADATION OF CASSAVA WASTEWATER  
USING PERIWINKLE SHELL, ROOF TILES AND TITANIUM  
DIOXIDE AS PHOTOCATALYSTS**

**BY**

**NMOSI SARAH OZAOMA**

**ENG1804648**

**DEPARTMENT OF CHEMICAL ENGINEERING**

**FACULTY OF ENGINEERING**

**UNIVERSITY OF BENIN**

**BENIN-CITY**

**APRIL, 2024**

**PHOTODEGRADATION OF CASSAVA WASTEWATER  
USING PERIWINKLE SHELL, ROOF TILES AND  
TITANIUM DIOXIDE AS PHOTOCATALYST**

**BY**

**NMOSI SARAH OZAOMA**

**ENG1804648**

**A PROJECT SUBMITTED TO THE DEPARTMENT OF  
CHEMICAL ENGINEERING, FACULTY OF ENGINEERING,  
UNIVERSITY OF BENIN, BENIN-CITY, EDO STATE,  
NIGERIA**

**IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR  
THE AWARD OF BACHELOR OF ENGINEERING IN  
CHEMICAL ENGINEERING.**

**APRIL, 2024**

# CERTIFICATION

This is to certify that this research project was carried out by NMOSI SARAH OZAOMA with matriculation number ENG1804648 of the Department of Chemical Engineering at the University of Benin, Benin City, Edo State, Nigeria.

-----

PROF. F. A. AISIEN

Project Supervisor

-----

DATE

-----

PROF. S.E UWADIAE

Project Coordinator

-----

DATE

-----

ENGR. DR. (MRS) E. T. AKHIHIERO

Acting head of department

-----

DATE

-----

EXTERNAL EXAMINER

-----

DATE

## **DEDICATION**

First and foremost, I want to dedicate this project work to God for the life, grace and strength given to me. I also want to dedicate this work to my family and friends for their help and support academically and lastly, to everyone that has contributed to this success.

## **ACKNOWLEDGEMENT**

I want to express my deepest gratitude to God for helping me and seeing me through during this project and my stay in this university.

I want to specially thank my family for their love and unwavering support throughout this period.

I sincerely want to appreciate Professor F. A. Aisien, whose leadership, insight, and mentoring have greatly influenced this research. His commitment to perfection and discipline has motivated me tremendously. Being able to work under his guidance has been a blessing as his skills and mentorship have been essential.

To Mr Okhuoya Moses, all I can say is a big thank you for the sacrifice, help and guidance. This project was successful because of you. Thank you for the times you motivated me to continue even when I don't see reasons to.

## ABSTRACT

This study focused on the photodegradation of cassava wastewater. The potential use of titanium dioxide, periwinkle shell and roof tiles, a sustainable and biodegradable catalyst to adsorb the pollutant from the aqueous solutions was investigated.

The catalyst was prepared by calcination and characterised by X-ray fluorescence (XRF), Brunauer-Emmet-Teller (BET), Scanning Electron Microscopy (SEM) and Fourier transform infrared spectrometry (FTIR) analysis. In this study, we explore the viability of using both activated and unactivated periwinkle shell and roof tiles powder to effectively the contaminants from the cassava wastewater. During the degradation process, the effects of some process variables such as contact time, concentration of the wastewater, and catalyst dose were investigated.

The results of batch adsorption study showed that for unmodified and modified catalyst, increasing the catalyst dosage and contact time resulted in increased percentage removal while increasing the concentration lead to a decrease in percentage removal. The optimum conditions for maximum percentage removal for unmodified and modified adsorbent are 3g catalyst dosage, 150 minutes contact time, and 100ml/l concentration of the wastewater. For adsorption Isotherm, Langmuir model was the best model for modified catalyst with a correlation coefficient of  $r^2 \geq 0.2989$  and in comparing the correlation coefficient  $r^2$  obtained from the Langmuir and Freundlich model, it clearly shows that the experimental analysis fit Freundlich model with  $r^2 \geq 0.8742$  for unmodified catalyst. For adsorption kinetics, Pseudo second order reaction showed a better fit ( $r^2 \geq 0.9999$ ,  $r^2 \geq 0.9998$ ) than both Langrande pseudo first-order ( $r^2 \geq 0.9782$ ,  $r^2 \geq 0.9982$ ) and the intra particle diffusion ( $r^2 \geq 0.9552$ ,  $r^2 \geq 0.9494$ ) for the modified and unmodified catalyst.

# TABLE OF CONTENT

<b>Title Page</b>	<b>i</b>
<b>Cover Page</b>	<b>ii</b>
<b>Certification</b>	<b>iii</b>
<b>Dedication</b>	<b>iv</b>
<b>Acknowledgement</b>	<b>v</b>
<b>Abstract</b>	<b>vi</b>
<b>Table of Content</b>	<b>vii</b>
<b>List of Figures</b>	<b>xi</b>
<b>List of Tables</b>	<b>xii</b>
<b>CHAPTER ONE</b>	<b>1</b>
<b>INTRODUCTION</b>	<b>1</b>
1.1 Overview of Wastewater Treatment	1
1.2 Problem Statement	3
1.3 Aim and Objectives	3
1.4 Scope of Study	4
1.5 Relevance of Study	4
<b>CHAPTER TWO</b>	<b>5</b>
<b>LITERATURE REVIEW</b>	<b>5</b>
2.1 What is Wastewater	5
2.2 Types of Wastewater	5
2.2.1 Domestic Wastewater	5

2.2.2	Stormwater runoff	6
2.2.3	Agricultural Wastewater	6
2.2.3	Industrial Wastewater	7
2.3	Characteristics of Wastewater	9
2.3.1	Physical Characteristics of Wastewater	9
2.3.2	Chemical Characteristics of Wastewater	10
2.3.3	Biological Characteristics of Wastewater	13
2.4	Stages of Wastewater Treatment	13
2.5	Wastewater Treatment Methodology	15
2.5.1	Physical Methods	15
2.5.2	Biological Methods	18
2.5.3	Chemical Methods	19
2.6	Types of Photodegradation	22
2.7	Photodegradation Rate Affecting Parameters	23
2.8	Uses of Photodegradation	26
2.9	Illumination source for Photodegradation	28
2.10	Titanium Dioxide as a Photocatalyst	29
2.10.1	Benefits of Titanium Dioxide	29
2.10.2	Drawbacks of Titanium Dioxide	30
2.10.3	Modification of Titanium Dioxide	31
2.11	Periwinkle Shell	31
2.11.1	Application of Periwinkle Shell	32
2.12	Clay Roof Tiles	34

2.12.1	Properties of Clay Roof Tiles	34
2.13	Cassava	35
2.13.1	Composition of Cassava Wastewater	36
2.14	Adsorption	37
2.14.1	Advantages of Adsorption	38
2.14.2	Adsorption Mechanism	38
2.14.3	Adsorption Isotherm	39
2.14.3.1	Langmuir Isotherm Model	39
2.14.3.2	Freundlich Isotherm Model	40
2.14.4	Adsorption Kinetics	41
2.14.4.1	Pseudo First-Order Kinetic Model	41
2.14.4.2	Pseudo Second-Order Kinetic Model	41
2.14.4.3	Intra-Particle Diffusion Model	42
	<b>CHAPTER THREE</b>	<b>43</b>
	<b>MATERIALS AND METHODS</b>	<b>43</b>
3.1	Materials	43
3.2	List of reagents and their Uses	43
3.3	Equipment	43
3.3.1	Multi Lamps UV Flow through Photocatalytic Reactor	43
3.3.2	Electronic Weighing Balance	44
3.3.3	pH Meter	44
3.4	Activation of Periwinkle Shell and Roof Tiles	46
3.5	Characterization of Periwinkle Shell and Roof Tiles	46

3.6	Photodegradation Treatments Procedures	47
	<b>CHAPTER FOUR</b>	<b>49</b>
	<b>RESULTS AND DISCUSSION</b>	<b>49</b>
4.1	Characterization Results of Periwinkle Shell and Roof Tiles	49
4.2	Photodegradation Treatment	49
4.2.1	Effect of Catalyst Dosage	50
4.2.2	Effect of Contact Time	52
4.2.3	Effect of Concentration	54
4.3	Isotherm Model for Modified Catalyst	56
4.4	Isotherm Model for Unmodified catalyst	58
4.5	Kinetic Model for Modified Catalyst	63
4.6	Kinetic Model for Unmodified Catalyst	66
	<b>CHAPTER FIVE</b>	<b>70</b>
	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>70</b>
5.1	Conclusions	70
5.2	Recommendations	70
	<b>REFERENCE</b>	<b>71</b>
	<b>APPENDIX</b>	<b>93</b>

## LIST OF FIGURES

Fig 2.1	Periwinkle Shell	32
Fig 2.2	Clay Roof Tiles	34
Fig 2.3	Cassava	36
Fig 3.1	Multi Lamps UV flow through Photocatalytic Reactor	43
Fig 3.2	Electronic Weighing Balance	44
Fig 3.3	pH Meter	44
Fig 4.1	Effect of Modified and Unmodified Catalyst Dosage	50
Fig 4.2	Effect of Contact Time	52
Fig 4.3	Effect of Concentration	54
Fig 4.4	Langmuir Isotherm for COD Reduction for Modified Catalyst Dosage	56
Fig 4.5	Freundlich Isotherm for COD Reduction for Modified Catalyst Dosage	57
Fig 4.6	Langmuir Isotherm for COD Reduction for Unmodified Catalyst Dosage	58
Fig 4.7	Freundlich Isotherm for COD Reduction for Unmodified Catalyst Dosage	59
Fig 4.8	Langrange Pseudo-First Order for COD Reduction for Modified Catalyst Dosage	63
Fig 4.9	Pseudo-Second Order for COD Reduction for Modified Catalyst Dosage	64
Fig 4.10	Intra Particle Diffusion for COD Reduction for Modified Catalyst Dosage	65
Fig 4.11	Langrange Pseudo-First Order for COD Reduction for Unmodified Catalyst Dosage	66
Fig 4.12	Pseudo-Second Order for COD Reduction for Unmodified Catalyst Dosage	67
Fig 4.13	Intra Particle Diffusion for COD Reduction for Unmodified Catalyst Dosage	68

## LIST OF TABLES

Table 4.1	Adsorption Modelling of COD	61
Table 4.2	$R_L$ and their Isotherm Type	62
Table 4.3	Kinetic Modelling	69
Table A.1	Physicochemical Properties of Cassava Wastewater	93
Table A.2	Effect of Modified Catalyst Dosage	94
Table A.3	Effect of Unmodified Catalyst Dosage	94
Table A.4	Effect of Contact Time Variation (Modified Catalyst)	95
Table A.5	Effect of Contact Time Variation (Unmodified Catalyst)	95
Table A.6	Effect of Concentration (Modified Catalyst)	96
Table A.7	Effect of Concentration (Unmodified Catalyst)	96
Table A.8	Adsorption Isotherm for Modified Catalyst	97
Table A.9	Adsorption Isotherm for Unmodified Catalyst	98
Table A.10	Kinetics Isotherm for Modified Catalyst	98
Table A.11	Kinetics Isotherm for Unmodified Catalyst	99

# CHAPTER ONE

## INTRODUCTION

### 1.1 OVERVIEW OF WASTE WATER TREATMENT

Water represents an invaluable commodity crucial to various human endeavours, yet only a tiny fraction of Earth's water reserves (roughly 0.03%) is readily available for human use (Allègre et al., 2006). The discharge of wastewater into aquatic environments poses a significant water pollution threat, escalating oxygen consumption and enriching water bodies with nutrients, leading to toxic and destabilised aquatic ecosystems. Extreme pH levels in a water body can adversely affect aquatic organisms, impairing recreational uses and hindering its solubility (Ekubo and Abowei, 2011).

Water quality management in aquaculture is often overlooked until its effects on production become apparent. Nonetheless, numerous factors influence water quality including temperature, phytoplankton, photosynthesis, pH equilibrium, carbon dioxide, alkalinity, and hardness (Verma et al., 2022). These variables encompass all these physical, chemical, and biological aspects that impact the effective utilisation of water. In the context of aquaculture, any water attribute that influences the health, growth, reproduction, or management of and associated aquatic species constitutes a water quality variable.(Malik et al., 2020).

Moreover, water quality can be influenced by the interplay of these factors. Several contaminants can pollute cassava wastewater and pose risks to the diverse life forms they support:

1. Microorganisms: Microorganisms, such as bacteria and viruses, may harbour pathogens that induce illnesses in aquatic organisms (Obasohan et al., 2010). Certain algae release toxic substances that pose threats to animals that come into contact with the water.

Excessive algae growth can also be problematic, obscuring sunlight from aquatic plants and depleting oxygen levels (Yeh et al., 2015)

2. Chemicals – Agricultural chemicals, such as pesticides can harm animals and plants (Kumar et al., 2013). Fertilizers can also present challenges by fueling algae growth, exacerbating the problems mentioned above (Savci, 2012). Industrial pollutants, including heavy metals, often exhibit toxicity to aquatic life and disrupt the functionality of cassava wastewater ecosystems.
3. Suspended Particles – Particles, including soil and organic debris, can pollute cassava wastewater. They can also impede sunlight penetration, which is essential for photosynthesis by aquatic plants. These particles frequently harbour unwanted microorganisms, so their removal can alleviate the pathogen load in the cassava wastewater.

Photo-Catalysis is defined as "acceleration facilitated by the presence of a catalyst". Catalysts remain unaltered and are not consumed during the chemical reaction. Photocatalysis involves photosensitization, a process in which a photochemical alteration occurs in one molecular entity as a result of the initial absorption of radiation by another molecular entity known as the photosensitizer.

In photo generated catalysis, the photocatalytic activity (PCA) hinges on the catalyst's ability to generate electron-hole pairs, which in turn produce free radicals (e.g., hydroxyl radicals: -OH) capable of secondary reactions. Two main types of photocatalysis exist: homogeneous and heterogeneous photocatalysis.

*In homogeneous photocatalysis*, the reactants and photo-catalysts are present in the same phase. The most commonly employed photo-catalysts include ozone and photo-Fenton systems ( $\text{Fe}^+$  and  $\text{Fe}^+/\text{H}_2\text{O}_2$ ). In contrast, *heterogeneous photocatalysis* features catalysts in a different phase

from the reactants. Metal oxides and semiconductors serve as heterogeneous photocatalysts due to their unique properties and attributes.

A photochemical multi-flow-through reactor for fluid treatment employs a substantially uniform light dosage from a linear light source. It comprises: a reactor housing containing an internal space with a fluid entry region, a fluid exit region, a core photochemical treatment zone consisting of a casing, a means for radially distributing fluid flow circumferentially toward and perpendicular to a line-type light source, and a fluid exit region, wherein the core photochemical treatment portion of the housing possesses rotational symmetry about a central axis and one or more line-type light sources mounted within the treatment zone substantially at the central axis of the housing, the axis of the lamps being oriented parallel to the rotational axis of the treatment zone housing. Techniques are also provided utilising the circumferential distribution of fluid flow radially toward and perpendicular to the line-type light source.

## **1.2 PROBLEM STATEMENT**

All living organisms rely on water for survival. Over two-thirds of the planet Earth is covered by ocean water, and there are also numerous freshwater habitats. However, certain activities tend to contaminate it at an alarming rate. One such activity is the discharge of wastewater into large bodies of water, such as rivers, seas, and oceans. Oceans are interconnected, and as a result, pollutants are transported by currents and tides, spreading around the globe. These pollutants enter the oceans' food chains and work their way up from phytoplankton to higher animals. As such, wastewater requires treatment prior to disposal to prevent widespread water pollution.

## **1.3 AIM AND OBJECTIVES**

To ascertain the optimal operating conditions for the photocatalytic treatment process of cassava wastewater using  $\text{TiO}_2$ , Periwinkle shell and Roof tiles as a catalyst and UV as a light

source, and to determine the isotherm and kinetic model that most accurately describes the process. The objectives encompass:

1. To establish the extent to which the wastewater can be treated using photocatalysis.
2. To examine how variations in experimental parameters such as catalyst dosage, concentration and contact time affect cassava wastewater treatment.
3. To determine the isotherm and kinetic model that best describes the photocatalytic process.

#### **1.4 SCOPE OF STUDY.**

The study's scope encompasses the following:

1. Subjecting the cassava wastewater to photocatalytic treatment using TiO<sub>2</sub>, Periwinkle shell, Roof tiles and UV light.
2. Analysing the treated cassava wastewater to determine its physicochemical properties.
3. Determining the optimal values.

#### **1.5 RELEVANCE OF STUDY**

Pristine cassava wastewater guarantees a salubrious environment for the organisms inhabiting it. However, over time, cassava wastewater becomes polluted by contaminants from natural and man-made sources. The polluted cassava wastewater necessitates treatment before it can be discharged into water bodies. This research investigates the efficacy of photocatalytic treatment of cassava wastewater using TiO<sub>2</sub>, Periwinkle shell and Roof tiles as a catalyst and UV as a light source.

# **CHAPTER TWO**

## **LITERATURE REVIEW**

### **2.1 WHAT IS WASTEWATER?**

Wastewater is any water contaminated by human activity, rendering it unfit for its original purpose. Wastewater primarily consists of 99.9% water, with the remaining 0.1% comprising organic matter, dissolved contaminants, microorganisms, and inorganic compounds (Nahiun et al., 2021). Additionally, wastewater includes storm runoff, containing harmful substances washed off roads and urban surfaces. Wastewater is discharged into various ecosystems, including lakes, streams, and oceans.

### **2.2 TYPES OF WASTEWATER**

#### **2.2.1 DOMESTIC WASTEWATER**

Domestic wastewater is wastewater generated from residential and commercial areas, including salons, restaurants, hospitals, and office buildings. It primarily originates from toilets, bathrooms, laundry, and kitchens (Mara, 2013), containing high levels of biological oxygen demand (BOD), ammonium, organic matter, and pathogenic microorganisms.

Domestic wastewater is typically transported through sewer systems.

1. **Blackwater:** Blackwater refers to wastewater that includes discharge from toilets and kitchen sinks. Contaminants in blackwater include urine, fecal matter, toilet paper, soaps, discarded food, and chemicals, making it highly polluted and posing a potential health hazard (Yin et al., 2019). It contains disease-causing bacteria, protozoa, viruses, and other pathogens that can cause illness if ingested or through skin contact.  
(J. Ahmed et al., 2021).

2. Greywater: Greywater is a less contaminated type of wastewater generated from baths, washing machines, and bathroom sinks. (Al- Jayyousi, 2003). It is domestic wastewater without fecal matter, urine, or food waste. While not considered pathogenic, greywater contains detergents, soaps, and chemicals, requiring treatment before reuse. It typically contains fewer contaminants than blackwater and can be reused for non-potable purposes such as irrigation or toilet flushing after appropriate treatment.(J. Ahmed et al., 2021)

### **2.2.2 STORMWATER RUNOFF**

Stormwater runoff is water that does not infiltrate the ground and flows over pavements, roads, rooftops, or open surfaces during precipitation events (Bani, 2011). It is a major source of water pollution, as toxic substances such as plastics, pesticides, herbicides, oils, chemicals, heavy metals, and pathogens are washed off into stormwater runoff from various sources. Stormwater runoff often flows directly or through channeled drains into nearby water bodies without treatment, threatening aquatic life and the environment (J. Ahmed et al., 2021).

### **2.2.3 AGRICULTURAL WASTEWATER**

Agricultural wastewater is wastewater contaminated by agricultural activities such as irrigation, livestock farming, crop production, and pesticide or fertilizer application. Excess water running off fields during irrigation can carry sediment and nutrients into water sources. Agricultural wastewater also contains agrochemicals such as fertilizers, pesticides, herbicides, crop residues, animal wastes, and dairy farming waste (Evans et al., 2019). Various farm management techniques are employed to minimize surface runoff and treat agricultural wastewater (Ongley, 1996, Vymazal, 2009).

## 2.2.4 INDUSTRIAL WASTEWATER

Industrial wastewater is water discharged from industrial processes, such as manufacturing, cleaning and other commercial activities (Munter, 2003). It contains dissolved and suspended substances, including organic and inorganic chemicals, suspended solids, heavy metals, oils, pesticides, silt, pharmaceuticals, and industrial byproducts (Azimi et al., 2017, Fu and Wang 2011). The composition of industrial wastewater varies depending on the industry. Examples of industries generating wastewater include mining, steel production, industrial laundries, power plants, oil and gas fracking, textiles, pharmaceuticals, and food/beverage industries. Industrial wastewater treatment is complex and requires specific examination of individual setups and treatment plants (Jern and Wun 2006).

### 1. Effluents Produced by Pharmaceutical Manufacturing Processes

The pharmaceutical manufacturing industry encompasses the creation, extraction, processing, refinement, and packaging of chemical and biological substances in various forms such as solids and liquids to be employed as medications for humans and animals. Wastewaters generated within this industry are commonly a byproduct of the processes involved in the creation and preparation of pharmaceutical products. A significant proportion of active pharmaceutical ingredients circulated globally are synthesized through chemical reactions employing organic, inorganic, and biological mechanisms (Gadipelly et al., 2014).

Pharmaceutical industry wastewater is characterized by its poor suitability for treatment. The chemical oxygen demand (COD) typically ranges from 5000 to 15000 mg/L, while the biochemical oxygen demand (BOD<sub>5</sub>) is relatively low. The BOD<sub>5</sub>/COD ratio is below 30%, indicating poor biodegradability. The wastewater often exhibits poor color, pH extremes, and requires extensive pretreatment followed by biological treatment with extended reaction times (Shi, 2009).

## 2. Effluents from Tannery Operations

The composition of tannery wastewater varies significantly among tanneries due to factors such as size, process chemicals, water usage, and products. Typical tannery wastewater exhibits characteristics based on parameters like Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Suspended Solids (SS), Chromium, and sulfide (Buljan et al., 2011). Typically, composite tannery wastewater is alkaline with a pH above 7.5, containing high levels of organic substances, including slowly biodegradable compounds, as well as significant suspended solids, nitrates, and total chromium. Additionally, it may contain substantial amounts of sulfide/sulfate, chlorides, and other metals. Biological treatment of tannery wastewater faces challenges due to inhibitory effects of chromium, sulfide, and chloride, often resulting in poor effluent quality regarding these contaminants. Discharge of such wastewater into water sources can have detrimental environmental consequences (Buljan et al., 2011).

## 3. Effluents Generated by Breweries

Barley is the primary grain utilized in beer brewing, with occasional additions of rice, oats, rye, wheat, and millet. Beer production encompasses three main stages: malt preparation from barley, wort preparation, and fermentation (Shi, 2009). The beer production process employs various batch-type operations to transform raw ingredients into the final beer product. Substantially, the process necessitates copious amounts of water for beer production, equipment cleansing, sanitation, and sterilization after each batch. A considerable portion of this utilized water is subsequently released through drainage systems. The primary water consumption areas within a typical brewery encompass the brewhouse, cellars, packaging, and general water utilization. Water consumption in these areas incorporates all water

utilized for product manufacturing, vessel washing, and cleaning in place (CIP), which significantly impact both water intake and effluent production (Van der Merwe and Friend, 2002).

4. Fermentation contributes another wastewater stream with significantly elevated COD and BOD<sub>5</sub> due to dissolved and suspended organic matter. Brewery wastewater is three to four times more concentrated than domestic sewage in terms of organic content. While it lacks toxic contaminants and most of the organic matter is biodegradable, suspended solids removal is essential before anaerobic and aerobic biological treatment steps to reduce organic concentrations and meet discharge standards (Shi, 2009).

## **2.3 CHARACTERISTICS OF WASTEWATER**

### **2.3.1 PHYSICAL CHARACTERISTICS OF WASTEWATER**

1. Solids: Solids can be categorized into dissolved solids, settle-able solids, suspended solids, and filterable solids. Dissolved solids encompass inorganic salts and organic matter present in water. Major components include calcium, magnesium, sodium, potassium cations, and carbonate, hydrogen carbonate, chloride, sulfate, and nitrate anions. Settle-able solids (silt and heavy organic solids) settle due to gravity. Suspended solids and filterable solids are classified by particle size; suspended solids remain at the top of a sample when filtered through a standard glass-fibre filter (APHA, 2005). Suspended solids hinder light penetration in surface waters, affecting aquatic plants. Their deposition in rivers and lakes may lead to septic and unpleasant conditions, indicating inadequate sewage treatment.

Water classifications based on total dissolved solids include:

- i. Potable water – Less than 1,500 mg/L TDS
- ii. Slightly saline water – 1,500-5,000 mg/L TDS

- iii. Highly saline water – Over 5,000 mg/L TDS
2. Color: Color is a qualitative attribute used to assess wastewater condition. Light brown wastewater is less than six hours old, light-to-medium grey indicates some decomposition or extended residence in collection systems, while dark grey or black wastewater is septic, showing significant bacterial decomposition under anaerobic conditions. Blackening often results from sulfide formation, particularly ferrous sulfide, when hydrogen sulfide combines with divalent metals like iron. Color is determined by comparison to standards (El-azim, 2019).
  3. Odor: Odor assessment has gained importance due to public concerns about wastewater treatment. Fresh wastewater has a generally inoffensive odor, but decomposition under anaerobic conditions releases odorous compounds. The primary odorous compound is hydrogen sulfide, produced when anaerobic microorganisms convert sulfates to sulfides (Gao et al., 2017). Odor is measured by diluting the sample with odor-free water until the odor becomes undetectable (Hawko et al., 2021).
  4. Temperature: Wastewater temperature is often higher than water supply temperature due to the influx of warm household and industrial waste (Rangarajan et al., 2019). Water temperature is crucial for aquatic life and its suitability for various uses (Khan et al., 2016). Temperature measurement is important because wastewater temperature varies seasonally (Arora and Kazmi, 2015).

### **2.3.2 CHEMICAL CHARACTERISTICS OF WASTEWATER**

1. pH value: Wastewater acidity or alkalinity is indicated by its pH value. Raw sewage has a slightly alkaline pH of 7.3-7.5. Over time, bacterial acid production lowers the pH, making the sewage more acidic (Sharma, 2023). Safe water has a pH between

6.5- 8.5 (WHO, 2011). Changes in pH can have various effects on plants and animals (Mesner and Geiger, 2010):

- i. Slightly acidic water can harm fish gills, damage membranes, and reduce egg hatching success.
  - ii. Water with extreme pH levels is fatal to aquatic life.
  - iii. Low pH can kill amphibians due to their sensitive skin.
2. Dissolved Oxygen: This is a critical water quality parameter that indicates the extent of pollution in water bodies. Dissolved oxygen is a result of oxygen solubility. High dissolved oxygen concentrations indicate good water quality. Its presence in untreated wastewater suggests freshness. In treated wastewater, it signifies effective oxidation throughout the treatment process. Low dissolved oxygen levels in disposal areas can lead to the death of fish and other aquatic organisms. Dissolved oxygen can be measured using a colorimeter or electrometric methods (APHA, 2005).
3. Biological Oxygen Demand: Microorganisms such as bacteria utilize organic matter as nourishment. Oxygen is consumed during this metabolic process. Dissolved oxygen in a water sample will deplete if this process occurs in water. High organic matter concentrations in the water cause excessive dissolved oxygen consumption to ensure organic matter decomposition. This poses a problem because aquatic life relies on DO for survival. High BOD levels indicate water contamination (Tchobanoglous et al., 2003). The dilution method can be used to determine biological oxygen demand. Temperature, dilution, nitrification, toxicity, and anaerobic organism presence can affect this test.

The BOD test involves two decomposition phases ( Delzer and Mckenzie, 2003):

- i. Carbonaceous stage: This encompasses oxygen demand associated with organic carbon conversion to carbon dioxide.

- ii. Nitrogenous stage: This incorporates combined carbonaceous and nitrogenous demand during organic nitrogen, ammonia, and nitrite transformation into nitrate.
- 4. Chemical Oxygen Demand (COD): The COD test measures oxygen consumption resulting from chemical oxidation of organic matter. The obtained value indirectly reflects the level of organic matter present. Potassium dichromate, a potent chemical oxidizing agent in acidic conditions, is used to determine the organic matter's oxygen equivalent that can be chemically oxidized. The test requires elevated temperatures and silver nitrate as a catalyst to facilitate oxidation (Samudro and Mangkoedihardjo, 2010).

COD values for wastes tend to be higher than BOD values since more compounds can be chemically oxidized than biologically oxidized (Tchobanoglous et al., 2003). This test is widely used due to its shorter duration (around 3 hours) compared to tests like BOD, which take 5 days (Samudro and Mangkoedihardjo, 2010). BOD involves biochemical oxidation of organic matter entirely by microorganisms, while COD represents chemical oxidation

- 5. Heavy Metals: Heavy metals refer to metallic elements with high densities and toxicity at elevated concentrations. Examples include mercury, cadmium, arsenic, chromium, nickel, copper, cobalt, and lead (Garbarino et al., 1995). Natural sources of heavy metals in wastewater include weathering, soil erosion, and volcanic activity, while human activities include industrial and municipal effluents (Florea et al., 2004). These heavy metals pose significant concerns due to their toxicity, bioaccumulation potential, and environmental and health risks (Monisha et al., 2014). Human exposure can occur through food, drinking water, and inhalation. Certain heavy metals, such as copper, iron, cobalt, selenium, and zinc, are essential in trace amounts but can become toxic at higher concentrations (Vardhan et al., 2019).

### **2.3.3 BIOLOGICAL CHARACTERISTICS OF WASTEWATER**

1. **Microorganisms:** Wastewater contains microorganisms such as bacteria, viruses, Algae fungi, and protozoa. Disease-causing microorganisms can spread to aquatic organisms and potentially humans. They can also deplete oxygen levels, affecting aquatic life.
2. **Organic Matter:** Organic matter encompasses carbon-based compounds originating from living organisms. It includes carbohydrates, lipids, proteins, and nucleic acids. These compounds are broken down through decomposition into simpler forms.

### **2.4 STAGES OF WASTEWATER TREATMENT**

The rising demand for water underscores the need for wastewater reuse and improved treatment strategies. Advanced approaches address these challenges by eliminating pollutants at treatment plants or preventing contamination at the source. New technologies for pollutant removal ensure effective water purification before discharge into water bodies. These systems achieve varying levels of pollution control, enabling treated wastewater to be repurposed for manufacturing, recreational, and agricultural uses.

1. **Preliminary Treatment Stage:** The foundational phase of wastewater treatment entails equalizing and integrating wastewater streams discharged intermittently from distinct manufacturing stages. Equalization guarantees consistency in waste characteristics, including pH, pollutant concentration, and temperature (Atul et al., 2012).

This stage also removes large or heavy debris that could hinder operations. Raw wastewater is screened to eliminate grit, large floating objects, and heavy inorganic solids. Organic material is largely unaffected by screening. Steroid hormones and micropollutants are minimally removed at this stage (Agarwal and Singh, 2017).

Screened material is typically disposed of in landfills or incinerated.

2. **Primary Treatment Stage:** This step involves the physical separation of suspended solids from wastewater through sedimentation. Solids and greases are removed from the wastewater. Screened wastewater enters a primary settling tank, where it is detained for several hours. Solid particles settle, forming sludge at the bottom and scum float up to the top (Demirbas et al., 2017). Scum is skimmed off, sludge is extracted, and partially treated wastewater advances to secondary treatment. Primary treatment typically removes about 50% of biochemical oxygen demand (BOD), 70% of suspended solids, and up to 65% of grease and oil. While this stage effectively removes substantial pollutants like organic nitrogen and phosphorus and heavy metals, it does not eliminate all harmful contaminants. The primary treated effluent still contains significant organic materials and a relatively high BOD (FAO, 2006).
3. **Secondary Treatment Stage:** This stage employs biological processes to reduce BOD, organic matter, and a significant portion of suspended solids. Microorganisms convert pollutants into less harmful substances. This treatment is categorized as either anaerobic or aerobic. In aerobic treatment, microorganisms utilize dissolved organic impurities as nourishment, converting them into water, carbon dioxide, and energy to sustain their growth (Higgins et al., 2018). Oxygen is essential for these microorganisms, necessitating continuous aeration through the treatment tanks. Forced air, supplied by a blower or compressor, mixes with wastewater, facilitating microbial consumption of organic waste. Anaerobic treatment offers energy efficiency, as microorganisms convert wastewater pollutants into biogas in the absence of oxygen. Methane-rich biogas is produced as a byproduct. In addition to removing organic matter and BOD, secondary treatment also removes nutrients such as nitrogen and phosphorus through processes like nitrification and luxury cell uptake

(Templeton and Butler, 2011.) These removals prevent eutrophication and oxygen depletion in receiving water bodies upon discharge of treated wastewater.

4. Tertiary Treatment Stage: This stage further purifies wastewater to meet specific industrial or domestic requirements or to ensure safe discharge. Treated water is disinfected using chlorination or ultraviolet (UV) radiation prior to release into water streams or reuse (Praveen and Loh, 2016). Tertiary treated wastewater can approach drinking water standards. However, this stage is costly and rarely implemented by industries.

## **2.5 WASTEWATER TREATMENT METHODOLOGY**

Industrial water treatment aims to reduce harmful pollutants from water. Water treatment techniques include:

### **2.5.1 PHYSICAL METHODS**

This preliminary treatment removes solids from wastewater. Methods include:

1. Screening and Filtering: This process separates floating or suspended particles. Different screen sizes remove different particle types. During wastewater treatment, particle filtration serves as a paramount initial step. Its purpose is to eliminate solids exceeding one micron in size. The selection of filters employed in the filtration process hinges on particle characteristics such as shape, size, texture, density, and quantity (Medeiros et al., 2020).
2. Sedimentation: This process allows solid particles to settle. Chemicals can be added to accelerate the process. Efficiency hinges on flow rate, detention time, and solid loading.

3. **Coagulation:** Coagulation, a crucial wastewater treatment method, involves adding positively charged metal salts or polyelectrolytes to destabilize particles. Ferric and aluminum salts are typically employed as coagulants and flocculating agents (Bratby, 2006). Coagulation targets particles from  $10^{-7}$  to  $10^{-14}$  centimeters. These colloid particles, with their Brownian movement and negative surface charge, resist coagulation unless positive charges neutralize their negative charge (Bache et al., 1999).
4. **Flocculation:** After coagulation, flocculation occurs, where destabilized particles collide, driven by hydraulic shear force or flocculant addition. This allows solids to form clumps, enhancing their removal via sedimentation or filtration (Sahu and Chaudhari, 2013).
5. **Membrane Separation:** This process employs a semipermeable membrane that forces feed water under pressure to separate specific particles. Molecules pass through the membrane by diffusion, with the rate influenced by pressure, temperature, and the membrane's permeability. This process is categorized as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), electrodialysis, or reverse osmosis (RO), based on pore size (Nqombolo et al., 2018)
  - i. **Microfiltration:** Microfiltration uses a barrier membrane to remove fine suspended solids. It efficiently targets particles from 0.1 to  $10\mu\text{m}$  (Wang et al., 2011).  
Microfiltration effectively removes not only heavy metal ions but also efficiently filters total dissolved solids (TDS), bacteria, algae, microorganisms larger than viruses, and micropollutants (Baruah et al., 2006).
  - ii. **Nanofiltration:** Nanofiltration exhibits increased permeability and lower transmembrane pressure compared to microfiltration (Cao et al., 2019). It involves liquid-phase separation of inorganic and organic substances in solutions. Diffusion

through the membrane occurs at pressure differentials less than reverse osmosis but higher than ultrafiltration. Nanofiltration membranes, with pore sizes from 1-10 nanometers, are smaller than microfiltration and ultrafiltration but larger than reverse osmosis membranes. Their porosity is influenced by pH, temperature, and processing time, with pore densities varying from 1 to  $10^6$  pores per  $\text{cm}^2$ .

- iii. Ultrafiltration: Ultrafiltration is a water filtration technique that employs lower pressure (compared to reverse osmosis and nanofiltration) to separate solids from water through a permeable barrier (Aouni et al., 2012). It removes suspended solids, bacteria, and viruses within a size range of 0.005 to 0.01 micron and can be sometimes utilized as a preliminary step before reverse osmosis (Li et al., 2006). The thickness of the membrane's surface layer typically falls between 150–250  $\mu\text{m}$ . This membrane filters out macromolecules, proteins, viruses, and polysaccharides (Abdel-Fatah, 2018, Obotey and Rathilal, 2020). It is an energy-efficient process with high removal efficiency, but it cannot remove dissolved solids.
- iv. Reverse Osmosis: Reverse osmosis is a widely employed water treatment method for industrial applications. It forces water through a semi-permeable membrane using applied pressure, removing contaminants such as dissolved ions (e.g., sodium), bacteria, viruses, and other impurities ranging from 0.005 to 0.0001 micron in size (Sonune and Ghate, 2004). The surface film's thickness is generally 150  $\mu\text{m}$ . This membrane also removes compounds of varying molecular weights, including glucose, proteins, sodium chloride, and amino acids (Azimi et al., 2017; Abdel-Fatah, 2018). Reverse osmosis and ultrafiltration differ in their membrane permeability and pore structure (size and porosity) (Murthy and Chaudhari, 2009).

6. **Electrodialysis:** Electrodialysis is a membrane separation technique that utilizes an electrical potential to drive ionized species through an ion-exchange membrane (Rodrigues et al., 2008). The membranes are thin plastic sheets with cationic or anionic properties. The ionic species solution flows through cell compartments, with cations moving towards the cathode and anions towards the anode, facilitating wastewater treatment (Ariffin et al., 2017).
7. **Ion Exchange:** Ion exchange involves the exchange of ions between liquid and solid phases. Ion exchange and complex formation occur as heavy metal ions are adsorbed onto the surface. Hydration takes place at the solution surface or in the adsorbent pores, resulting in the removal of ions from the electrolyte solution by resins (natural or synthetic). Ions with the same charge enter the solution. Advantages include material regeneration and selectivity for metal ions. However, high resin costs and sensitivity to removed particles limit its efficiency. (Darban et al., 2020). Additionally, resins require frequent replacement due to deterioration and foul odor.
8. **Wastewater Treatment through Flotation:** Flotation utilizes fine gas bubbles to transport dispersed or suspended substances to the surface, where they can be removed. This process is employed in wastewater treatment to separate oils, fats, and suspended solids and particles. Smaller microbubbles enhance particle and droplet collection. Dissolved Air Flotation (DAF) is a cost-effective method commonly used in wastewater treatment (Sonune and Ghate, 2004).

## **2.5.2 BIOLOGICAL METHODS**

Biological approaches offer an alternative to conventional metal recovery processes.

Microorganisms like bacteria, fungi, and algae play a crucial role in treating wastewater biologically. These microorganisms convert heavy compounds into simpler forms, facilitating

their separation from mixed solutions (Samer, 2015). A variety of processes have been established based on their mode of action, as discussed in this section.

1. **Biosorption:** Biosorption utilizes microorganisms, plant material, agricultural waste, and biopolymers to eliminate metals from aqueous solutions. These "biosorbents" possess functional groups (hydroxyl, carboxyl, etc.) that bind metals through a physicochemical process, circumventing metabolic processes and oxidation (Davis et al., 2003). Biosorption offers advantages such as low cost, high uptake capacity, and no toxic effects, making it a potential alternative to conventional metal recovery methods (Chojnacka, 2010).
2. **Bio-Precipitation:** Bio-precipitation employs biological agents to precipitate metals, reducing chemical dependency and sludge production (Ahalya et al., 2003). Metabolites released by immobilized cells facilitate precipitation through sulfide, carbonate, and phosphate formations, with metal-sulfide precipitation being particularly stable.
3. **Bioaccumulation:** Bioaccumulation involves the active uptake of metals by living cells. Metal ions are adsorbed into cells (adsorption phase) and then actively transported intracellularly (transport phase). Unlike biosorption, this irreversible process is metabolism-dependent and requires cultivation of microorganisms in the presence of the target metal (Mrvčić et al., 2012).

### **2.5.3 CHEMICAL METHODS**

1. **Chemical Precipitation:** Chemical precipitation is a simple and economical process for primary wastewater treatment due to its effectiveness in removing heavy metals (Matlock, et al., 2002). It involves adjusting the pH (basic pH) of heavy metals and adding chemical reagents (e.g., lime, hydroxides, sulphides), leading to the formation

of insoluble particles that are removed by sedimentation. The process efficiency is influenced by metal concentration in the wastewater, wastewater type, reaction conditions, and the presence of compounds that inhibit reactions (Pohl, 2020).

However, the major limitation is the inability to achieve discharge-acceptable heavy metal concentrations, requiring additional post-treatments. Furthermore, significant sludge generation, disposal, and potential secondary pollution pose additional challenges (Bolisetty et al., 2018).

2. **Chemical Oxidation:** This reliable method employs minimal setup. It involves adding an oxidizing agent to wastewater, triggering electron transfer from the oxidant to contaminants, inducing structural changes. Oxidation can eliminate organic and certain inorganic compounds like iron and manganese from water. Typical oxidants used include chlorine, chlorine dioxide, permanganate, oxygen, and ozone. Advanced oxidation technologies, incorporating processes like steam stripping or activated carbon adsorption, assist in removing toxic chemical oxidation by-products (Bolisetty et al., 2018). The key advantage of this method is its destructive nature, preventing secondary pollution (Herrmann, 1999, Ibadon and Fitzpatrick 2013).
3. **Electrochemical Treatment:** Three significant electrochemical treatment technologies are electrocoagulation (EC), electro flotation (EF), and electrode position. Pollutants like heavy metal ions are retained in wastewater due to surface electrical charges or hydrogen bonds. Applying an electric field neutralizes electrostatic charges binding suspended or emulsified pollutants, causing them to coagulate from the aqueous phase. Heavy metal particles aggregate like small magnets, forming sludge or floc. EC-produced flocs have larger sizes, reduced bound water, and enhanced stability compared to other techniques. Flocs can be efficiently removed from the solution at minimal expense. EF separates pollutants by floating them to the liquid phase surface.

Electro deposition offers benefits such as requiring no additional reagents, producing no sludge during the process, and being highly selective and cost-effective. It transforms dissolved metal ions into solid particles by deposition on ionic conductors (cathode and anode), protecting them from corrosion. Advantages of this method include the removal of most metals, eliminating chemical consumption, and selectively targeting metal ions. Drawbacks include high energy consumption, as well as high operational and capital costs (Elimelech et al., 1998).

4. Adsorption: Adsorption's principle involves mass transfer between the liquid phase and the solid-phase adsorbent. The process of absorbing contaminants on the adsorbent includes three key steps (Darban et al., 2020):
  - i. Pollutant penetration from solution to the adsorbent surface.
  - ii. Pollutant adsorption on the adsorbent surface
  - iii. Infiltration into the adsorbent structure. A widely used and effective adsorbent is activated carbon.

Advantages of this method include its high performance and reduced treatment time. Disadvantages include limited regeneration, high cost, and efficiency dependence on the adsorbent (Darban et al., 2020).

5. Photodegradation: Photodegradation involves the chemical breakdown of complex molecules into smaller, non-toxic, and lighter molecular weight species using a broad spectrum of light. It is a light-induced photocatalytic reaction that effectively oxidizes/reduces organic pollutants through simple redox reactions (Nagajyothi et al., 2019). The process initiates with photon absorption in the UV, visible, or IR spectral ranges (Yousif and Haddad, 2013, IUPAC, 1996). Photodegradation is a promising energy-saving technology that directly converts light energy into chemical energy for degrading and eliminating organic compounds (Tolia et al., 2012, Burrows et al.,

2002). Significantly, photodegradation outperforms other conventional methods due to complete pollutant mineralization, simplicity, absence of harmful byproducts, cost-effectiveness, operation at ambient pressure and temperature, and reduction of pollutants to ppm and ppb concentrations (Pouretedal and Kiyani, 2014, Zheng et al., 2019). Additionally, the process utilizes solar and visible light as economical energy sources (Ahmed et al., 2011). Available photodegradation techniques include UV photolysis, photooxidation using oxidants (e.g., hydroxyl radicals, H<sub>2</sub>O<sub>2</sub>, ozone), and UV photocatalytic oxidation (PCO) (Ray, 2000). Notably, photodegradation eliminates conventional wastewater treatment methods, making it a green technology in the field of environmental purification (Pouretedal and Kiyani, 2014, Saeed et al., 2015). Another key feature of photodegradation is its adaptability to both air (Julson and Ollis, 2006) and aqueous environments (Vallejo et al., 2020).

## **2.6 TYPES OF PHOTODEGRADATION**

1. Homogeneous photodegradation: Reactants and catalysts are uniformly distributed in liquid solution. Molecular catalysts mediate oxidation and reduction reactions. Examples include ozone and photo-Fenton systems. The reactive species is OH• radicals (Devi et al., 2022).
2. Heterogeneous Photodegradation: The photocatalyst and pollutants reside in different phases. Semiconductor-mediated photocatalysis is widely used for its ease of catalyst separation and energy efficiency (Devi et al., 2022).  
Heterojunction photocatalysts, composed of different materials, enhance photocatalytic activity (Wang et al., 2014):
  - i. Semiconductor-semiconductor (S-S)
  - ii. Semiconductor-metal (S-M)

- iii. Semiconductor-carbon group (S-C)
- iv. Multicomponent heterojunction

Semiconductor photocatalysts absorb light energy to generate electron-hole pairs, which produce highly reactive radicals that degrade pollutants through secondary reactions or direct electron/hole transfer.

The efficiency of a photocatalyst is heavily influenced by its capacity to produce an e-h pair upon light absorption. The photo-generated e-h pair in the semiconductor catalyst usually has a very short lifetime, necessitating the quick use of these free electrons and holes in secondary reactions before they recombine (Bora and Dutta, 2014). For instance, the holes in TiO<sub>2</sub>'s valance band (VB) are strong oxidizing agents with a redox potential of about +1.0 to +3.5V against NHE (normal hydrogen electrode), while electrons in the conduction band (CB) are strong reducing agents NHE (Zoski, 2007). As a result, the holes oxidize surface-adsorbed organic molecules with a redox potential of around +0.5 to -1.5 V versus NHE, while electrons reduce them either directly or indirectly, as previously stated. Heterogeneous photocatalytic oxidation has been demonstrated to be highly effective in degrading and transforming persistent organic pollutants like chlorobenzene into more biodegradable and less toxic compounds. Under normal conditions, this reaction produces hydroxyl radicals, resulting in end products like CO<sub>2</sub> and H<sub>2</sub>O (Trapalis et al., 2016).

## **2.7 PHOTODEGRADATION RATE AFFECTING PARAMETERS**

Certain factors can influence the rate of photodegradation, including temperature, pH, contact time, light intensity, wastewater concentration, and catalyst dosage. These are explained further below.

1. Effect of Temperature: According to numerous studies, temperature has a significant impact on the rate of photocatalytic reactions (Malato et al., 2009, Malato et al., 2016, Chong et al., 2010). Shen et al investigated and compared the adsorption rates of  $\text{Cu}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  on  $\text{Fe}_3\text{O}_4$  at various temperatures. This study found that the adsorption rates of  $\text{Cr}^{6+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  increased with temperature, whereas the adsorption rate of  $\text{Cu}^{2+}$  remained largely unaffected (Shen et al., 2009). It has been shown that adsorption of reactants on the  $\text{TiO}_2$  surface is hindered at temperatures above  $80^\circ\text{C}$  (Malato et al., 2009, Malato et al., 2016, Chong et al., 2010). However, temperatures as low as  $0^\circ\text{C}$  have been found to enhance the apparent activation energy, impeding the desorption of the final product (Malato et al., 2009). As a result, the reaction's optimal temperature range is reported to be between  $20^\circ\text{C}$  and  $80^\circ\text{C}$ .
2. Effect of pH: pH is a crucial operating parameter that affects the size of catalyst aggregates, the charge on catalyst particles, and the position of conduction and valence bands. Hydroxyl radicals (which are strong oxidizing agents) are generated by establishing alkaline conditions and changing the pH, enhancing the efficiency of pollutant removal. The pH of the solution is known to affect the surface charges present on adsorbent surfaces, which in turn can significantly impact the adsorption process. The ionization of contaminants in the solution can also be substantially affected by the solution's pH (Naveen et al. 2016). This improvement in removal rate is due to the deprotonation of the adsorbent surface, which is likely to result in a negative surface charge at that pH (Badmus and Audu 2009).
3. Effect of Contact time: The efficiency of absorption or removal is heavily influenced by the reactants' contact time as well as the semiconductor's irradiation time. Adsorption rate has been found to be directly proportional to contact time (Li et al., 2012, Shen et al., 2009). However, some pollutants, such as  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$ , have been

found to adsorb more readily than  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ , indicating that the rate of adsorption for  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  is more dependent on contact time (Ahmed and Haider, 2018). By extending the contact period, the removal efficiency is increased to a maximum before reaching a constant rate. The number of metal hydroxides produced rises as the contact time increases.

4. **Effect of Catalyst Dosage:** Generally, increasing the catalyst quantity enhances photodegradation. This stems from increased fresh active sites that absorb more photons and produce more  $\text{OH}\cdot$  radicals and positive holes. However, beyond an optimal threshold, an increase in catalyst dosage may lower the photodegradation rate due to a turbid solution inhibiting UV penetration (Coleman et al., 2007).
5. **Effect of Light Intensity:** While the initial onset of photocatalytic reactions is largely independent of light intensity, higher intensity is required for an efficient reaction rate. Increased light intensity ensures sufficient photon energy for each catalyst active site. More photons per unit area lead to increased reactive radical generation and enhanced photocatalytic outcomes (Chong et al., 2010). However, excessive light intensity should be avoided, as it elevates the reaction temperature, potentially leading to thermal reactions (Yadav and Meena, 2010). The wavelength and intensity of light significantly influence the photocatalytic reaction and vary depending on the photocatalyst employed (Chong et al., 2010).
6. **Effect of Concentration:** In photocatalytic degradation, initial concentration plays a crucial role. Increasing pollutant concentration with a fixed amount of photocatalyst decreases the degradation rate as more organic pollutants cover the photocatalyst surface, limiting photon access. This results in reduced active species formation and a decrease in decolorization. Conversely, decreasing concentration enhances

degradation because fewer active sites are covered, promoting the generation of OH radicals on the catalyst surface.

## 2.8 USES OF PHOTODEGRADATION

1. **Water and Wastewater Treatment:** Photocatalysis, utilizing semiconductor photocatalysts, is widely employed in water and wastewater purification. In photocatalysis, the primary function of these semiconductors is to facilitate the transfer of light energy to charge carriers (Zhao et al., 2015). Semiconductors like TiO<sub>2</sub> and ZnO possess strong UV absorption and can efficiently photodegrade organic contaminants and toxic metal ions. This technology can also be applied to seawater treatment, particularly for removing water-soluble fractions of crude oil after spills (Ziulli and Jardim, 2001; Rocha et al., 2010).
2. **Removal of Organic Contaminants:** Photocatalysis has proven effective in degrading harmful organic contaminants in water into benign byproducts, primarily carbon dioxide and water. Various types of alcohols, carboxylic acids, phenolic derivatives, and chlorinated aromatic contaminants have been successfully targeted using this technique (Bhatkhande et al., 2001; Mills et al., 1993). In developing nations, the release of pollutants from industries into rivers is a significant concern, and semiconductor metal oxides have shown promise in photocatalytically degrading these pollutants (Chan et al., 2011; Danwittayakul et al., 2013)
3. **Removal of Inorganic Contaminants:** Photocatalysis can effectively decompose inorganic contaminants such as halide ions, cyanide, thiocyanate, ammonia, nitrates, and nitrites (Hoffmann et al., 1995; Mills et al., 1996). TiO<sub>2</sub> has been extensively studied for its photocatalytic activity against silver nitrate by Chakhtouna et al. Serpone et.al, worked on the photo-reduction and elimination of Hg (II) and CH<sub>3</sub>Hg

(II) chloride salts from aqueous suspensions of titanium dioxide using AM1 simulated sunlight. TiO<sub>2</sub> nanoparticles have also shown high efficiency in photocatalytically converting ammonia to nitrogen under visible irradiation according to Lee et al.

4. **Removal of Heavy Metals:** Heavy metal removal from wastewater is crucial for treatment plants, as the presence and quantity of these metals vary depending on the wastewater source. Removing toxic heavy metals from water bodies is paramount for human health and water quality. Photocatalysis offers a promising method for recovering rare and expensive metals (Bora and Dutta, 2014). Gold (III), platinum (IV), and rhodium (III) have been successfully recovered using TiO<sub>2</sub> dispersions by Minero and co-workers as early as in 1986 (Borgarello et al., 1986). Cadmium removal from wastewater using nanosized TiO<sub>2</sub> particles has also been investigated, with high reduction and recovery rates reported (Skubal et al., 2002). Recovery of gold from samples consisting of cyanide ions was also shown by Serpone et al. along with the degradation of CN<sup>-</sup> by utilizing two peroxides, H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (Serpone et al., 1987).
5. **Eradication of Microbes:** Many photocatalysts also demonstrate antibacterial properties and inhibit microbial growth. The mechanism primarily involves the destruction of the microbes' cell wall by highly reactive radicals generated during photocatalysis, leading to their eventual destruction. Various pathogenic bacteria and viruses, including *Streptococcus mutans*, *Streptococcus natans*, *Streptococcus cricetus*, *Escherichia coli*, *Scaccharomyces cerevisias*, and *Lactobacillus acidophilus*, can be eradicated using heterogeneous photocatalysis (Mills and Hunte, 1997). Zinc oxide (ZnO) has also shown promising antimicrobial effects against *Escherichia coli* and *Staphylococcus aureus* (Baruah et al., 2012; Jaisai et al., 2012; Ajaya et al., 2011).

6. **Air Treatment:** Air pollutants, particularly sulfur dioxide and nitrates, can pose long-term health hazards. Similar to water purification, TiO<sub>2</sub> is the most widely investigated photocatalyst for air purification. TiO<sub>2</sub> coatings and nanotubes have effectively removed acetone (Rao et al., 2010), ethanol (Rao et al., 2010), toluene (Shiraishi and Ishimatsu, 2009, Rao et al., 2010), and volatile organic compounds (Chen and Zhang, 2008). In recent years, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has also shown significant potential for air purification, even under visible light irradiation (Dong et al., 2014).

## **2.9 ILLUMINATION SOURCE FOR PHOTODEGRADATION**

1. **Natural Sunlight:** Put simply, natural light is light that occurs naturally, primarily emitted by the sun. It is a cost-effective light source. Solar irradiation is an economical alternative light source due to its abundance, accessibility, and non-hazardous nature (Reza et al., 2017). However, solar light consists of 5% UV light (200–400 nm), 43% visible light (400–800 nm), and 52% IR (> 52%) (Sarina et al., 2013)
2. **Artificial Light:** Sources can be employed to maintain consistent intensities unaffected by cloud cover or other environmental factors. Compared to solar irradiation, artificial light can enhance the efficiency of photocatalytic activity. It offers greater reproducibility than sunlight. Examples include ultraviolet light, visible light, etc. The energy of visible light photons is lower than that of UV light photons. Therefore, photocatalysts with wider bandgaps, such as TiO<sub>2</sub>, can only absorb UV light for activation (Sarina et al., 2013).

## **2.10 TITANIUM DIOXIDE AS A PHOTOCATALYST**

When photons interact with semiconductor materials, a catalytic process known as photocatalysis occurs on their surface. Developing photocatalysts that improve charge carrier separation and enable practical applications in environmental remediation and hydrogen production is a key challenge for photocatalysis researchers (Verma et al., 2014).  $\text{TiO}_2$  acts as a medium and is a semiconductor when stimulated by light, allowing electrons to transition from the valence band to the conduction band while holes ( $h^+$ ) remain in the valence band. Consequently, electrons and holes migrate to the semiconductor's surface and participate in a series of reduction and oxidation reactions (Zhao et al., 2017). Upon irradiation by photons, electrons on  $\text{TiO}_2$ 's surface are excited to the conduction band, and positive holes are formed in the valence band. The electrons and holes can either recombine and release thermal energy or interact with other molecules (Venkatadri and Peters, 1993). The holes can react with electron donors in the solution to generate potent oxidizing free radicals, such as hydroxyl radicals, which oxidize the surface organics. Additionally, the holes can oxidize the substrate through direct electron transfer. Among commonly used semiconductors,  $\text{TiO}_2$  and  $\text{ZnO}$  have demonstrated wide-ranging environmental applications. Although  $\text{ZnO}$  possesses unique physical and chemical characteristics as a photocatalyst, including a wide band gap (3.2 eV) and high exciton binding energy (60 meV) at room temperature, its use is limited due to its tendency to dissolve in acidic solutions.

### **2.10.1 BENEFITS OF TITANIUM DIOXIDE**

1. It is frequently utilized in hydrogen production and energy conversion. Titanium dioxide, among numerous photocatalysts, stands out due to its non-toxic nature, exceptional physical properties and strong oxidizing power (Pirkanniemi and Sillanpaa, 2002).

2. It is highly significant as it ensures that organic pollutants are generally completely degraded into non-toxic substances like CO<sub>2</sub>, HCl, and water, thereby avoiding the disadvantages of photolysis reactions in terms of intermediate product formation. Furthermore, the reaction can occur at ambient temperature (Aramendia et al. 2005; Malato et al. 2003; Chatterjee and Dasgupta 2005).
3. It has strong activity and is economical and accessible. Factors enriching TiO<sub>2</sub> photocatalytic action are its specific surface area, the adsorption potency and potential for organic contaminants, electron-hole recombination procedure in the volume and on the surface of the catalyst as well as the force and spectral circulation of the shining light.
4. Titanium dioxide is a widely accepted photocatalyst due to high photo stability, chemical inertness and environmental friendly nature (Cai et al., 2015; Jongprateep et al., 2015).

### **2.10.2 DRAWBACKS OF TITANIUM DIOXIDE**

A disadvantage of employing TiO<sub>2</sub> is the quick electron/hole recombination rate, which is paired with the scattering of energy as heat. Additionally, the substantial electron pair recombination rate decreases the success of the photocatalytic procedure. The deficiency of proper electron acceptors is a significant energy-wasting phase. Using oxygen as an electron scavenger partly resolves this problem but results in low mineralization photo-efficiency (Malato et al., 2009). Titanium dioxide has restrictions as a photocatalyst due to its large band gap. These traits confine its photocatalytic performance. TiO<sub>2</sub>'s significant band gap restricts its reaction to light, leading to limited photo-efficiency. Attempts have been made to increase the photocatalytic performance of TiO<sub>2</sub> to address these restrictions, including changing the composition, doping additional metals, and creating junctions with other metal oxides.

### **2.10.3 MODIFICATION OF TITANIUM DIOXIDE**

Untainted and unaltered TiO<sub>2</sub> works under subdued situations with subdued oxidants and only utilizes the UV range. But, the procedure gets harder at higher contaminant levels due to catalyst deactivation, slow kinetics, and low photo-efficiencies. To employ unaltered TiO<sub>2</sub> for practical purposes like treating industrial and environmental effluents, artificial light must be utilized, raising the price of the procedure. However, altering or doping TiO<sub>2</sub> can eliminate this high cost and prevent catalyst deactivation (Malato et al., 2009).

Modifying regular titanium dioxide to enhance photocatalytic activity is imperative and crucial. Titanium-based composites incorporating precious metals, transition metals, non-metallic elements, metal ions, and rare earth metal ion doping have demonstrated efficacy as methods for boosting photocatalytic activity (Nam et al., 2018; Kaur and Singh, 2017; Panwar et al., 2022; Obotey and Rathilal 2020; Fernandes, et al., 2020; Alosfur et al., 2018).

### **2.11 PERIWINKLE SHELLS**

Periwinkle shell is a waste byproduct from eating periwinkles, a tiny greenish-blue sea snail with a V-shaped spiral shell (Olutoge et al., 2012). The climbing use of shelly seafood, especially in beachfront neighborhoods, as a nutritional protein source, cannot be understated. Periwinkles (*Tympanotonus fuscatus*) are common in the Niger Delta's coastal areas of mangroves, swamps, and mudflats (Olutoge, et al. 2012; Fayeofori, 2012). Its shell, around 70% of its weight (Yao, et al. 2014), is considerably harder and more robust than that of a regular snail. *Tympanotonus* has only one species with two subspecies, *Tympanotonus fuscatus* var *fuscatus* (Jamabo, et al. 2010) and *Tympanotonus fuscatus* var *radula* (Moruf, 2015). *Tympanotonus fuscatus* var *fuscatus* is known for its turreted, granular, and thorny shells. On the contrary, the absence of a thorny tubercle on the shell differentiates

*Tympanotonus fuscatus* var *radula* from the other subspecies. Herbivores make up a significant portion of these invertebrates. They range in size from small (about 2.5cm long) to large (about 5cm long). Locals in the area frequently refer to these periwinkles as male and female due to their distinct characteristics. Nigeria generates around twelve million tons of waste shells yearly, which are thrown away on land and on seashores. Periwinkle shells make up a sizable portion of this waste. These shells litter marketplaces, residential areas, and local garbage dumps without a reliable waste disposal system, contributing to environmental and air pollution.(Aimikhe and Gospel, 2021)



Fig 2.1 Periwinkle shell

### **2.11.1 APPLICATION OF PERIWINKLE SHELL**

1. **Building Materials and Construction:** Periwinkle shells are commonly employed in the building and construction industries. Locals in coastal areas with a lot of shell waste utilize it as a partial replacement for cement, fine aggregates, or coarse aggregates to create mostly pavement slabs. Studies by Soneye et al, Otunyo et al. and Agbede and Manasseh looked at how periwinkle shells could be used instead to make composite blocks and concrete.

2. **Wastewater Treatment and Bio-filters:** Like other waste shells, periwinkle shells have been utilized in wastewater treatment and biofilters to mostly eradicate harmful and poisonous contaminants from wastewater (Okwo and Ozioko; 2011, Akanbi and Babayemi, 2019)
3. **Suspension Loss Additive in Drilling Fluids:** Drilling fluid, commonly known as mud, represents a thick liquid compound utilized in oil and gas well construction processes to facilitate the removal of excavated materials. To enhance the filtration control efficiency of the drilling fluid, fibrous, flaky, or granular substances have been suggested as suspension loss additives, effectively sealing pores and mitigating fluid loss.(Aimikhe and Gospel, 2021)
4. **Biomedical Applications:** In the field of orthopedic medicine, biomaterials serve as the foundation of prosthetic devices, replacing human bones and providing bone filler solutions. Nevertheless, these biomaterials must exhibit compatibility within their target environment, possessing adequate physicochemical characteristics and thermal stability (Saji et al. 2018). Research (Rujitanapanich et al. 2014, Karunakarana et.al 2019; Wu et al. 2017) has demonstrated that  $\text{CaCO}_3$  chitin materials derived from discarded shells can be employed in the synthesis of calcium phosphate (hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), the primary mineral component of human bones.
5. **Development of Asbestos-free Brake Pads:** Brake pads are essential components within industrial machinery, particularly automobiles, playing a crucial role in decelerating and eventually halting a moving object through the conversion of kinetic energy into heat energy via friction between the pads and the disc. Brake pads consist of steel plates bonded to a friction material (Aigbodion et al. 2010), typically

composed of a variable mix of abrasives, lubricants, binders, fillers, and performance modifiers.

## **2.12 CLAY ROOF TILES**

Through a baking process, molded clay forms the basis of clay roof tiles. The tile's density is dictated by the temperature and duration of the heating process. Variations in color exist, with shades ranging from white to yellow, orange, and even brown. However, Terra-cotta stands as the most common color encountered. High baking temperatures fuse the color into the tile, ensuring resistance to peeling or fading, contributing to their exceptional longevity and insulation qualities.



Fig 2.2 Clay Roof Tiles

### **2.12.1 PROPERTIES OF CLAY ROOF TILES**

Characterized by a large surface area and abundant active sites, clay roof tiles display remarkable chemical and mechanical stability, featuring a layered structure and high porosity. Their low cost, ample availability, and non-toxic nature render them ideal as efficient

adsorbents, complemented by their exceptional adsorption properties and robust ion exchange capabilities.

## **2.13 CASSAVA**

Cassava (*Manihot esculenta* Crantz), belonging to the Euphorbiaceae family is a major staple crop cultivated in different parts of Sub-Saharan Africa, Central and South America, and Southeastern Asia by most peasants and smallholder farmers. Its roots boast a wealth of carbohydrates, proteins, and additional nutrients (Assanvo et al., 2017; Barceloux, 2009). Consequently, it serves as a vital crop in over 89 nations, making substantial contributions to rural socio-economic conditions, particularly in developing regions, and encompassing all economic sectors (Santos et al., 2020; Watthier et al., 2019). Nigeria being the world leading producer of cassava accounts for 52,403 million tons annually (FAO, 2012). Amongst its diverse applications for human and animal consumption, cassava holds significant value in the food, textile, alcohol, pharmaceutical, and paper industries (De Souza Fernandes et al. 2019; Acchar and Da Silva 2021). Cassava tubers can be processed into a variety of high calorific foods such as garri (toasted granules), fufu (fermented cooked paste), flour, starch, tapioca (kpokpo-garri flakes) and other confectioneries (Coker et al., 2015; Oghenejoboh, 2012). The roots of some cassava varieties that have low cyanide content can even be cooked and eaten without further processing (Onwuka and Ogbogu, 2007 ; Oghenejoboh, 2012). The different products derived from cassava makes it especially fitting as low cost and high calorific food for many poor Nigerians. However, the cassava processing industry generates abundant waste, including effluent from cassava processing and solid residue (peels, bagasse, stem, and leaves) (Tumwesigye et al. 2016).



Fig 2.3 Cassava

### **2.13.1 COMPOSITION OF CASSAVA WASTEWATER**

The wastewater derived from cassava processing refers to the residue remaining after the washing and peeling of cassava roots (Chisté et al. 2006). It is a yellowish liquid generated during the pressing stage of cassava flour production. It contains residues composed of starch, glucose, cyanide, carbohydrates, proteins, lipids, and minerals. Its composition varies with environmental factors (climate, soil, and cassava cultivar).

Constituting roughly 30% of the original material, cassava wastewater can present an environmental challenge (Wosiacki and Cereda 2002). Its potential for environmental pollution stems from the high content of organic matter (composition) and the presence of glycosides capable of generating cyanide (Kuyucak and Akcil 2013; Tumwesigye et al. 2016). Boadi et al. (2008) reported that cyanide range in raw cassava root and its peels is between 360.05 to 509.51 mg/kg. Ingestion of cyanide above 30 ppm can lead to respiratory problems and eventually death (Ogunyemi et al., 2018). This is the reason why cassava root should be thoroughly prepared through peeling, slicing, crushing, draining and roasting before consumption. Cyanide possesses the ability to bind with metals, such as the iron in

hemoglobin, impeding oxygen delivery to cells and promoting asphyxiation. Due to its toxicity, wastewater treatment prior to discharge requires heightened attention for both human and animal safety (Kuyucak and Akcil 2013).

The organic load of cassava wastewater highlights its potential as a pollutant if not properly treated or utilized (Pinto 2008; Acchar and da Silva 2021). Alternatively, its high concentration of micro and macronutrients makes it a viable substrate for biotechnological applications.

## **2.14 ADSORPTION**

Adsorption refers to the process by which gaseous or liquid substances (adsorbates) accumulate on the surface of a solid. The adsorbate is the substance being adsorbed, while the adsorbent is the material that adsorbs it (Do, 1998). Adsorption results from unbalanced molecular forces on the solid surface. The solid surface compensates for these forces by attracting and retaining molecules or ions from the surrounding medium

Adsorption can be classified based on the nature of surface forces, which can be chemical (chemisorption) or physical (physisorption). In chemisorption, chemical forces or valency forces between the adsorbate and adsorbent form chemical bonds, such as ionic, metallic, or covalent bonds. Chemisorption is typically limited to a monolayer, and the bond is stronger and more specific than in physisorption forces (Ruthven 2008).

Physisorption involves the attraction of the adsorbate to the solid surface by weak physical forces, primarily van der Waals interactions (Ruthven 2008). Physisorption forces are also known as dispersion forces. Due to the low energy requirements, physisorption typically reaches equilibrium rapidly and is easily reversible. Physisorption can involve the formation of multilayer structures.

Surface diffusion, defined as the movement of atoms between adjacent adsorption sites on metal surfaces, can also play a role in adsorption processes (Antczak and Ehrlich 2004).

Activated carbon and silica gel have been known to exhibit surface diffusion when relative humidity exceeds 40% (Bart and Gemmingen 2005).

#### **2.14.1 ADVANTAGES OF ADSORPTION**

1. Allows for the selective recovery of specific chemicals from dilute solutions.
2. Its design, operation, and scale-up processes are relatively simple and straightforward.
3. It exhibits a high capacity and a favourable rate, and it remains unaffected by the presence of harmful substances (Soto et al. 2011).
4. Adsorbed compounds can also be recuperated through desorbing agents, chemical reagent leaching, biological procedures, and thermal treatment (Kikuchi and Tanaka 2012).

#### **2.14.2 ADSORPTION MECHANISM**

Researchers have suggested that adsorption presents a highly effective approach for the removal of pollutants from wastewaters (Kulkarni, et al., 2013; Cotman and Gotvajn, 2010; Lorenc, et al., 2013 and Hua, et al., 2012). Adsorption involves the mass transfer of material from a liquid phase to a solid phase, where physical and chemical interactions occur at the interface. Physical attributes, substantial surface area, microporous framework, high adsorption capacity, and surface reactivity of the adsorbent significantly influence the adsorption process.

### 2.14.3 ADSORPTION ISOTHERMS

Generally, an adsorption isotherm represents the result of equilibrium interactions between the adsorbent and adsorbate species (Al-ghouti and Da, 2020). This study employed the Langmuir and Freundlich isotherms.

#### 2.14.3.1 LANGMUIR ISOTHERM MODEL

Langmuir Isotherm describes the quantitative formation of a monolayer adsorbate on the external surface of the adsorbent. The adsorbent is assumed to possess a finite adsorption capacity  $q_{\max}$ . Langmuir proposed the following equation (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (2.1)$$

$q_m$  is the maximum sorption capacity (mg/g) of the adsorbent,  $q_e$  (mg/g) represents the quantity of adsorbed COD,  $C_e$  (mg/L) represents the pollutant concentration at equilibrium and  $K_L$  is the Langmuir constant (L/mg).

A linear plot of  $\frac{C_e}{q_e}$  against  $C_e$  was used to calculate the values of  $q_o$  and  $K_L$ .

The key characteristics of the Langmuir isotherm can be described using a dimensionless constant separation factor  $R_L$ , defined as:

$$R_L = \frac{1}{1 + K_L C_o} \quad (2.2)$$

$C_o$  is the initial concentration of solute

The  $R_L$  number indicates whether the isotherm is favourable ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), or reversible ( $R_L = 0$ ). If the values of  $R_L$  range from 0 to 1, the isotherm is likely to be favourable under the tested conditions (Hamzaoui et al., 2018).

### 2.14.3.2 FREUNDLICH ISOTHERM MODEL

The Freundlich isotherm describes a heterogeneous system and reversible adsorption. It assumes that an adsorbent has a finite number of sites, and once these sites are occupied by adsorbed molecules, no further adsorption can occur. The Freundlich equation is expressed as follows:

$$q_e = K_f C_e^{1/n} \quad (2.3)$$

The above equation can be expressed in its linearized form as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2.4)$$

Here,  $q_e$  (mg/g) represents the quantity of adsorbed COD,  $C_e$  (mg/L) represents the pollutant concentration at equilibrium,  $k_f$  (mg/g) represents the adsorption capacity (also known as the Freundlich constant) and  $n$  (L/mg) represents the adsorption constant.

A linear plot of  $\ln q_e$  against  $\ln C_e$  was employed to calculate the values of the constants. The values of  $n$  between 1 and 10 typically indicate beneficial and favourable adsorption.

The mass balance equation was used to calculate  $q_e$  (mg/g) (the quantity of adsorbed COD):

$$q_e = \frac{v(C_o - C_e)}{m} \quad (2.5)$$

Where  $C_o$  is the initial concentration of solute,  $C_e$  is the pollutant concentration at equilibrium,  $m$  is the mass of adsorbent and  $V$  is the isotherm solution volume

#### 2.14.4 KINETIC MODELLING

In engineering applications, it is essential to determine an appropriate rate equation that accurately reflects experimental observations. As adsorption is believed to play a crucial role in the heterogeneous photocatalytic degradation process, the kinetics of the photodegradation process were investigated using three different kinetic models: pseudo first order, pseudo second order and intra-particle diffusion kinetic models. These models are described in detail in the following sections.

##### 2.14.4.1 PSEUDO-FIRST -ORDER KINETIC MODEL

Lagergren (1898) established the pseudo-first order kinetic model, which is commonly utilized to define the rates of adsorption processes. The pseudo-first-order kinetic model is represented by the equation (Lagergren et al., 1898):

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (2.6)$$

$K_1$  represents the pseudo-first order rate constant (1/min), and  $q_e$  and  $q_t$  represent the amounts adsorbed (mg/g) at equilibrium and at time  $t$ .

The gradient and intercept of the plot of  $\ln(q_e - q_t)$  against  $t$  create a linear relationship from which the  $k_1$  and  $q_e$ , are calculated.

##### 2.14.4.2 PSEUDO-SECOND -ORDER KINETIC MODEL

As it accurately models experimental data, the pseudo-second order kinetic model based on adsorption equilibrium capacity is also extensively employed. The model can predict behavior across the entire adsorption range (Ho and McKay 1999). The equation (Ho and McKay 1998) representing the pseudo-second-order kinetic model is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (2.7)$$

$K_2$  is the rate constant of the pseudo second order process (g/mg.min).

The plot of  $\frac{t}{q_t}$  versus  $t$  was used to calculate the values of the model parameters.

#### 2.14.4.3 INTRA-PARTICLE DIFFUSION MODEL

The diffusion mechanism of the process was modelled using the intra-particle diffusion model as follows:

$$q_t = k_p t^{1/2} + C \quad (2.8)$$

$K_p$  is the intra-particle diffusion rate constant (mg/g.min<sup>1/2</sup>) and  $C$  is a measure of the boundary layer effect.

The plot of  $q_t$  versus  $t^{1/2}$  was used to calculate the values of the constants.

## **CHAPTER THREE**

### **MATERIALS AND METHODS**

#### **3.1 MATERIALS**

For this study, the photocatalysts chosen were Periwinkle shell ash, Clay roof tiles, and titanium dioxide (TiO<sub>2</sub>). Periwinkle shell ash was sourced from the Department of Chemical Engineering Laboratory at the University of Benin, in Benin City, Edo State, Nigeria. Roof tiles were acquired at Cook road in Benin City, while titanium dioxide was procured at Ring road in Benin City. The cassava wastewater was obtained at Okada in Benin City

#### **3.2 LIST OF REAGENTS AND THEIR USES**

1. Sodium Hydroxide (NaOH) and Hydrochloric (HCl) Acid was used for pH adjustment.
2. Hydrogen Tetraoxosulphate (VI) acid (H<sub>2</sub>SO<sub>4</sub>) was used for the activation of the periwinkle shell and roof tiles.

#### **3.3 EQUIPMENT**

##### **3.3.1 MULTI-LAMPS UV FLOW THROUGH PHOTOCATALYTIC REACTOR**



Fig 3.1 Multi-Lamps UV flow through photocatalytic reactor

### 3.3.2 ELECTRONIC WEIGHING BALANCE

The weight of the various catalyst used in the course of the experiment were measured with the aid of a weighing balance.



Fig 3.2: Electronic weighing balance

### 3.3.3 pH METER

The pH of the various solutions was measured with an electronic pH meter. The pH of the solution was adjusted with help of HCL and NaOH. The pH meter was calibrated with a buffer solution.



Fig 3.3: pH Meter

The following apparatus were used:

1. Conical flask: It was used in the preparation of the different solutions and also for the storage of the solutions.
2. Beaker: It was also used in the preparation of the different solutions.
3. Spatula: It was used to transfer the solid into their respective containers.
4. Measuring cylinder: It was used to measure the required volumes of liquid when preparing a solution.
5. Volumetric Flask: It was used for the preparation of the concentrations of cassava wastewater from the stock solution
6. Filter paper: It was used to filter each sample after the experiment.
7. Tight Lid Plastic Containers: It was used to store the prepared concentrations and modified sample to avoid contamination.
8. Stirrer: It was used for stirring the solution during preparation.
9. Sieve: It was used to sieve the crushed adsorbent fiber into fine particle size.
10. Masking Tape: It was used to label the containers used for easy identification.
11. Plastic Funnel: It was used to aid in the transferring of solution from one container to another.

### **3.4 ACTIVATION OF THE PERIWINKLE SHELL AND ROOF TILES**

The periwinkle shell and roof tiles were thermally activated by calcination in a furnace at 800°C for 4 hours (Calcination eliminates carbon-based and volatile substances, enhancing the surface area of the photocatalyst. This facilitates adsorption and effective utilization of light energy) prior to activation using a 0.1M solution of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). The powdered periwinkle shell and roof tiles was impregnated with the acid in a ratio of 1:2. The mixture was mechanically agitated for uniform distribution of the acid throughout the powder. The acid-infused periwinkle shell and roof tiles was left for 24 hours for thorough saturation. The activated powder was subsequently cleansed using distilled water to eliminate any remaining acid until a pH of 7 (neutral) was achieved. The activated powder was subjected to drying at 150°C in an oven to eliminate moisture and stored in an airtight container until required for use.

### **3.5 CHARACTERIZATION OF THE PERIWINKLE SHELL AND ROOF TILES**

The Rolab Research and Diagnostic Laboratory in Ibadan received 20g of each of the activated and unactivated samples, and used a range of analytical techniques to investigate and describe them. These techniques included:

1. Fourier Transform Infrared (FTIR) spectroscopy: The functional groups on the Periwinkle shell and Roof tiles surface were determined by Fourier transform infrared spectrometry (FTIR) using a Perkin Elmer spectrum 3000 MX spectrometer in the frequency range 4000 to 400 cm<sup>-1</sup>. The purpose of this technique is to get some insight into how these groups could inherently affect the adsorption process.
2. Brunauer-Emmet-Teller (BET): The surface area, the pore size, pore volume of the catalyst was determined using the standard BET techniques (Aisien et al., 2014).

3. Scanning Electron Microscopy (SEM): This produces detailed and magnified images of the catalyst by scanning its surface to create a high resolution image. SEM does this using a focused beam of electrons. The resulting images show information about what the catalyst is made of and its physical features.
4. X-ray Fluorescence (XRF): The prepared catalyst was characterised by using XRF analysis to determine its oxide composition (Aku et al., 2012).

### **3.6 PHOTODEGRADATION TREATMENT PROCEDURE**

#### **Effect of modified catalyst variation**

In investigating the effect of modified catalyst variation on the photodegradation of the cassava wastewater;

1. Titanium dioxide was modified with the absorbent using a ratio of 1 to 2. i.e for every 1g of titanium dioxide that was added, we use 2g of the absorbent
2. The concentration of the catalyst was varied at 0.4, 0.8, 1.2,2 and 3 g/L
3. 2L of the cassava wastewater was measured and mixed with the modified catalyst
4. The other variables were left constant; temperature at 25°C, UV light at 450W, pH at 3.6, agitation speed at 1200rpm and flow rate at 120L/min.

#### **Effect of unmodified catalyst variation**

In investigating the effect of unmodified catalyst variation on the photodegradation of the cassava wastewater;

1. The concentration of titanium dioxide was varied at 0.4, 0.8, 1.2,2 and 3 g/L
2. 2L of the cassava wastewater was measured and mixed with the unmodified catalyst
3. The other variables were left constant; temperature at 25°C, UV light at 450W, pH at 3.6, agitation speed at 1200rpm and flow rate at 120L/min.

### **Effect of cassava wastewater concentration variation**

In investigating the effect of the concentration of the wastewater variation on the photodegradation of the cassava wastewater;

1. The concentration of the wastewater was varied at 100, 200, 300, 400, 500 ml/L using the best dosage between the modified and unmodified catalyst obtained from the previous runs of experiment
2. The other variables were left constant; temperature at 25°C, UV light at 450W, pH at 3.6, agitation speed at 1200rpm and flow rate at 120L/min.

### **Effect of time variation**

In investigating the effect of time variation on the photodegradation of the cassava wastewater;

1. The time was varied at 30, 60, 90, 120 and 150 minutes for different dosage of the modified and unmodified catalyst dosage and the wastewater concentration to obtain the best dosage of the modified and unmodified catalyst and concentration.
2. The other variables were left constant; temperature at 25°C, UV light at 450W, pH at 3.6, agitation speed at 1200rpm and flow rate at 120L/min.

## **CHAPTER FOUR**

### **RESULTS AND DISCUSSION**

#### **4.1 CHARACTERIZATION RESULT OF PERIWINKLE SHELL AND ROOF TILES**

Chemical characterisation of the Periwinkle shell and Roof tiles revealed that the major oxides present were calcium oxide (CaO), silica (SiO<sub>2</sub>) and magnesium oxide (MgO) which accounted for 61.6%, 26.95% and 3.07% of the weight of the activated catalyst characterized and 61.8%, 26.75% and 3.07% of the weight of the unactivated catalyst. The surface area of the PSA were obtained as 72.220 m<sup>2</sup>/g for the activated catalyst and 76.500m<sup>2</sup>/g for the unactivated catalyst. Some of the elements and oxides present in PSA are semiconductors and oxides of the semiconductors respectively and they have been reported to possess photocatalytic properties thus supporting the choice of PSA for this study.

#### **4.2 PHOTODEGRADATION TREATMENT**

Several variables affect the performance of photocatalytic degradation. This study considers the rate of degradation of organic compounds (cassava waste water) by the photocatalytic treatment using the following: Catalyst dosage (modified and unmodified), contact time, and concentration of the wastewater. Hence, these methods were studied, and the results are interpreted below.

#### 4.2.1 EFFECT OF CATALYST DOSAGE

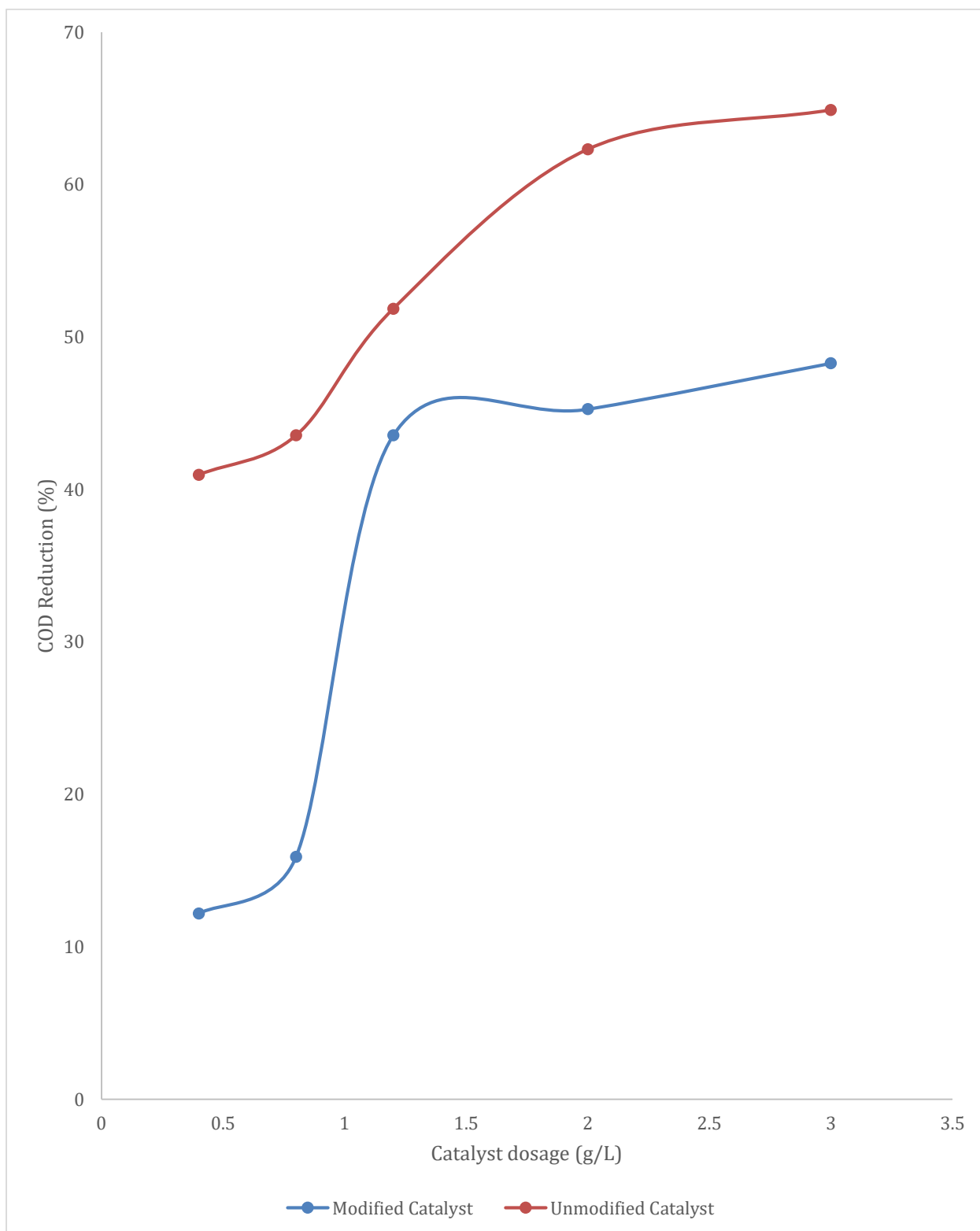


Figure 4.1 Effect of catalyst dosage on the photodegradation process of cassava wastewater.

Figure 4.1 shows the effect of increased modified and unmodified catalyst dose on percentage COD reduction. With increase in the catalyst dosage from 0.4 to 3 g/L, there was a steady decrease in COD reduction from 12.18% to 48.28% for modified catalyst and 40.97% to 64.90% for unmodified catalyst

The decrease in COD observed might be due to the increase in the number of active sites on the photo-catalyst surface.

#### 4.2.2 EFFECT OF CONTACT TIME

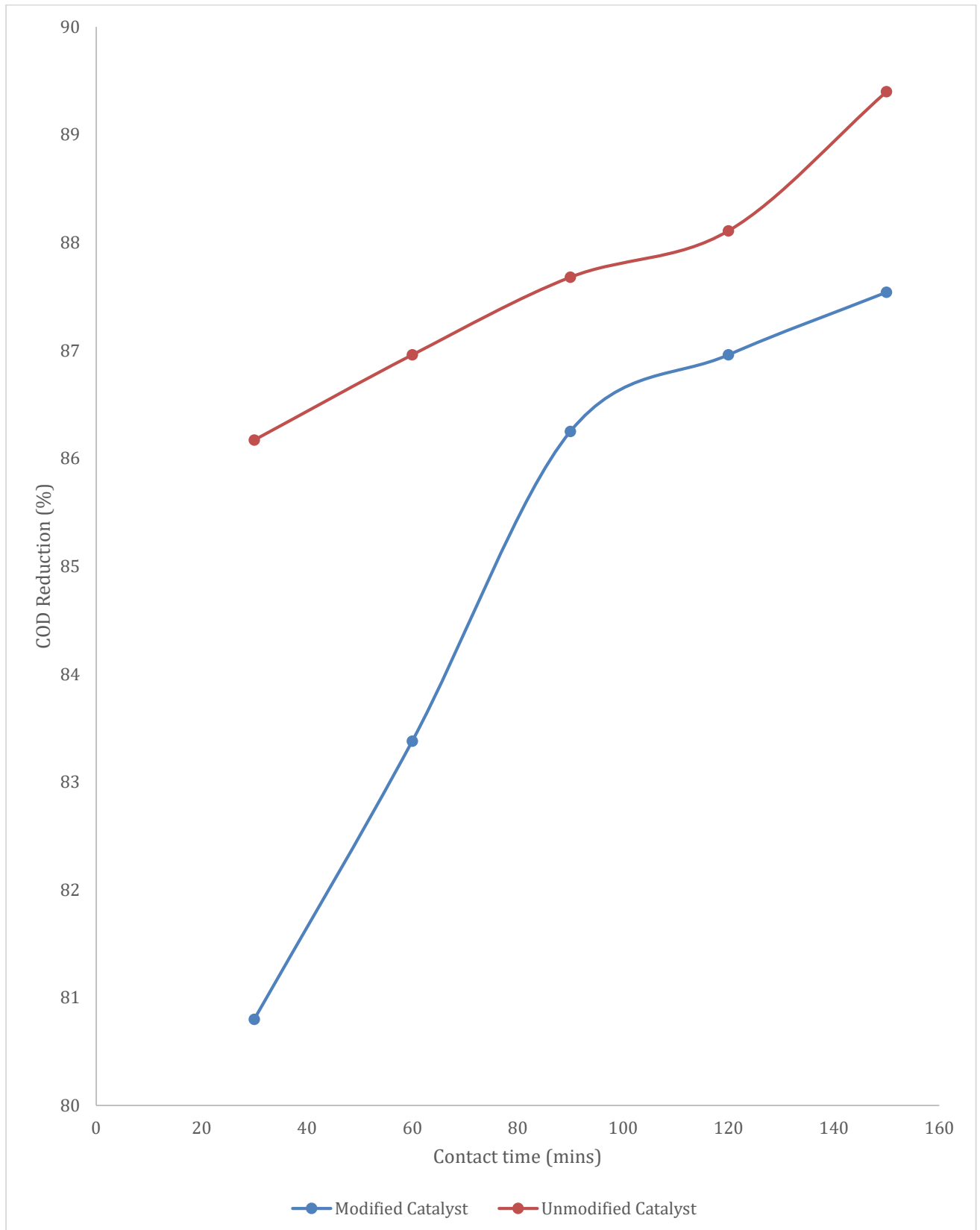


Figure 4.2 Effect of contact time on the photodegradation process of cassava wastewater.

Figure 4.2 shows how the percentage reduction of COD of the waste water was affected by the contact time of the photo-chemical reactor. The contact time was varied between 30 mins to 150 mins. It was observed that there was an increase in COD reduction from 80.80% to 87.54% as the contact time was increased from 30 to 150 mins for modified catalyst and 86.17% to 89.40% for unmodified catalyst

The reason for the increase in percentage removal is as a result of the exposure of the active sites to photons for a longer time and the production of more  $\text{OH}\cdot$  radicals and positive holes which will increase photodegradation efficiency.

### 4.2.3 EFFECT OF CONCENTRATION

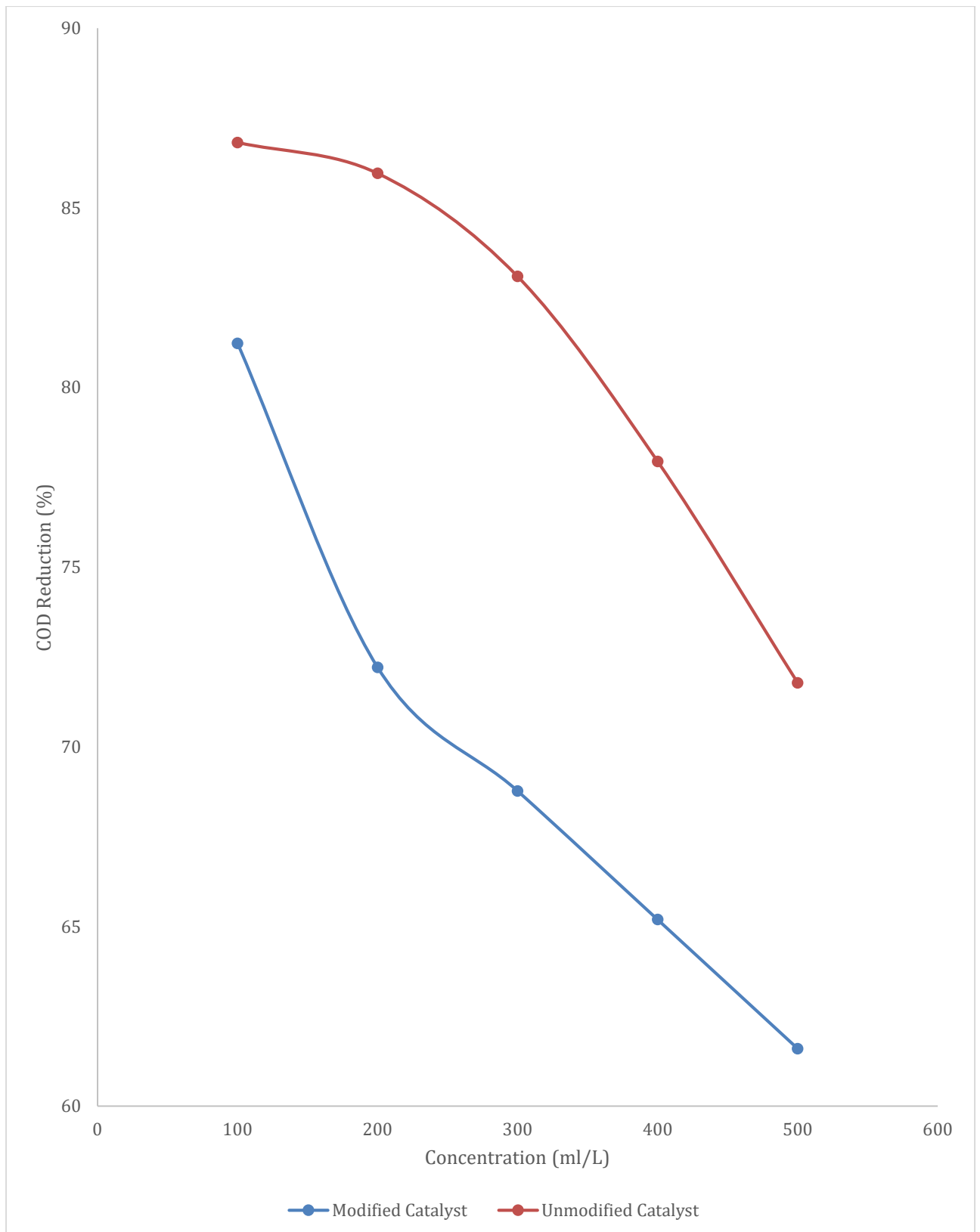


Figure 4.3 Effect of concentration on the photodegradation process of cassava wastewater.

Fig 4.3 shows how the COD of the treated cassava waste water varied with concentration between 100ml/L to 500ml/L for modified catalyst. It was observed that the COD increases from 1310 to 2680 mg/L representing a 51.12% increase as the concentration increased from 100 to 500ml/L for modified catalyst. Similar trend was observed for unmodified catalyst where there was an increase in COD from 920 to 1970 mg/L indicating a percentage reduction of 53.30% as the concentration of the wastewater was increased from 100 to 500ml/L.

This might be due to the presence of less organic pollutants adsorbed on the surface of the photocatalyst so, photons are able to get on the catalyst surface faster compared to a higher concentration of the wastewater.

### 4.3 ISOTHERM MODEL FOR MODIFIED CATALYST

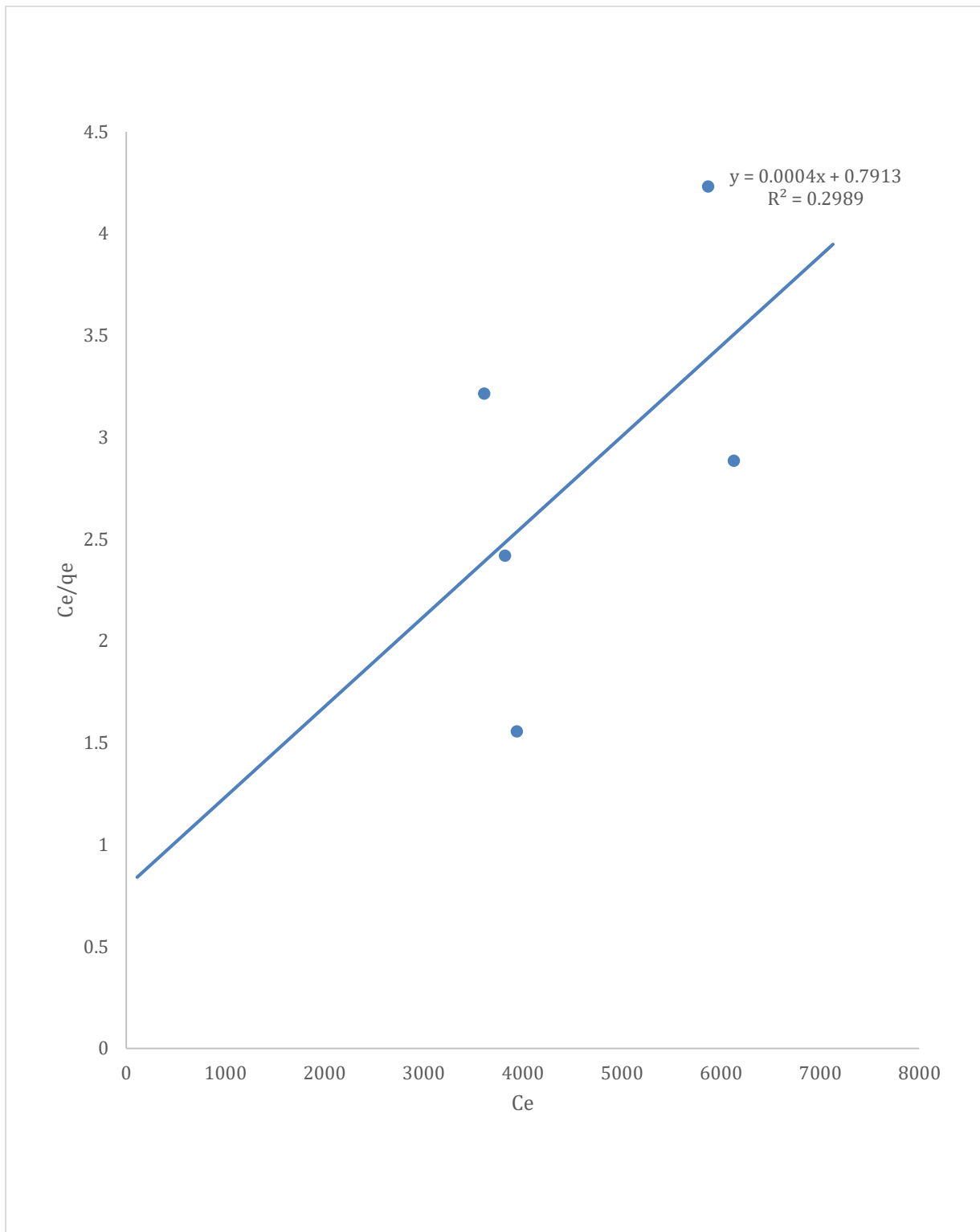


Fig 4.4: Langmuir Isotherm for COD reduction for modified catalyst dosage

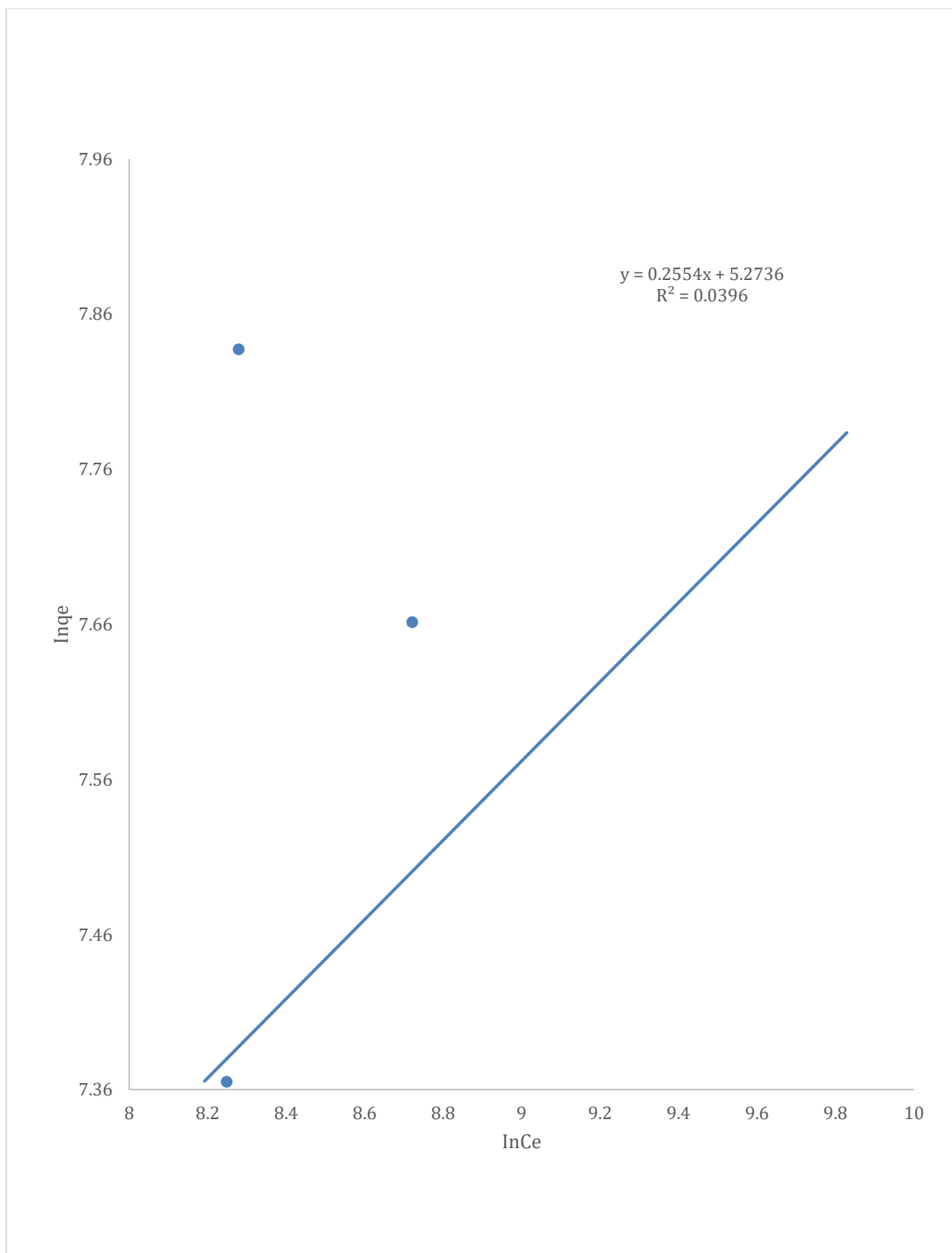


Fig 4.5: Freundlich Isotherm for COD reduction for modified catalyst dosage

#### 4.4 ISOTHERM MODEL FOR UNMODIFIED CATALYST

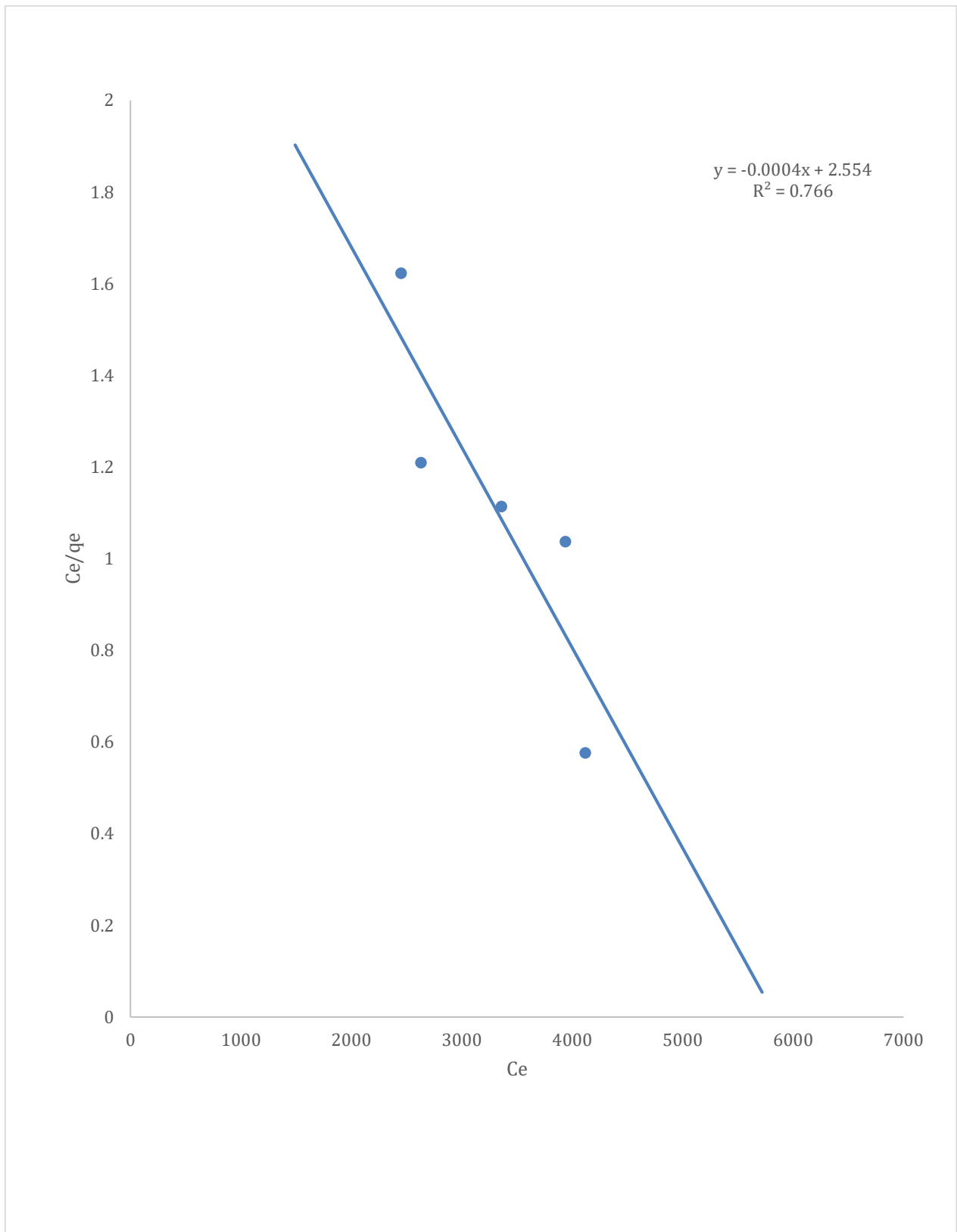


Figure 4.6: Langmuir Isotherm for COD reduction for unmodified catalyst dosage

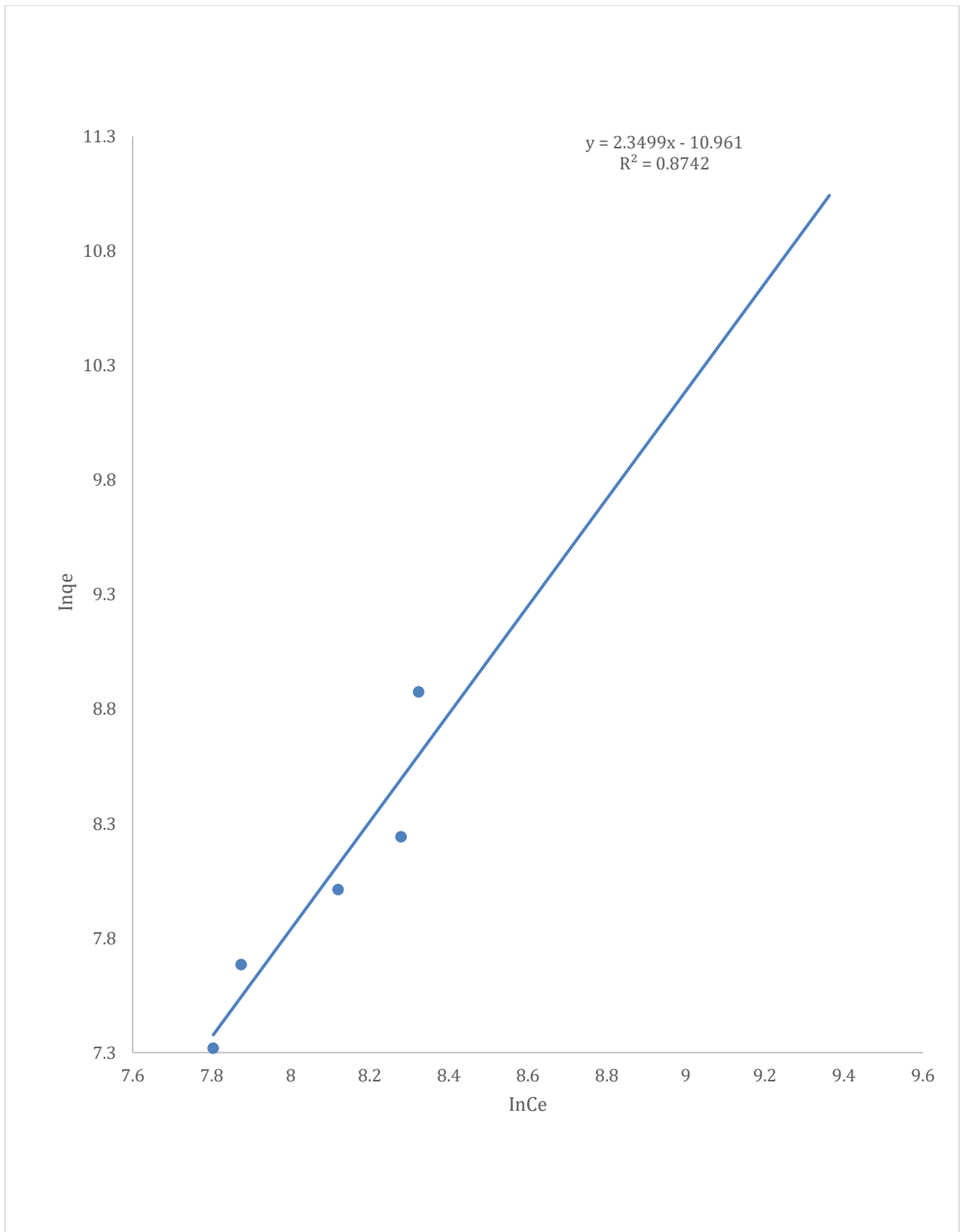


Figure 4.7: Freundlich Isotherm for COD reduction for unmodified catalyst dosage

### **Adsorption Isotherm Model**

It is clear from the plot of Fig 4.4-4.5 above that Langmuir model was the best model for modified catalyst with a correlation coefficient of  $r^2 \geq 0.2989$  for COD. Also for Fig 4.6 to 4.7, In comparing the correlation coefficient  $r^2$  obtained from the Langmuir and Freundlich model, it clearly shows that the experimental analysis fit Freundlich model with  $r^2 \geq 0.8742$  for unmodified catalyst.

**Table 4.1:** Adsorption Modelling of COD

Isotherm model	Langmuir Isotherm				Freundlich Isotherm		
Equation	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$				$q_e = K_F C_e^{1/n}$		
Linear Equation	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$				$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$		
Plot	$\frac{C_e}{q_e}$ against $C_e$				$\ln q_e$ against $\ln C_e$		
Parameters	$q_m$ (mg/g)	$K_L$ (l/mg)	$R_L$	$r^2$	$K_F$	n	$r^2$
COD (Modified)	2500	0.000505	0.2210	0.2989	195.12	3.915	0.0396
COD (Unmodified)	-2500	-0.000157	-10.4319	0.766	$1.737 \times 10^{-5}$	0.4256	0.8742

It should be noted that the essential features of the Langmuir isotherm model is the term ( $R_L$ ) which is a non – dimensional constant called separation factor or equilibrium parameter, and it is derived from the following equation.

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

Where  $C_o$  (mg/l) is the initial concentration of adsorbate,  $K_L$  (l/mg) is the Langmuir constant. The compatibility of adsorption for adsorption-adsorption pair is expressed by  $R_L$  in the table below.

**Table 4.2:**  $R_L$  and their isotherm type

If $0 < R_L < 1$	Adsorption is favourable
If $R_L > 1$	Adsorption is unfavourable
If $R_L = 1$	Adsorption is linear
If $R_L = 0$	Adsorption is irreversible

From the study,  $R_L$  values for the Langmuir isotherm are less than 1 which means that favourable adsorption was achieved.

## 4.5 KINETICS MODEL FOR MODIFIED CATALYST

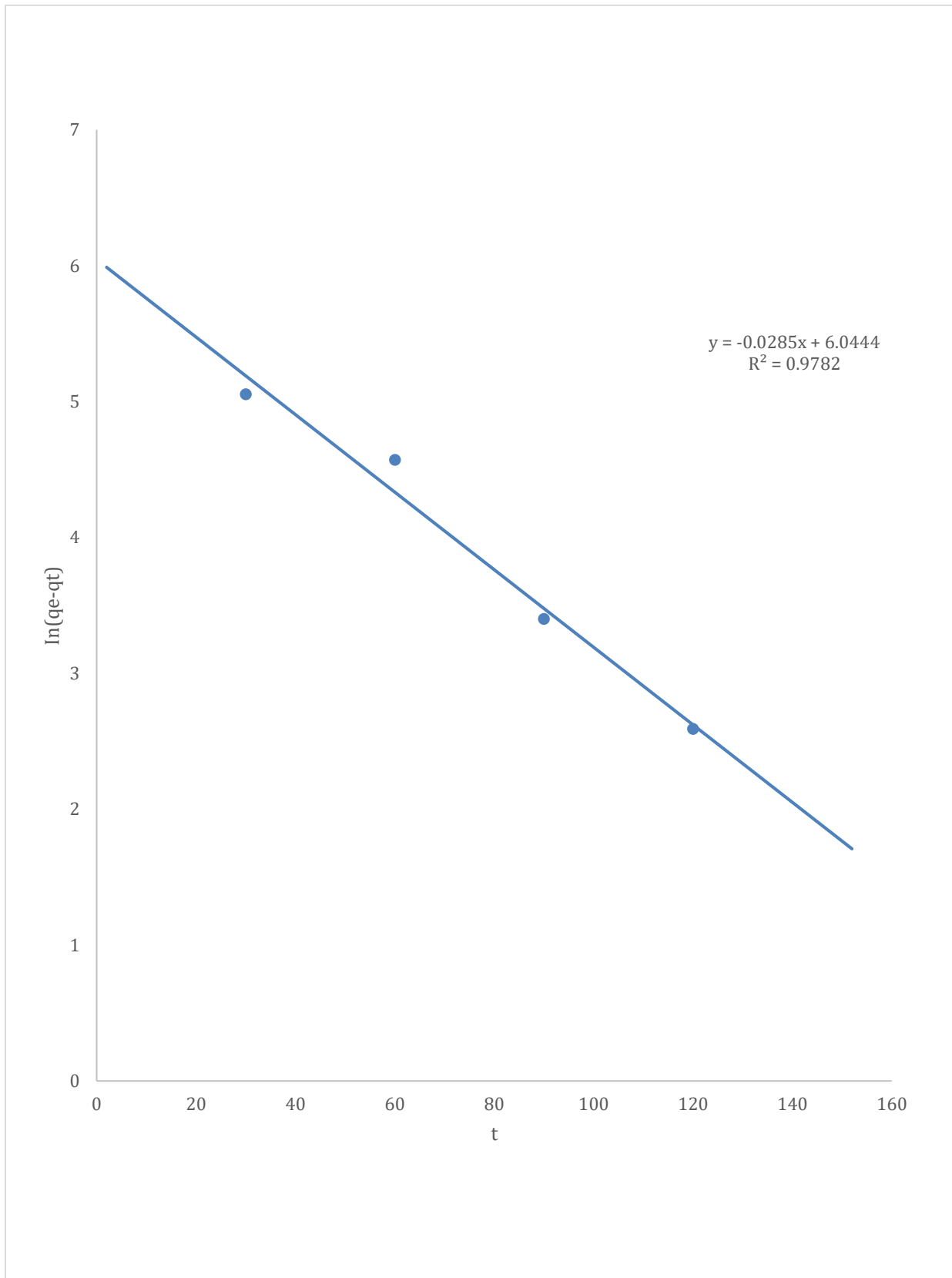


Figure 4.8 Langrange pseudo first-Order for COD reduction for modified catalyst dosage

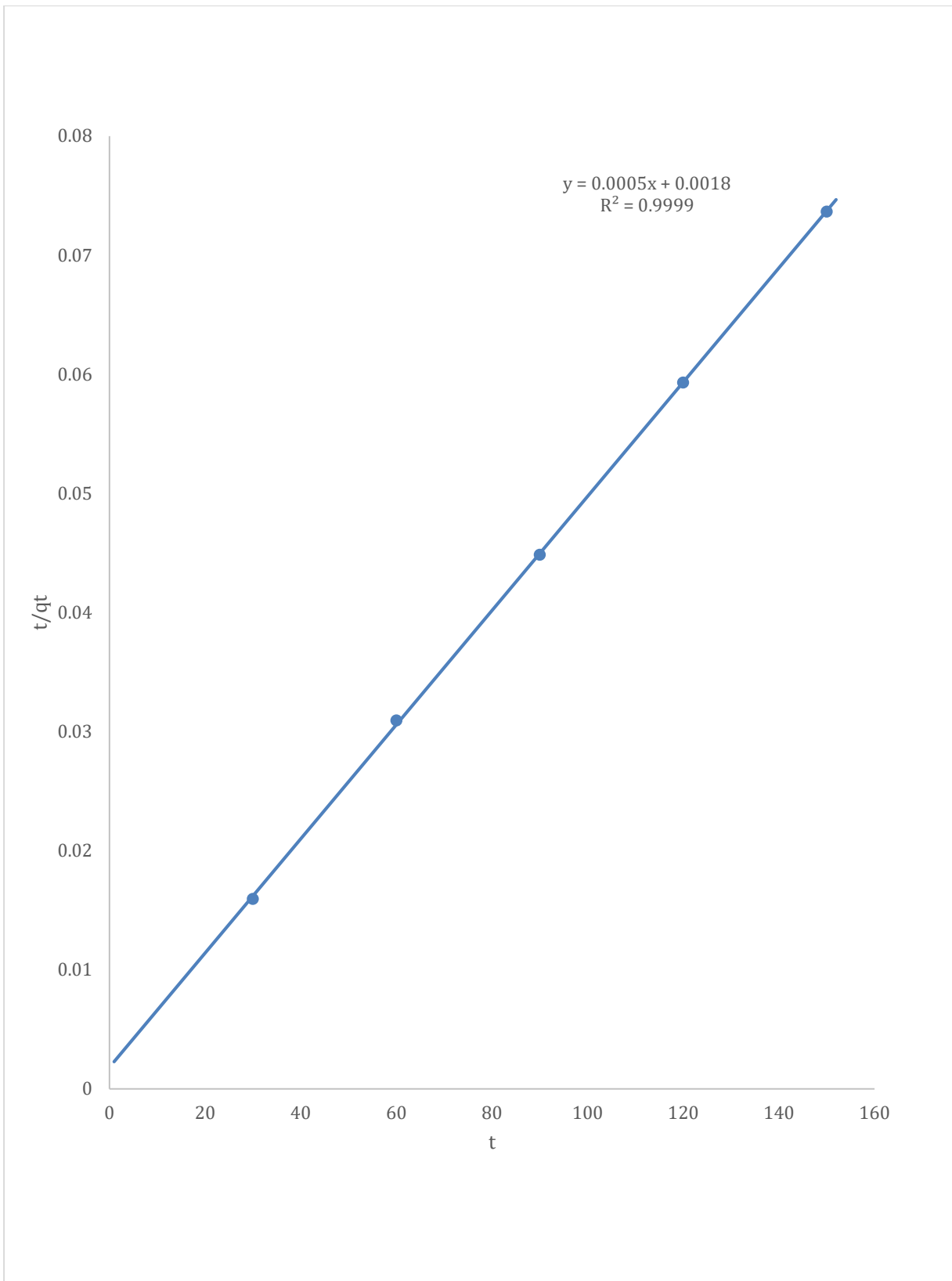


Figure 4.9: Pseudo Second-Order for COD reduction for modified catalyst dosage

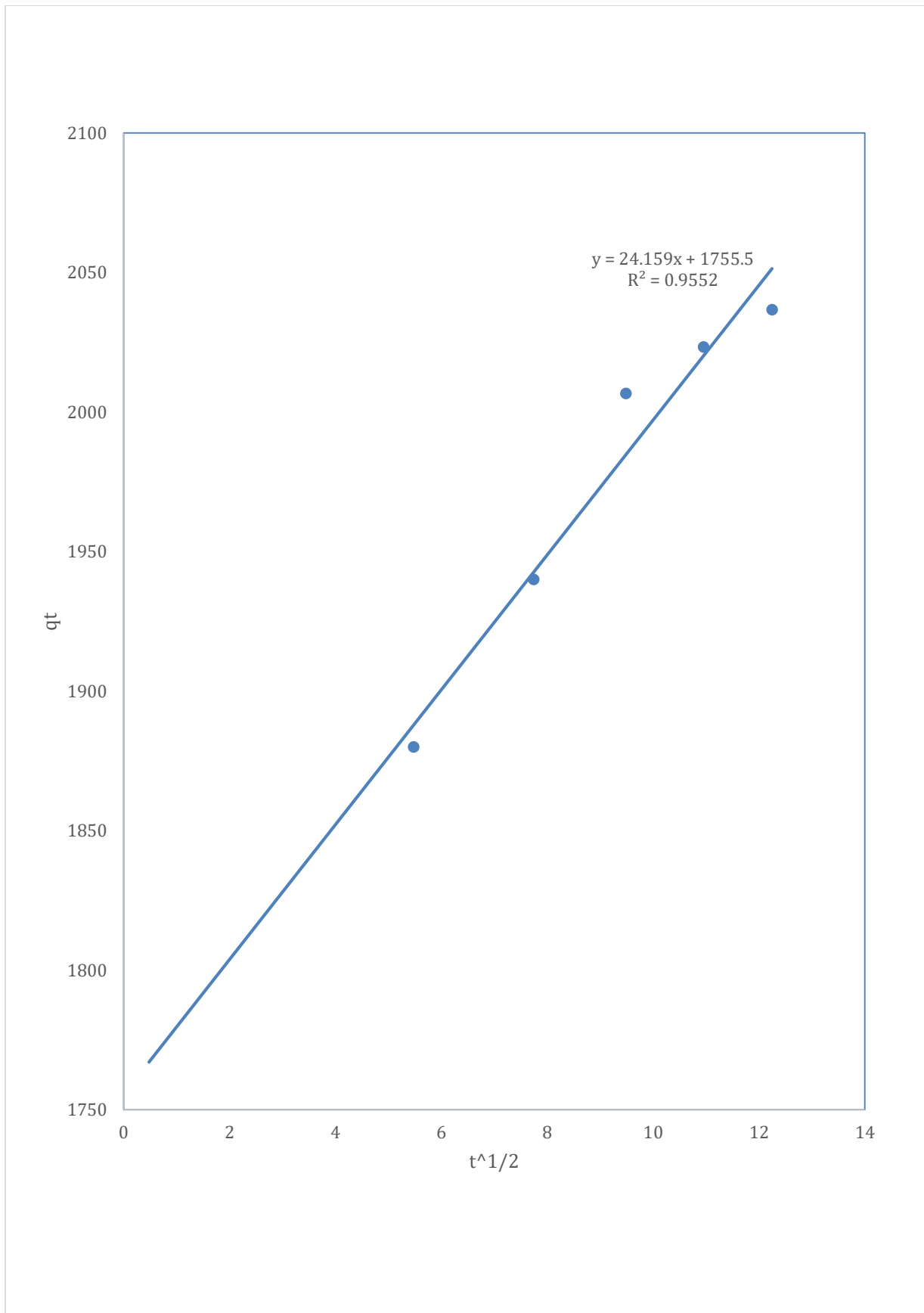


Figure 4.10: Intra Particle Diffusion for COD reduction for modified catalyst dosage

## 4.6 KINETICS MODEL FOR UNMODIFIED CATALYST

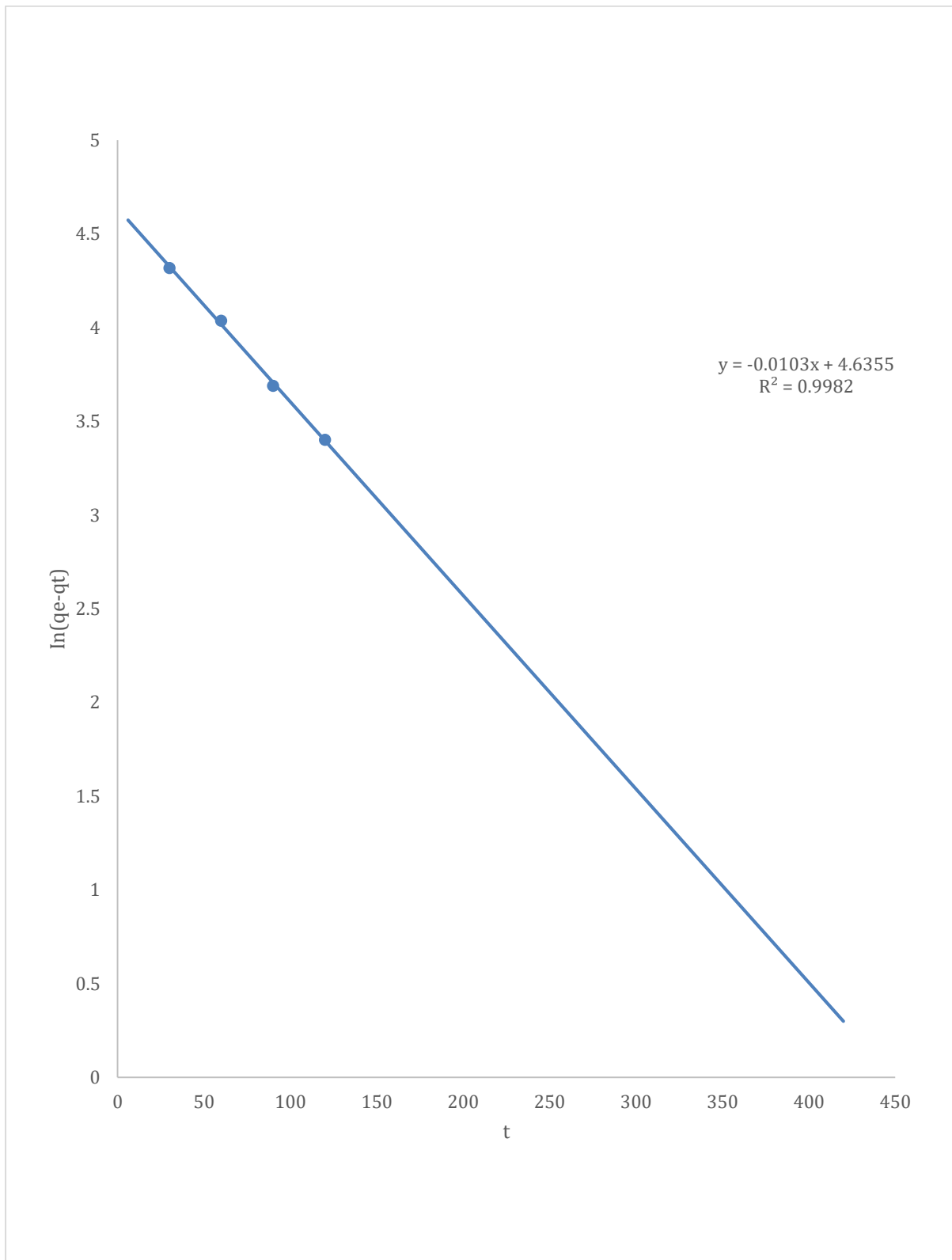


Figure 4.11 Langrange pseudo first-Order for COD reduction for unmodified catalyst dosage

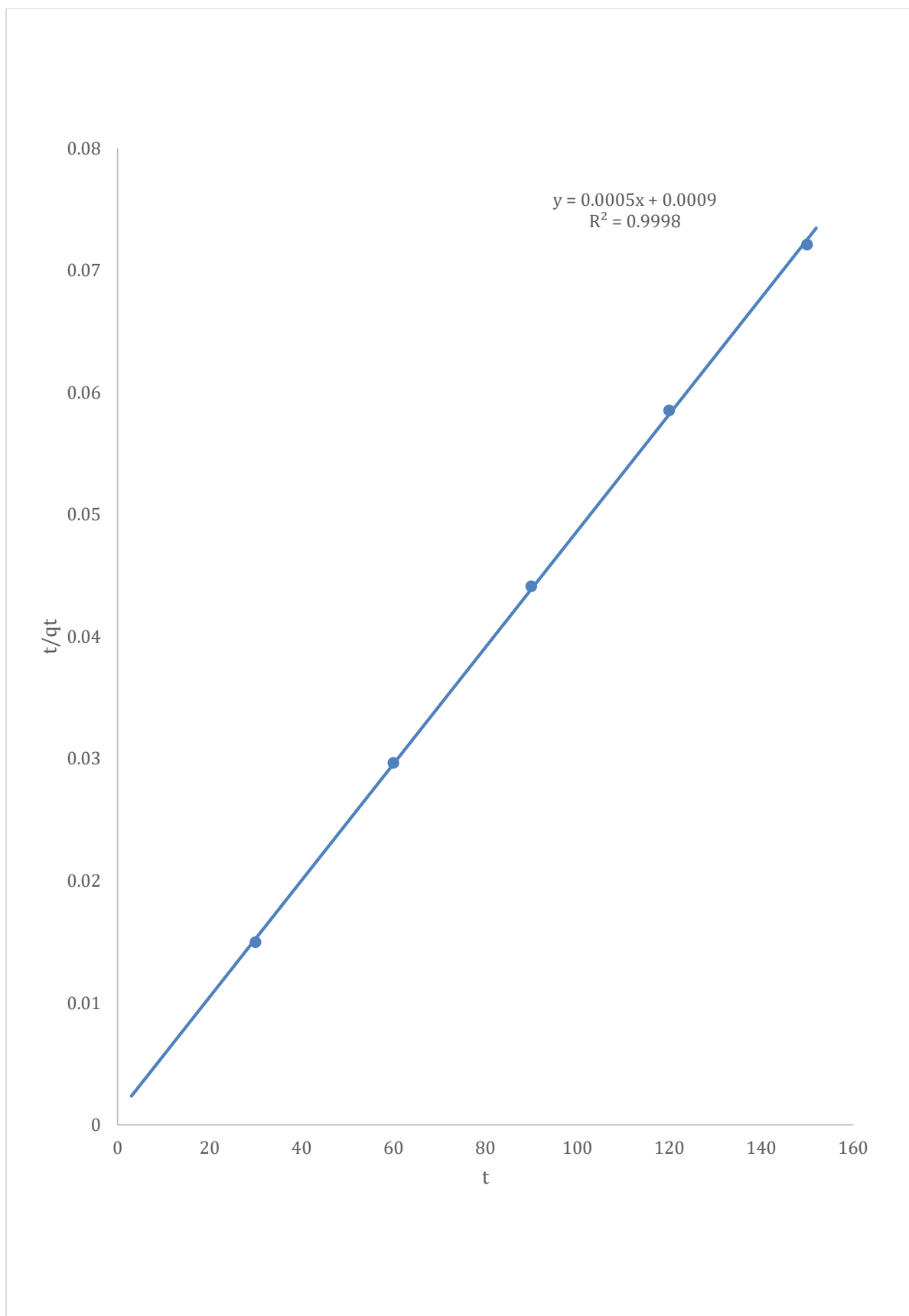


Figure 4.12: Pseudo Second-Order for COD reduction for unmodified catalyst dosage

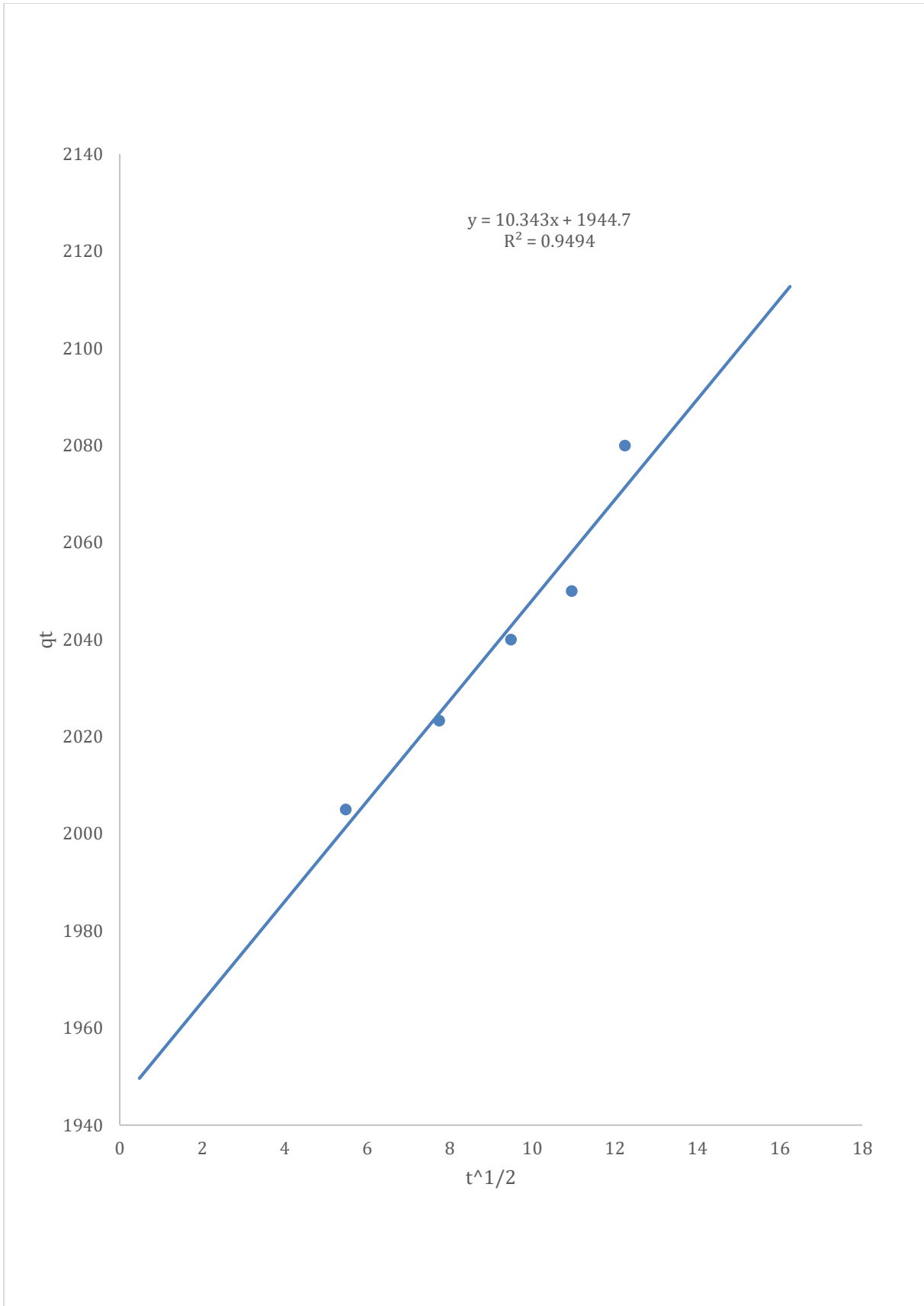


Figure 4.13: Intra Particle Diffusion for COD reduction for unmodified catalyst dosage

**Table 4.3:** Kinetic modelling

Kinetic Model	Langrange pseudo first order			Pseudo second order			Intra particle diffusion		
Equation	$\frac{dqt}{dt} = Ke_1(qe - qt)$			$\frac{dqt}{dt} = Ke_2(qe - qt)^2$			$q_t = k_p^{t^{(1/2)}} + C$		
Linearly	$\ln(qe - qt) = \ln(qe) - ke_1t$			$\frac{t}{qt} = \frac{1}{k_2q_e^2} + \frac{t}{qe}$					
Plot	$\ln(qe - qt)$ against $t$			$\frac{t}{qt}$ against $t$			$q_t$ against $t^{1/2}$		
Parameters	$K_1$	$q_e$	$r^2$	$K_2$	$q_e$	$r^2$	$K_p$	$c$	$r^2$
COD (Modified)	0.0285	421.745	0.9782	0.0001389	2000	0.9999	24.159	1755.5	0.9552
COD (Unmodified)	0.0103	103.079	0.9982	0.0002778	2000	0.9998	10.343	1944.7	0.9494

From table 4.8 to 4.13, the pseudo second order reaction showed a better fit ( $r^2 = 0.9999$ ,  $r^2 = 0.9998$ ) than both Langrange pseudo first-order ( $r^2 = 0.9782$ ,  $r^2 = 0.9982$ ) and the intra particle diffusion ( $r^2 = 0.9552$ ,  $r^2 = 0.9494$ ) for the modified and unmodified catalyst.

## CHAPTER FIVE

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

It is evident from the experiment results that photocatalysis can be used to treat cassava waste water to a considerable level of purity. The treated water can be safely discharged into water bodies. The optimum values of catalyst dosage, contact time and concentration were gotten to be 3g, 150mins, 100ml/L respectively.

The adsorption isotherm study shows that Langmuir isotherm is best fit with correlation coefficient ( $r^2 \geq 0.2989$ ) for modified catalyst and Freundlich model with correlation coefficient ( $r^2 \geq 0.8742$ ) for unmodified catalyst.

The Pseudo second order kinetic model was able to sufficiently describe the kinetics of the process for the modified and unmodified catalyst with a high correlation coefficient ( $r^2 \geq 0.9999$ ,  $r^2 \geq 0.9998$ ), reaction rate ( $K_2 = 1.389 \times 10^{-4} \text{mg/l.hr}$ ,  $2.778 \times 10^{-4} \text{mg/l.hr}$ ) and adsorption equilibrium constants ( $q_e = 2000$ ,  $q_e = 2000$ ) respectively

#### 5.2 RECOMMENDATIONS

Further experiments should be done to determine how variations of UV light intensity and other light source e.g. sunlight affects the photocatalytic treatment rate of cassava waste water.

Experiments should be done to determine how other photocatalysts e.g. zinc oxide, snail shell ash, can affect the photocatalytic treatment of the cassava waste water.

## REFERENCE

Abdel-Fatah, M. A. (2018). Nanofiltration systems and applications in wastewater treatment : Review article. *Ain Shams Engineering Journal*, 9(4), 3077–3092.

<https://doi.org/10.1016/j.asej.2018.08.001>

Acchar W and Da Silva V., (2021) Ecological brick of mineral residues and cassava wastewater. In: Acchar W, Da Silva V. (eds) Use of cassava wastewater and scheelite residues in ceramic formulations. Springer International Publishing, Cham, pp 33–51.

Agarwal M and Singh K., Heavy metal removal from wastewater using various adsorbents: A review. *J Water Reuse Desalin* 2017; 7(4): 387-419.(<http://dx.doi.org/10.2166/wrd.2016.104>)

Agbede O. I and Manasseh J. Suitability of periwinkle shell as partial replacement for river gravel in concrete, *Leonardo Electronic Journal of Practices and Technologies*. 2009;15:59-66.

Ahalya N., Ramachandra T. V., Kanamadi R.D., Biosorption of heavy metals, *Res. J. Chem. Environ.* 7 (2003) 71-79 [http://wgbis.ces.iisc.ernet.in/energy/water/paper/biosorption\\_heavymetals/Biosorption.pdf](http://wgbis.ces.iisc.ernet.in/energy/water/paper/biosorption_heavymetals/Biosorption.pdf).

Ahmed, J., Thakur, A., and Goyal, A. (2021). and Its Toxic Effects. *Industrial Wastewater and Its Toxic Effects*, 5, 1–14. <https://doi.org/10.1039/9781839162794-00001>

Ahmed S., Rasul M.G., Martens W. N., Brown R., Hashib M. A., Advances in heterogeneous photocatalytic degradation of phenols and dyes in wastewater: a review, *Water Air Soil Pollut.* 215 (2011) 3–29.

Ahmed, S. N., and Haider, W. (2018). Heterogeneous photocatalysis and its potential applications in water and wastewater treatment : a review.

Aigbodion V, Akadike U, Hasssn SB, Asuke F, Agunsoye JO. Development of asbestos-free brake pad using bagasse. *Tribology in Industry*. 2010;32(1):12 – 18.

Aimikhe, V., and Gospel, L. (2021). An Overview of the Applications of Periwinkle (*Tympanotonus fuscatus*) Shells An Overview of the Applications of Periwinkle (*Tympanotonus fuscatus*) Shells. August. <https://doi.org/10.9734/CJAST/2021/v40i1831442>

Aisien, F.A.; Amenaghawon, N.A.; and Assogba, M.M. (2014). Heterogeneous photocatalytic degradation of naphthalene using periwinkle shell ash: Effect of operating variables, kinetic and isotherm study. *South African Journal of Chemical Engineering*, 19(1), 31-45.

Ajaya S., Alfredo J. A., Sunandan B., Oleg V. S., and Joydeep D., *Nanotechnology* 22, 215703 (2011)

Akanbi O, Babayemi AK. Comparative Analysis of heavy metal removing using activated bamboo and periwinkle shell, a case study of Cr (III) ion, *Global Journal of Researches in Engineering: (C) Chemical Engineering*. 2019;19(6).

Aku, S.Y.; Yawas, D.S.; Madakson, P.B.; and Amaren, S.G. (2012). Characterization of periwinkle shell as asbestos-free brake pad materials. *The Pacific Journal of Science and Technology*, 13(2), 57-63.

Al-ghouti, M. A., and Da, D. A. (2020). Guidelines for the use and interpretation of adsorption isotherm models : A review. *Journal of Hazardous Materials*, 393(January), 122383. <https://doi.org/10.1016/j.jhazmat.2020.122383>.

Al- Jayyousi O. R., Greywater reuse: towards sustainable water management, *Desalination*, 2003, 156, 181–192.

Allegre, C., Moulin, P., Maisseu, M., and Charbit, F. (2006). *Treatment and reuse of reactive dyeing effluents*. 269, 15–34. <https://doi.org/10.1016/j.memsci.2005.06.014>.

Alofsur F. K. M., Ridha N. J, Jumali M. H, Radiman S. (2018) One-step formation of TiO<sub>2</sub> hollow spheres via a facile microwave-assisted process for photocatalytic activity. *Nanotechnology*, 29, 1–7

Antczak, G., and Ehrlich, G. (2004). *Long jumps in surface diffusion*. 276, 1–5. <https://doi.org/10.1016/j.jcis.2003.11.035>

Aouni A, Fersi C, Cuartas-Uribe B, et al. Reactive dyes rejection and textile effluent treatment study using ultrafiltration and nanofiltration processes. *Desalination*. 2012;297:87–96.

APHA. *Standard Methods for the Examination of Water and Wastewater*. 21st ed. Washington, DC: American Public Health Association; 2005

Aramendia M. A, Marinas A, Marinas J. M, Moreno J. M, Urbano F. J (2005) Photocatalytic degradation of herbicide fluroxypyr in aqueous suspension of TiO<sub>2</sub>. *Catal Today* 101:187–193

Ariffin N, Abdullah MMAB, Zainol MRRMA, Murshed MF, Faris MA, Bayuaji R. Review on adsorption of heavy metal in wastewater by using geopolymer. *MATEC Web Conf* 2017; 97: 8. [<http://dx.doi.org/10.1051/mateconf/20179701023>]

Arora, S., and Kazmi, A. A. (2015). ScienceDirect The effect of seasonal temperature on pathogen removal efficacy of vermifilter for wastewater treatment. *Water Research*, 74, 88–99. <https://doi.org/10.1016/j.watres.2015.02.001>.

Assanvo, J. B. et al. Influence of microbiological and chemical quality of traditional starter made from cassava on “attiéké” produced from four cassava varieties. *Food Control*, v. 78, p. 286–296, 1 ago. 2017.

Atul K, Pratibha C, Poonam V. A comparative study on the treatment methods of textile dye effluents. *J Chem Pharm Res*. 2012;4(1):763–771.

Azimi A., Azari A., Rezakazemi and Ansarpour M., removal of heavy metals from industrial wastewaters: a review, *ChemBioEng Rev.*, 2017, 4, 37–59.

Bache, D. H., Johnson, C., Papavasiliopoulos, E., Rasool, E., and McGilligan, F. J., 1999. "Sweep coagulation: structures, mechanisms and practice." *Journal of Water Supply: Research and Technology- Aqua*, vol. 48, pp. 201-210.

Badmus M. A. O and Audu T. O. K (2009) Periwinkle shell: based granular activated carbon for treatment of chemical oxygen demand (COD) in industrial wastewater. *Can J Chem Eng* 87:69–77.

Bani R., *Wastewater management, Waste Water: Evaluation and Management*, 2011, p. 379.

Barceloux, D. G. Cyanogenic Foods (Cassava, Fruit Kernels, and Cycad Seeds). *Disease-a-Month*, v. 55, n. 6, p. 336–352, 1 jun. 2009.

Bart H. J and Gemmingen, V. U.: Adsorption in Ullmann’s Encyclopedia of Industrial Chemistry. Wiley-VCH, Weinheim (2005). Published Online: 15 Jan. 2005.  
doi:10.1002/14356007.b03\_09.pub2

Baruah G. L., Nayak A. and Belfort G., *Journal of Membrane Science*, 2006, 274, 56–63

Baruah S., Jaisai M., and Dutta J., *Catal. Sci. Technol.* 2, 918 (2012).

- Bhatkhande D. S., Pangarkar V. G., and Beenackers A. A. C. M, *J. Chem. Technol. Biotechnol.* 77, 102 (2001).
- Boadi, N. O., Twumasi, S. K., Ephraim, J. H. 2008. Impact of cyanide utilization in mining on the environment. *International Journal of Environmental Resources* 3(1): 101–108.
- Bolisetty, S. (2018). *Chem Soc Rev Sustainable technologies for water purification from heavy metals : review and analysis.* <https://doi.org/10.1039/c8cs00493e>
- Bora, T., and Dutta, J. (2014). *Applications of Nanotechnology in Wastewater.* 14(1), 613–626. <https://doi.org/10.1166/jnn.2014.8898>
- Borgarello E., Serpone N., Emo G., Harris R., Pelizzetti E., and Minero C., *Inorg. Chem.* 25, 4499 (1986).
- Bratby J., *Coagulation and flocculation in water and wastewater treatment*, IWA Publishing, London, 2nd edn, 2006.
- Buljan J. and I. Kral (2011); *Introduction to treatment of tannery effluents.* United Nations Industrial Development Organization (UNIDO) Vienna.
- Burrows H. D., Canle M. L., Santaballa J. A., Steenken S., *Reaction pathways and mechanisms of photodegradation of pesticides,* *J. Photochem. Photobiol. B, Biol.* 67 (2002) 71–108.
- Cai H., Mu W., Liu W, et al. *Sol– gel synthesis highly porous titanium dioxide microspheres with cellulose nano fibrils–based aerogel templates.* *Inorganic Chemistry Communications.* 2015;51:71–74.
- Cao X. L, Yan Y. N, Zhou F. Y, et al. *Tailoring nanofiltration membranes for effective removing dye intermediates in complex dye-wastewater.* *J Membr Sci.* 2019;595:117476.

Chan S. H. S., Yeong T., Wu, Juan J. C., and Teh C. Y, J. Chem. Technol. Biotechnol. 86, 1130 (2011).

Chakhtouna, H., Benzeid, H., Zari, N., & Bouhfid, R. (2021). *Recent progress on Ag / TiO<sub>2</sub> photocatalysts : photocatalytic and bactericidal behaviors*. 44638–44666.

Chatterjee D, Dasgupta S (2005) Visible light induced photocatalytic degradation of organic pollutants. J Photochem Photobiol C 6:186–205.

Chen W and Zhang J. S 2008 UV-PCO device for indoor VOCs removal: investigation on multiple compounds effect Build. Environ. 43 246–52

Chisté R. C, Cohen K de O (2006) Efeito do Processo da fabricação da farinha de mandioca. Efeito do Process Fabr da Farinha Mandioca.

Chojnacka K. Biosorption and bioaccumulation—the prospects for practical applications. Environment International. 2010;36:299-307

Chong M. N, Jin B, Chow C. W. K and Saint C 2010 Recent developments in photocatalytic water treatment technology: a review Water Res. 44 2997–3027

Coker, A.O, Achi, C.G., Sridhar, M.C.K. , 2015. Utilization of cassava processing waste as a viable and sustainable strategy for meeting cassava processing energy needs: case study from Ibadan City, Nigeria. J. Solid Waste Technol. Manag. 41 (4), 628–639.

Coleman, H. M., Vimonses, V., Leslie, G., and Amal, R. (2007). Degradation of 1, 4-dioxane in water using TiO<sub>2</sub> based photocatalytic and H<sub>2</sub>O<sub>2</sub> / UV processes. 146, 496–501.

<https://doi.org/10.1016/j.jhazmat.2007.04.049>

Cotman M. and Gotvajn A. Z., *Comparison of different physico-chemical methods for the removal of toxicants from landfill leachate* ~ gajnar Gotvajn b. (n.d.).

<https://doi.org/10.1016/j.jhazmat.2010.01.078>

Danwittayakul S., Jaisai M., Koottatep T., and Dutta J., *Ind. Eng. Chem. Res.* 52, 13629 (2013).

Darban, A. K., Shahedi, A., Ph, D., and Taghipour, F. (2020). A review on industrial wastewater treatment via electrocoagulation processes. *Current Opinion in Electrochemistry*.

<https://doi.org/10.1016/j.coelec.2020.05.009>

Davis T. A, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Research.* 2003;37:4311-4330.

De SouzaYes F. D, Dos Santos T. P. R, Fernandes A. M, Leonel M (2019) Harvest time optimization leads to the production of native cassava starches with different properties. *Int J Biol Macromol* 132:710–721. <https://doi.org/10.1016/j.ijbio mac.2019.03.245>.

Delzer G. C., and Mckenzie, S. W. (2003). Five-Day Biochemical Oxygen Demand. 7, 1–21.

Demirbas A, Edris G, Alalayah W. M. Sludge production from municipal wastewater treatment in sewage treatment plant. *Energy Sources A Recovery Util Environ Effects* 2017; 39(10): 999-1006. [<http://dx.doi.org/10.1080/15567036.2017.1283551>]

Devi M., Praharaj S., and Rout D., “Industrial problems and solution towards visible light photocatalysis,” in *Nano-structured Materials for Visible Light Photocatalysis*, pp. 535–567, Elsevier, Amsterdam, Netherlands, 2022.

Do D. D., *Adsorption analysis: equilibria and kinetics*, London: Imperial College Press, 1998.

Dong F, Ou M, Jiang Y, Guo S and Wu Z 2014 Efficient and durable visible light photocatalytic performance of porous carbon nitride nanosheets for air purification *Ind. Eng. Chem. Res.* 53 2138–40

Dong F, Wang Z, Li Y, Ho W and Lee S. C 2014 Immobilization of polymeric g-C<sub>3</sub>N<sub>4</sub> on structured ceramic foam for efficient visible light photocatalytic air purification with real indoor illumination *Environ. Sci. Technol.* 48 10345–53

Ekubo, A. A., and Abowei, J. F. N. (2011). Review of Some Water Quality Management Principles in Culture Fisheries. 3(12), 1342–1357.

El-azim, H. A. (2019). Pollution Impacts of industrial activities in Suez Bay with mitigation Hoda Abd El-Azim. September.

Elimelech M., Jia X., Gregory J., Williams R., Particle Deposition and Aggregation: Measurement, Modelling and Simulation (Colloid and Surface Engineering), First, Butterworth-Heinemann., 1998.

Evans A. E., Mateo- Sagasta J., Qadir M., Boelee E., and Ippolito A., agri- cultural water pollution: key knowledge gaps and research needs, *Curr. Opin. Environ. Sustainability.*, 2019, 36, 20–27.

FAO, 2006. FAOSTAT. Food and Agriculture Organization of the United Nations <http://faostat.fao.org>.

Fayeofori G.B, A preliminary study on the population estimation of the periwinkles *Tympanotonus fuscatus* (Linnaeus, 1758) and *Pachymelania aurita* (Muller) at the Rumuolumeni mangrove swamp creek, Niger Delta, Nigeria, *Agriculture and Biology Journal of North America.* 2012;3(6):265-270.

Fernandes, A., Makoś, P., Wang, Z., and Boczkaj, G. (2020). Synergistic effect of TiO<sub>2</sub> photocatalytic advanced oxidation processes in the treatment of refinery effluents. *Chemical Engineering Journal*, 391, 123488.

Florea A. M, Dopp E, Obe G, Rettenmeier A. W. Genotoxicity of organometallic species. In: Hirner

Food and Agricultural Organisation. (2012). State of the world's strategic environmental assessment: An assessment of the impact of cassava production and processing on the environment and biodiversity. Proceeding of the Validation Forum on the Global Cassava Development Strategy 5:26-28

Fu F., and Wang Q., removal of heavy metal ions from wastewaters: a review, *J. Environ. Manage.*, 2011, 92, 407–418.

Gadipelly, C., Rathod, V. K., and Marathe, K. V. (2014). Pharmaceutical Industry Wastewater : Review of the Technologies for Water Treatment and Reuse Raquel Iba n.

Gao, H., Zhang, W., Song, Z., Yang, X., Yang, L., Cao, M., et al. (2017). Transfer behavior of odorous pollutants in wastewater sludge system under typical chemical conditioning processes for dewaterability enhancement. *Scientific Reports*, 7(1), 1–12.  
<https://doi.org/10.1038/s41598-017-03727-4>.

Garbarino, J. R., Hayes, H., Roth, D., Antweider, R., Brinton, T. I. and Taylor, H. 1995. Contaminants in the Mississippi River, U. S Geological Survey Circular 1133, Virginia, U. S. A. Available online at: [pubs.usgs.gov/circ/circ1133](https://pubs.usgs.gov/circ/circ1133).

Hamzaoui, M., Bestani, B., and Benderdouche, N. (2018). *The use of linear and nonlinear methods for adsorption isotherm optimization of basic green 4-dye onto sawdust-based activated carbon*. 2508(4), 1110–1118

Hawko, C., Verrielle, M., Hucher, N., Crunaire, S., Leger, C., and Savary, G. (2021). A review of environmental odor quantification and qualification methods : the question of objectivity in sensory analysis.

Herrmann J. M., *Catal. Today*, 1999, 53, 115–129.

Higgins P. G, Hrenovic J, Seifert H, Dekic S. Characterization of *Acinetobacter baumannii* from water and sludge line of secondary wastewater treatment plant. *Water Res* 2018; 140: 261-7. [<http://dx.doi.org/10.1016/j.watres.2018.04.057>] [PMID: 29723815]

Ho, Y. S., and Mckay, G . (1998). *Kinetic Models For The Sorption Of Dye From Aqueous Solution By Wood*. 76(May).

Ho, Y. S., and Mckay, G. (1999). *Pseudo-second order model for sorption processes*. 34, 451–465.

Hoffmann M. R., Martin S.T., Choi W., and Bahnemann D.W., *Chem. Rev.* 95, 69 (1995).

Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L., and Zhang, Q. (2012). *Heavy metal removal from water / wastewater by nanosized metal oxides : A review*. 212, 317–331.

<https://doi.org/10.1016/j.jhazmat.2011.10.016>

Ibhadon O. A.and Fitzpatrick P., *Catalysts*, 2013, 3, 189–218

International Union of Pure and Applied Chemistry, Glossary of terms used in photochemistry (IUPAC recommendations), *Pure Appl. Chem.* 68 (1996) 2223–2286 (1996).

Jaisai M., Baruah S., and Dutta J., *Beilstein J. Nanotechnol.* 3, 684 (2012).

Jamabo N, Chinda A. Aspects of the ecology of *tympanotonusfuscatus*Var*Fuscatuis* (Linnaeus, 1758) in the mangrove swamps of the upper bonny River, Niger Delta, Nigeria, *Current Research Journal of Biological Sciences*. 2010;2(1):42-47

Jern N. W., and Wun J., *Industrial Wasterwater Treatment*, imperial College Press Singapore, 2006.

Jongprateep O., Puranasamriddhi R, Palomas J. Nanoparticulate titanium dioxide synthesized by sol–gel and solution combustion techniques. *Ce- ramics International*. 2015;41(1):S169–S173.

Julson A. J., Ollis D. F., Kinetics of dye decolorization in an air–solid system, *Appl. Catal. B- Environ*. 65 (2006) 315–325.

Karunakarana G, Choa E, Kumarb G. S, Kolesnikovc E, Karpenkovd D. U, Gopinathane J, Pillaie MM, Selvakumare R, Boobalang S, Gorshenkov M. V. Sodium dodecyl sulfate mediated microwave synthesis of biocompatible super paramagnetic mesoporous hydroxyapatite nanoparticles using black *Chlamysvaria* seashell as a calcium source for biomedical applications, *Ceramics International*. 2019;45:15143–15155

Kaur N. and Singh V. (2017). Current status and future challenges in ionic liquids, functionalized ionic liquids and deep eutectic solvent-mediated synthesis of nanostructured TiO<sub>2</sub>: a review. *New Journal of Chemistry*. 41, 2844–2868.

Khan, M.Y.A.; Khan, B.; Chakrapani, G.J. Assessment of spatial variations in water quality of Garra River at Shahjahanpur, Ganga Basin, India. *Arab. J. Geosci*. **2016**, 9, 516.

Kikuchi, T., and Tanaka, S. (2015). *Biological Removal and Recovery of Toxic. August*.  
<https://doi.org/10.1080/10643389.2011.651343>

Kulkarni, S. J., Dr. Kaware J. P (2013). *Review on Research for Removal of Phenol from*. 3(4), 1–5.

Kumar S., Anil K. Sharma, Rawat S. S., Jain D. K. and Ghosh S. Use of pesticides in agriculture and livestock animals and its impact on environment of India. November 2013.

Kuyucak N., Akcil A., (2013) Cyanide and removal options from effluents in gold mining and metallurgical processes. *Miner Eng* 50–51:13–29. <https://doi.org/10.1016/j.mineng.2013.05.027>

Lagergren, S., (1898). About the theory of so-called adsorption of soluble substances., 24(4), 1-39. SID. <https://sid.ir/paper/563615/en>

Lee J., Park H., and Choi W., *Environ. Sci. Technol.* 36, 5462 (2002)

Langmuir I. (1918). *The adsorption of gases on plane surfaces of glass, mica and platinum*. 345(1914).

Li J, Zhang S, Chen C, Zhao G, Yang X, Li J and Wang X 2012 Removal of Cu(II) and fulvic acid by graphene oxide nanosheets decorated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles *ACS Appl. Mater. Interfaces* 4 4991–5000

Li, Y. S., Yan, L., Xiang, C. B., and Hong, L. J., 2006. "Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes." *Desalination*, vol. 196, pp. 76-83.

Lorenc-Grabowska, E., Gryglewicz, G., and Diez, M. A. (2013). Kinetics and equilibrium study of phenol adsorption on nitrogen-enriched activated carbons Kinetics and equilibrium study of phenol adsorption on nitrogen-enriched activated carbons. *Fuel*, 114(December), 235–243. <https://doi.org/10.1016/j.fuel.2012.11.056>

Malato S., Blanco J., Compos A., Caceres J., Guillard C., Herrmann J. M et al (2003) Effect of operating parameters on the testing of new industrial titania catalysts at solar pilot plant scale. *Appl Catal B: Environ* 42:349–357

Malato S, Fernandez-Ibanez P, Maldonado M. I, Blanco J and Gernjak W 2009  
Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends *Catal. Today* 147 1–59

Malato S, Maldonado M. I, Fernández-Ibáñez P, Oller I, Polo I and Sánchez-Moreno R 2016  
Decontamination and disinfection of water by solar photocatalysis: the pilot plants of the Plataforma Solar de Almeria *Mater. Sci. Semicond. Process.* 42 15–23

Malik, D. S., Sharma, A. K., Sharma, A. K., Thakur, R., and Sharma, M. (2020). A review on impact of water pollution on freshwater fish species and their aquatic environment. 10–28.  
<https://doi.org/10.26832/aesa>

Mara D., *Domestic Wastewater Treatment in developing Countries*, Routledge, 2013

Matlock M. M., Howerton B. S and Atwood D. A, *Water Res.*, 2002, 36, 4757–4764.

Medeiros, R.C., De M N Fava, N., Freitas, B.L.S., Sabogal-Paz, L.P., Hoffmann, M.T., Davis, J.Fernandez-Ibanez, P., Byrne, J.A., 2020. Drinking water treatment by multistage filtration on a household scale: efficiency and challenges. *Water Res.* 178, 115816.  
<https://doi.org/10.1016/j.watres.2020.115816>.

Mesner N., and Geiger J.,(2010). *What is pH? December*, 6–9.

Mills A., Belghazi A., and Rodman D., *Water Res.* 30, 1973 (1996)

Mills A., Davies R. H., and Worsley D., *Chem. Soc. Rev.* 22, 417 (1993).

Mills A. and Le Hunte S., *J. Photochem. Photobiol.*, A 108, 1 (1997)

Monisha J, Tenzin T, Naresh A, Blessy B. M, Krishnamurthy NB. Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*. 2014;7(2):60-72.

Moruf R. O., Some aspect of the biology of periwinkle (*Tympanotonus fuscatus*) var, *radula* in the mangrove swamp of Lagos Lagoon Front. Lagos, Nigeria. MSc Thesis, University of Lagos, Nigeria; 2015.

Mrvčić J, Stanzer D, Solić E, Stehlik-Tomas V. Interaction of lactic acid bacteria with metal ions: Opportunities for improving food safety and quality. *World J Microbiol Biotechnol* 2012; 28(9): 2771-82. [<http://dx.doi.org/10.1007/s11274-012-1094-2>] [PMID: 22806724]

Munter R., *Industrial Wastewater Characteristics*. The baltic university Programme (buP), Sweden, 2003, pp. 185–194.

Murthy Z.V.P and Chaudhari, L. B. (2009). *Treatment of distillery spent wash by combined *uf* and *ro* processes*. 11(2), 235–240.

Nagajyothi P. C., Vattikuti S. V. P., Devarayapalli K. C., Yoo K., Shim J., Sreekanth T. V. M, Green synthesis: photocatalytic degradation of textile dyes using metal and metal oxide nanoparticles-latest trends and advancements, *Crit. Rev. Environ. Sci. Technol.* (2019), <https://doi.org/10.1080/10643389.2019.1705103>.

Nahiun, K. M. (2021). *Scientific Review A Review on the Methods of Industrial Waste Water Treatment A Review on the Methods of Industrial Waste Water Treatment*. July. <https://doi.org/10.32861/sr.73.20.31>

Nam Y, Li L, Lee J. Y, Prezhdo O. V. (2018). Size and shape effects on charge dynamics of TiO<sub>2</sub> nanoclusters. *The Journal of Physical Chemistry, C122*, 5201–5208.

Naveen D, Chandrajit B, Prasenjit M (2016) Comparative investigation on the removal of cyanide from aqueous solution using two different bio adsorbents. *Water Res Indus* 15:28–40. <https://doi.org/10.1016/j.wri.2016.06.002>

Nqombolo A., Mpupa A., Moutloali R. M., Nomngongo P. N., Wastewater treatment using membrane technology, *Wastewater Water Qual.* 29 (2018).

Obasohan, E. E., Agbonlahor, D. E. and Obano, E. E. (2010). *Water pollution : A review of microbial quality and health concerns of water, sediment and fish in the aquatic ecosystem.* 9(January), 423–427.

Obotey Ezugbe, E., and Rathilal, S. (2020). Membrane technologies in wastewater treatment: a review. *Membranes*, 10(5), 89.

Oghenejoboh, K. M., 2012. Effects of starch fermentation on the shelf-life of cassava starch based adhesive. *Biotechnol. J. Int.* 2 (4), 257–268. doi: 10.9734/BBJ/2012/2308 .

Ogunyemi, A. K., Samuel, T. A., Amund, O. O. and Ilori, M. O. 2018. Toxicity evaluation of waste effluent from cassava-processing factory in Lagos State, Nigeria using the *Allium Cepa* assay. *Ife Journal of Science* 20 (2): 3015 – 315.

Okwo J. M, Ozioko A. C. Adsorption of lead and mercury ions on chemically treated periwinkle shell, *Journal of Chemical Society of Nigeria.* 2011;26:60- 65.

Olutoge FA, Okeyinka OM, Olaniyan OS. Assessment of the suitability of periwinkle shell ash (PSA) as partial replacement for ordinary Portland cement (OPC) in concrete, *International Journal of Research and Reviews in Applied Sciences.* 2012;10(3):428-434.

Ongley E. D., *Control of Water Organization Pollution from Agriculture, Food & agriculture Organization,* 1996.

Onwuka, G.I., Ogbogu, N.J., 2007. Effects of fermentation on the quality and physicochemical properties of cassava based fufu products made from two varieties, NR8212 and Nwangbisi. *J. Food Technol.* 5 (3), 261–264 [https://medwelljournals.com/abstract/?doi = jftech.2007.261.264](https://medwelljournals.com/abstract/?doi=jftech.2007.261.264) .

Otunyo A. W., Friday I. U., and Israel T.A. (2014). *Exploratory study of crushed periwinkle shell as partial*. 13(1), 151–159.

Panwar, S., Upadhyay, G. K., and Purohit, L. P. (2022). Gd-doped ZnO: TiO<sub>2</sub> heterogenous nanocomposites for advance oxidation process. *Materials Research Bulletin*,145, 111534.

Pinto P., (2008) Tratamento de manipueira de fecularia em biodigestor anaeróbio para disposição em corpo receptor, rede pública ou uso em fertirrigação: Dissertação para obtenção do título de Mestre em Agronomia. Universidade Estadual Paulista “Júlio Mesquita Filho 9:87

Pirkanniemi K., and Sillanpaa M., *Chemosphere*, 2002, 48, 1047–1060.

Pohl, A. (2020). Removal of Heavy Metal Ions from Water and Wastewaters by Sulfur-Containing Precipitation Agents. *Water, Air, & Soil Pollution*.  
<https://doi.org/10.1007/s11270-020-04863-w>

Pouretedal H. R., Kiyani M., Photodegradation of 2-nitrophenol catalyzed by CoO, CoS and CoO/CoS NPs, *J. Iran. Chem. Soc.* 11 (2014) 271–277.

Praveen P, Loh K. C. Nitrogen and phosphorus removal from tertiary wastewater in an osmotic membrane photobioreactor. *Bioresour Technol* 2016; 206: 180-7

Rangarajan, S.; Thattai, D.; Kumar, H.; Satish, N.; Rustagi, R.Y.P. Evaluation of water quality index for River Mahananda West Bengal India. *Int. J. Innov. Technol. Explor. Eng.* 2019, 8, 1307–1309

Rao N, Rani G, Bakardjieva S and Subrt J 2010 Thick film titania on glass supports for vapour phase photocatalytic degradation of toluene , acetone , and ethanol *Chem. Eng. J.* 163 219–29

Ray M. B., Photodegradation of the volatile organic compounds in the gas phase: a review, *Dev. Chem. Eng. Mineral Process.* 8 (2000) 405–439.

Reza K. M., Kurny A. S. W, F. Gulshan F., Parameters affecting the photocatalytic degradation of dyes using TiO<sub>2</sub>: a review, *Appl. Water Sci.* 7 (2017) 1569–1578.

Rocha O. R. S, Dantas R. F, Duarte M M B, Duarte M M L and Da Silva V. L 2010 Oil sludge treatment by photocatalysis applying black and white light *Chem. Eng. J.* 157

Rodrigues M., Amado F. D. R., Xavier J., Streit K., Bernardes A., Ferreira J. Z., Application of photoelectrochemical–electrodialysis treatment for the recovery and reuse of water from tannery effluents, *J. Clean. Prod.* 16 (2008) 605–611.

Rujitanapanich S, Kumpapan P, Wanjanoi P. Synthesis of hydroxyapatite from oyster shell via precipitation, *Energy Procedia.* 2014;56:112–117.

Ruthven, D. M. (2008). *Fundamentals of Adsorption Equilibrium and Kinetics in Microporous Solids.* January 2006, 1–43.

Saeed K., Ali G., Khan I., Khan H., TiO<sub>2</sub>/Carbon nanotubes composites used for the photocatalytic degradation of organic dye, *J. Chem. Eng. Chem. Res.* 2 (2015) 671–676.

Santos, M. N. et al. Intraspecific variation, knowledge and local management of cassava (*Manihot esculenta* Crantz) in the semiarid region of Pernambuco, Northeast Brazil.

*Environment, Development and Sustainability*, v. 22, n. 4, p. 2881–2903, 7 abr. 2020.

Sahu, O. P. and Chaudhari, P. K., 2013. "Review on chemical treatment of industrial waste water." *Journal of Applied Sciences and Environmental Management*, vol. 17, pp. 241-257.

Saji G. S, Shamnadh M, Varma S, Amanulla S, Bharath RS, Oommen C. Experimental evaluation of compressive strength of PMMA-seashell based biocomposites for orthopedic applications. *Materials Today: Proceedings*. 2018;5:16509-16515.

[DOI.org/10.1016/j.matpr.2018.06.005](https://doi.org/10.1016/j.matpr.2018.06.005)

Samer, M. (2015). *Biological and Chemical Wastewater Treatment Processes*. InTech. doi: 10.5772/61250

Samudro, G., & Mangkoedihardjo, S. (2021). Review on BOD, COD and BOD / COD ratio : a triangle zone for toxic , biodegradable and stable levels. June.

Sarina S., Waclawik E. R., Zhu H., Photocatalysis on supported gold and silver nanoparticles under ultraviolet and visible light irradiation, *Green Chem.* 15 (2013) 1814–1833

Savci, S. (2012). An Agricultural Pollutant : Chemical Fertilizer. 3(1), 11–14.

Serpone N., Ah-You Y. K., Tran T. P., Harris R., Pelizzetti E., and Hidaka H. Solar Energy. Volume 39, Issue 6 (1987).

Serpone N., Borgarello E., Barbeni M., Pelizzetti E., Pichat P., Hermann J. M., and Fox M. A., *J. Photochem.* 36, 373 (1987).

Sharma K. 2023.Characteristics of Wastewater: Physical, Chemical, Biological

<https://scienceinfo.com/characteristics-of-wastewater>.

Shen Y. F., Tang J, Nie Z. H., Wang Y. D., Ren Y and Zuo L., 2009 Preparation and application of magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles for wastewater purification Sep. Purif. Technol. 68 312–9

Shi Hanchang Industrial wastewater-types, amounts and effects. Point sources of pollution: Local effects and their control, 2009.

Shiraishi F., and Ishimatsu T., 2009 Toluene removal from indoor air using a miniaturized photocatalytic air purifier including a preceding adsorption/desorption unit Chem. Eng. Sci. 64 2466–72

Skubal L. R., Meshkov N. K., Rajh T., and Thurnauer M., J. Photochem. Photobiol. A 148, 393 (2002).

Soneye, T., Ede, A. N., Bamigboye, G. O., and Olukanni, D. O. (2016). *The Study of Periwinkle Shells as Fine and Coarse Aggregate in Concrete Works*. 361–364.

Sonune, A. and Ghate, R., 2004. "Developments in wastewater treatment methods." Desalination, vol. 167, pp. 55-63.

Soto L. M., Moure, A., Domínguez, H., and Carlos, J. (2011). *Recovery , concentration and purification of phenolic compounds by adsorption : A review*. 105, 1–27.

<https://doi.org/10.1016/j.jfoodeng.2011.02.010>

Trapalis A, Todorova N, Giannakopoulou T, Boukos N, Speliotis T, Dimotikali D and Yu J 2016 TiO<sub>2</sub>/graphene composite photocatalysts for NO<sub>x</sub> removal: a comparison of surfactant-stabilized graphene and reduced graphene oxide Appl. Catal. B.

Tolia J. V., Chakraborty M., Murthy Z. V. P., Photocatalytic degradation of malachite green dye using doped and undoped ZnS nanoparticles, Pol. J. Chem. Technol. 14 (2012) 16–21.

Tchobanoglous G, Burton F. L, Stensel H. D. Metcalf and Eddy Wastewater Engineering: Treatment and Reuse. 4th ed. New Delhi: Tata McGraw-Hill Limited; 2003

Templeton, M. R and Butler, P. D. (n.d.). Introduction to Wastewater Treatment.

Tumwesigye K. S, Oliveira J. C, Sousa-Gallagher M. J (2016) Integrated sustainable process design framework for cassava biobased packaging materials: critical review of current challenges, emerging trends and prospects. Trends Food Sci Technol 56:103–114. <https://doi.org/10.1016/j.tifs.2016.08.001>

Vallejo W., Cantillo A., Uribe C. D., Methylene blue photodegradation under visible irradiation on Ag-Doped ZnO thin films, Int. J. Photoenergy (2020), <https://doi.org/10.1155/2020/1627498>.

Van der Merwe, A. I. and Friend, J. F. C. (2002). *Water management at a malted barley brewery*. 28(3), 313–318.

Vardhan, K.H.; Kumar, P.S.; Panda, R.C. A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. J. Mol. Liq. 2019, 290, 111197.

Venkatadri R., Peters R.W., (1993) Chemical oxidation technologies: ultraviolet light/hydrogen peroxide, Fenton's reagent, and titanium dioxide-assisted photocatalysis. Hazard Waste Hazard Mater 10:107–149

Verma, A., Prakash, N. T., and Toor, A. P. (2014). An efficient TiO<sub>2</sub> coated immobilized system for the degradation studies of herbicide isoproturon: Durability studies. Chemosphere, 109, 7-13

Verma, D. K., Maurya, N. K., and Kumar, P. (2022). Important Water Quality Parameters in Aquaculture : An Overview Important Water Quality Parameters in Aquaculture : An Overview. March.

Vymazal J., The use constructed wetlands with horizontal sub- surface flow for various types of wastewater, *Ecol. Eng.*, 2009, 35, 1–17.

Wattthier, E. et al. Cassava Wastewater Treatment in Fixed-Bed Reactors: Organic Matter Removal and Biogas Production. *Frontiers in Sustainable Food Systems*, v. 3, p. 6, 13 mar. 2019.

Wosiacki G., Cereda M. P., (2002) Valorização De Resíduos Do Pro- cessamento De Mandioca. *Publ UEPG—Ciencias Exatas e Da Terra, Agrar e Eng* 8:27–43. <https://doi.org/10.5212/publi.catio.v8i01.762>

Wang H., Zhang L., Chen Z., et al., “Semiconductor heterojunction photocatalysts: design, construction, and photo- catalytic performances,” *Chemical Society Reviews*, vol. 43, no. 15, p. 5234, 2014.

Wang, L. K., Chen, J. P., Hung, Y. T. and Shammass, N. K. *Membrane and Desalination Technologies*. Membrane and Desalination Technologies vol. 13 (2011). Springer.

World Health Organization Guidelines for drinking-water quality.4th ed. Geneva:WHO;2011

Yadav P., and Meena R. C., Photo catalytic bleaching of Amaranth by MB immobilized resin Dowex-11, *Der Pharm. Lett.* 2 (2010) 66–71.

Yao Z, Xia M, Li H, Chen T, Ye Y, Zheng H. Bivalve shell: not an abundant useless waste but a functional and versatile biomaterial, *Critical Reviews in Environmental Environmental Science and Technology*. 2014;44 (22):2502–2530. DOI.org/10.1080/10643389.2013.829763.

Yeh, T. Y., Ke, T. Y., and Lin, Y. L. (2015). Algal Growth Control Within Natural Water Purification Systems : Macrophyte Light Shading Effects Algal Growth Control Within Natural Water Purification Systems : Macrophyte Light Shading Effects. December. <https://doi.org/10.1007/s11270-010-0447-4>

Yin H., Xie M., Zhang I., Huang J., Xu Z., Li H., Jiang R., Wang R. and Zeng X., identification of sewage markers to indicate sources of contamination: low cost options for misconnected non-stormwater source tracking in stormwater systems, *Sci. Total Environ.*, 2019, 648, 125–134.

Yousif E., Haddad R., Photodegradation and photostabilization of polymers, especially polystyrene: review, *SpringerPlus* 2 (2013) 398–429.

Zhao, X., Liu, X., Yu, M., Wang, C., and Li, J. (2017). The highly efficient and stable Cu, Co, Zn-porphyrin–TiO<sub>2</sub> photocatalysts with heterojunction by using fashioned one-step method. *Dyes and Pigments*, 136, 648-656.

Zhao Z, Tian J, Sang Y, Cabot A and Liu H 2015 Structure, synthesis, and applications of TiO<sub>2</sub> nanobelts *Adv. Mater.* 27 2557–82

Zheng Y., Cao L., Xing G., Bai Z., Huang J., Zhang Z., Microscale flower-like magnesium oxide for highly efficient photocatalytic degradation of organic dyes in aqueous solution, *RSC Adv.* 9 (2019) 7338–7348.

Ziulli R. L and Jardim W. F 2001 Photocatalytic decomposition of seawater-soluble crude oil fractions using high surface area colloid nanoparticles of TiO<sub>2</sub> *J. Photochem. Photobiol. A*

Zoski C. G., *Handbook of Electrochemistry*, Elsevier, Amsterdam (2007).

## APPENDIX (A)

Table A.1 Physicochemical Properties of Cassava Wastewater

Parameters	Values
pH	3.6
Electrical Conductivity ( $\mu\Omega$ )	7890
Turbidity (NTU)	973
Suspended solid (mg/l)	572
Chloride (mg/l)	184.6
Hardness (mg/l)	875
Phosphate (mg/l)	9.26
Nitrate (mg/l)	0.53
Calcium (mg/l)	123.6
Magnesium (mg/l)	156.8
Dissolved Oxygen (mg/l)	133.5
BOD	85.4
COD	6980
Iron (mg/l)	398.67
Zinc (mg/l)	129.54
Copper (mg/l)	11.63

$$\text{Percentage Decrease} = \frac{C_o - C_e}{C_o} \times 100\% \quad (\text{A.1})$$

Table A.2 Effect of modified catalyst dosage variation

<b>Catalyst Dosage (g/L)</b>	<b>BOD (mg/l)</b>	<b>COD (mg/l)</b>	<b>Initial COD (mg/l)</b>	<b>Percentage decrease (%)</b>
0.4	83	6130	6980	12.18
0.8	65	5870	6980	15.90
1.2	62	3940	6980	43.55
2	53	3820	6980	45.27
3	47	3610	6980	48.28

Table A.3 Effect of unmodified catalyst dosage variation

<b>Catalyst Dosage (g/L)</b>	<b>BOD (mg/l)</b>	<b>COD (mg/l)</b>	<b>Initial COD (mg/l)</b>	<b>Percentage decrease (%)</b>
0.4	76	4120	6980	40.97
0.8	58	3940	6980	43.55
1.2	51	3360	6980	51.86
2	43	2630	6980	62.32
3	39	2450	6980	64.90

Table A.4 Effect of contact time variation (modified catalyst)

<b>Contact time (mins)</b>	<b>BOD (mg/l)</b>	<b>COD (mg/l)</b>	<b>Initial COD (mg/l)</b>	<b>Percentage decrease (%)</b>
30	29.30	1340	6980	80.80
60	25.80	1160	6980	83.38
90	22.20	960	6980	86.25
120	20.70	910	6980	86.96
150	18.40	870	6980	87.54

Table A.5 Effect of contact time variation (unmodified catalyst)

<b>Contact time (mins)</b>	<b>BOD (mg/l)</b>	<b>COD (mg/l)</b>	<b>Initial COD (mg/l)</b>	<b>Percentage decrease (%)</b>
30	22.40	965	6980	86.17
60	20.10	910	6980	86.96
90	17.60	860	6980	87.68
120	17.20	830	6980	88.11
150	14.20	740	6980	89.40

Table A.6 Effect of concentration variation (modified catalyst)

<b>Concentration(ml/L)</b>	<b>BOD (mg/l)</b>	<b>COD (mg/l)</b>	<b>Initial COD (mg/l)</b>	<b>Percentage decrease (%)</b>
100	30.70	1310	6980	81.23
200	33.00	1940	6980	72.21
300	37.40	2180	6980	68.77
400	39.20	2430	6980	65.19
500	43.60	2680	6980	61.60

Table A.7 Effect of concentration variation (unmodified catalyst)

<b>Concentration(ml/L)</b>	<b>BOD (mg/l)</b>	<b>COD (mg/l)</b>	<b>Initial COD (mg/l)</b>	<b>Percentage decrease (%)</b>
100	21.00	920	6980	86.82
200	23.00	980	6980	85.96
300	27.70	1180	6980	83.09
400	30.50	1540	6980	77.94
500	34.30	1970	6980	71.78

$$q_e = \frac{v(C_o - C_e)}{w} \quad (\text{A.2})$$

$$q_t = \frac{v(C_o - C_e)}{w} \quad (\text{A.3})$$

Where,  $C_o$  = Initial concentration

$C_e$  = Final concentration

$V$  = Volume of wastewater

$W$  = Catalyst Dosage

Table A.8 Adsorption Isotherm for Modified Catalyst

<b>Qe</b>	<b>Ce</b>	<b>Ce/qe</b>	<b>Inqe</b>	<b>InCe</b>
2125	6130	2.8847	7.6615	8.7210
1387.5	5870	4.2306	7.2353	8.6776
2533.33	3940	1.5553	7.8 373	8.2789
1580	3820	2.4177	7.3652	8.2480
1123.33	3610	3.2137	7.0241	8.1915

Table A.9 Adsorption Isotherm for Unmodified Catalyst

<b>qe</b>	<b>Ce</b>	<b>Ce/qe</b>	<b>Inqe</b>	<b>InCe</b>
7150	4120	0.5762	8.8749	8.3236
3800	3940	1.0368	8.2428	8.2789
3016.67	3360	1.1138	8.0119	8.1197
2175	2630	1.2092	7.6848	7.8747
1510	2450	1.6225	7.3199	7.8038

Table A.10 Kinetics Isotherm for Modified Catalyst

<b>T</b>	<b>Ce</b>	<b>qe</b>	<b>qt</b>	<b>(qe-qt)</b>	<b>In(qe-qt)</b>	<b>t/qt</b>	<b>t<sup>1/2</sup></b>
30	1340	2036.67	1880	156.67	5.05414	0.01595	5.47722
60	1160	2036.67	1940	96.67	4.57130	0.03092	7.74596
90	960	2036.67	2006.67	30	3.40119	0.04485	9.48683
120	910	2036.67	2023.33	13.34	2.59076	0.05931	10.95445
150	870	2036.67	2036.67	0		0.07365	12.24745

Table A.11 Kinetics Isotherm for Unmodified Catalyst

<b>T</b>	<b>Ce</b>	<b>qe</b>	<b>qt</b>	<b>(qe-qt)</b>	<b>ln(qe-qt)</b>	<b>t/qt</b>	<b>t<sup>1/2</sup></b>
30	965	2080	2005	75	4.31749	0.01496	5.4772
60	910	2080	2023.33	56.67	4.03724	0.02965	7.746
90	860	2080	2040	40	3.68888	0.04412	9.4868
	830	2080	2050	30	3.40119	0.05854	10.9545
150	740	2080	2080	0		0.07211	12.2474