PHOTOCATALYTIC TREATMENT OF WASTEWATER FROM SELECTED TEA FACTORIES IN KENYA

BY

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2017
DECLARATION

“I declare that this thesis is my original work and has not been submitted elsewhere for examination, award of a degree or publication. Where other people’s work, or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi’s requirements”.

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ABSTRACT

Wastewater from black tea (Camellia sinensis) processing factories is characterized by a persistent brown colour that conventional treatment works are unable to remove. In this work photocatalytic decolourization of persistent brick-red colour of black tea processing wastewater was investigated. Forty eight wastewater samples each of 500 cm$^3$ were collected from three black tea processing factories in the western Kenya highlands, and subjected to treatment by Titanium dioxide and Zinc oxide photocatalysts. Wastewater physico-chemical parameters were determined by analyzing Total Organic Carbon, Chemical Oxygen Demand, Turbidity, Total Suspended Solids and Total Dissolved Solids levels. Total Organic Carbon concentration was determined using the direct method, where 30% sodium persulfate, oxidizes dissolved organic carbon to carbon dioxide. The carbon present, is proportional to concentration of carbonaceous material present. Chemical Oxygen Demand was determined by closed reflux titrimetric method measuring chromates calorimetrically. Untreated wastewater samples were analysed for total metals of Mn, Al, Fe and Ni levels by Atomic Absorption Spectroscopy equipped with a deuterium background correction and air-acetylene burner. Total Al metal was analysed using a nitrous oxide-acetylene burner. The results obtained indicate concentrations levels Fe=1.46 mg/L; Mn=1.17 mg/L; Al=18.89 mg/L and Ni=0.32 mg/L. Sample concentration ranged between 0.26 – 18.89 mg/L. A GC-MS analysis of untreated samples indicated the presence of organic macromolecules that were identifiable and quantifiable. The number of molecules were as follows; (CBH= 9, KBH=14 and NBH= 12) respectively. An amount of 500 cm$^3$ of each wastewater sample was put in a photocatalytic reactor with a floor coated with a thin layer of ZnO to give a wastewater liquid height of approximately 2 cm. This was illuminated with Ultra violet lamps at 365 nm wavelength of intensity 3.0 mW/cm$^2$ for 180 mins, and solar light of intensity 1.4 mW/cm$^2$. Samples of 5 cm$^3$ were drawn every 15 minutes and analyzed using Ultra Violet/Visible spectrophotometer at $\lambda = 410$ nm. These experiments were repeated using TiO$_2$ coated floors. ZnO results indicate decolourization of 77% - 87% of the wastewater in 180 mins. Solar illumination produced higher efficiency of decolourization of 3% above Ultra violet lamp. On average decolourization of 61% solar illumination and 58% Ultra violet lamp was achieved in 60 minutes. Solar illumination intensity was 47% that of Ultra violet lamp.TiO$_2$ results indicate that decolourization of 70.4% - 78.5% of the wastewater was achieved in 180 mins. Solar illumination produced higher efficiency of 2.3% above Ultra violet lamp irradiation. Decolourization of 59.7% solar and 54.4 % Ultra violet lamp was achieved in
the first 60 minutes Solar radiation intensity used was 47% that of Ultra violet lamp for both photocatalytic systems. ZnO and TiO$_2$ photocatalysts were characterized by Laser Induced Breakdown Spectroscopy, X-ray Diffraction, Scanning Electron Microscope, Energy Dispersive X-Ray Spectroscopy, and surface area measurements. Laser Induced Breakdown Spectroscopy analysis revealed discrete atomic lines, indicating Ti and Zn spectral peaks at $\lambda = 400$ nm, X-Ray Diffraction/Scanning Electron Microscope analysis showed particle sizes of ZnO of 16.21 nm ± 2 nm and TiO$_2$ of 16.00 nm ± 2 nm and spherical in morphology, Energy Dispersive X-Ray Spectroscopy showed active catalyst element present 61.5%, Zn in ZnO and 61%, Ti in TiO$_2$ and specific surface area of 40.14 m$^2$/g ZnO and 31.76 m$^2$/g TiO$_2$. After 180 mins, Total Organic Carbon, Chemical Oxygen Demand, Turbidity, Total Suspended Solids and Total Dissolved Solids levels decreased by 74.8%, 58.5%, 45.1, 58.01% and 41.52% respectively but pH increased from acidity towards neutrality from 5.8 to 6.7. Treatment by Solar/Ultraviolet/ZnO system, indicated a 9.7% efficiency compared to Solar/Ultraviolet/TiO$_2$ system.
DEDICATION

This dissertation is dedicated to my parents who instilled in me the virtues of perseverance and commitment and relentlessly encouraged me to strive for excellence.
ACKNOWLEDGEMENTS

Primarily I dedicate this dissertation to God almighty, without whose origin of wisdom and knowledge, my humanly endeavours would be futile.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>vi</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xvi</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS / ACRONYMS AND SYMBOLS</td>
<td>xviii</td>
</tr>
<tr>
<td>CHAPTER ONE</td>
<td>1</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Background</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Tea processing wastewater</td>
<td>3</td>
</tr>
<tr>
<td>1.2.1 Characteristics of tea processing wastewater</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2 Wastewater management- Tea processing wastewater</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2.1 Wetlands</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2.2 Lagoons</td>
<td>4</td>
</tr>
<tr>
<td>1.2.2.3 Stabilization ponds (SPs)</td>
<td>4</td>
</tr>
<tr>
<td>1.2.2.4 Electro-coagulation (EC)</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Pollution of water resources</td>
<td>5</td>
</tr>
<tr>
<td>1.4 National Environmental Legal Framework in Kenya</td>
<td>6</td>
</tr>
<tr>
<td>1.5 Problem Statement</td>
<td>6</td>
</tr>
<tr>
<td>1.6 Justification and significance of the study</td>
<td>7</td>
</tr>
<tr>
<td>1.7 Main Objective</td>
<td>7</td>
</tr>
<tr>
<td>1.7.1 Specific Objectives</td>
<td>7</td>
</tr>
<tr>
<td>CHAPTER TWO</td>
<td>9</td>
</tr>
<tr>
<td>2 Literature review</td>
<td>9</td>
</tr>
</tbody>
</table>
2.1 Tea Varieties

2.2 Tea pigments

2.2.1 Biochemical constituents of Tea

2.3 Tea processing in Kenya

2.3.1 Coloured wastewater treatment techniques

2.3.1.1 Phytoremediation

2.3.1.2 Physico-chemical techniques

2.3.1.3 Biological techniques

2.3.1.4 Electrochemical techniques

2.3.1.5 Electromagnetic radiation

2.3.1.6 Conventional methods

2.3.1.7 Advanced Oxidation Processes (AOPs)

2.4 Photocatalytic degradation mechanism

2.4.1 Applications of Photocatalytic degradation

2.4.1.1 Destruction of organics

2.4.1.2 Water disinfections

2.4.1.3 Photocatalytic treatment of natural organic matter

2.4.1.4 Seawater treatment

2.4.2 Principles of semi-conductor photocatalysis

2.4.2.1 Photocatalytic oxidation

2.4.2.2 Photosensitized oxidation

2.4.3 Heterogenous photocatalytic degradation

2.4.4 Homogenous photocatalytic degradation (Photo-Fenton Reaction)

2.5 Solar induced photocatalytic degradation

2.5.1 Solar Ultra-violet radiation (UVR)

2.5.2 Advantages of Solar induced photocatalytic degradation

2.5.3 Limitations of Solar induced photocatalytic degradation

2.6 Zinc oxide and Titanium dioxide photocatalysts

2.6.1 Theory of semi-conductors

2.7 Suspension photocatalysis

2.8 Thin film photocatalysis

2.8.1 Ideal Photocatalysts

2.8.1.1 Nano – photocatalysts
2.8.1.2 Titanium dioxide photocatalyst ........................................ 26
2.8.1.3 Zinc oxide photocatalyst .................................................. 27
2.8.2 Influence of TiO$_2$ and ZnO Structural and morphological character on wastewater photocatalytic treatment ........................................ 29
   2.8.2.1 Structural and Morphological characterization – ZnO/TiO$_2$ 29
      2.8.2.1.1 Scanning Electron Microscope (SEM)/ Brunauer Emmett Teller (BET) 29
      2.8.2.1.2 X-Ray Diffraction (XRD) ........................................ 30
      2.8.2.1.3 Energy Dispersive X-Ray Spectrometry (EDS) ............... 32
      2.8.2.1.4 Laser Induced Break-down Spectroscopy (LIBS) ............. 33
      2.8.2.1.5 Ultra-violet / visible spectrophotometer ..................... 34
      2.8.2.1.6 Atomic Absorption Spectroscopy (AAS) ....................... 35
      2.8.2.1.7 Gas Chromatography – Mass Spectroscopy (GC-MS) ....... 36

CHAPTER THREE ........................................................................... 37

3 Materials and methods .............................................................. 37
   3.1 Sample collection ................................................................. 37
      3.1.1 Sampling sites ............................................................... 37
      3.1.2 Sampling period and atmospheric temperature ....................... 38
         3.1.2.1 Map - Nandi County .................................................. 39
         3.1.2.2 Map - CBH factory .................................................. 40
         3.1.2.3 Map - NBH factory ................................................... 41
         3.1.2.4 Map - KBH factory ................................................... 42
         3.1.2.5 Rivers in Nandi County .............................................. 43
   3.2 Chemicals and Reagents ...................................................... 44
   3.3 Instruments ......................................................................... 45
      3.3.1 UV light source (UV lamps) ........................................... 46
      3.3.2 Solar light ..................................................................... 46
      3.3.3 Preparation of ZnO and TiO$_2$ surface layers ....................... 46
      3.3.4 Preparation of ZnO and TiO$_2$ pellets ............................... 46
      3.3.5 Fabrication of photocatalytic reactors ................................. 47
         3.3.5.1 Photocatalytic reactor fitted with UV lamps .................. 47
         3.3.5.2 Photocatalytic reactor irradiated by solar light ................ 48
      3.3.6 Experimental design ....................................................... 49
3.4  Methods

3.4.1 Measuring light intensity

3.4.1.1 UV lamps

3.4.1.2 Solar light

3.5  Physico-Chemical Characterization of Raw and Treated Wastewater

3.5.1 pH

3.5.2 Turbidity

3.5.3 Total Organic Carbon – Direct method

3.5.4 Chemical Oxygen Demand (COD) (mg/L) – closed reflux titrimetric method

3.5.5 Total Suspended Solids (TSS)

3.5.6 Total Dissolved Solids (TDS)

3.6  Decolourization of wastewater

3.6.1 Colour measurement by UV/Vis spectrophotometer

3.6.2 Spectral analysis of wastewater

3.6.3 Photocatalytic decolourization of wastewater

3.6.4 UV-ZnO film decolourization system

3.6.5 Solar-ZnO film decolourization system

3.6.6 UV/TiO₂ film – decolourization system

3.6.7 Solar /TiO₂ film – decolourization system

3.7  Macro-molecules in tea processing wastewater

3.7.1 Gas Chromatography – Mass Spectrometry

3.8  Chemical elements in tea processing wastewater

3.8.1 Atomic Absorption Spectroscopy

3.9  Surface morphology characterization of TiO₂ and ZnO

3.9.1 Laser Induced Breakdown Spectroscopy (LIBS)

3.9.2 Energy-Dispersive X-ray spectroscopy (EDS)

3.9.3 Scanning Electron Microscope (SEM) – Crystal size

3.9.4 X-Ray Diffractometry (XRD) – Crystallite size

3.9.5 Brunauer Emmett Teller (BET) – surface area analysis

CHAPTER FOUR

4  Results and Discussion
4.1 Physico-Chemical Characterization - untreated wastewater
4.1.1 pH
4.1.2 Turbidity
4.1.3 Total Organic Compounds (TOC)
4.1.4 Chemical Oxygen Demand (COD)
4.1.5 Total Suspended Solids (TSS)
4.1.6 Total Dissolved Solids (TDS)

4.2 Analysis of macro-molecules in tea processing wastewater
4.2.1 Gas Chromatography–Mass Spectrometry (GC-MS)

4.3 Total chemical elements in tea processing wastewater
4.3.1 Total Chemical element – Ni
4.3.2 Total Chemical element – Al
4.3.3 Total Chemical element – Mn
4.3.4 Total Chemical element – Fe

4.4 Photocatalytic treatment of tea processing wastewater
4.4.1 Spectral analysis of untreated CBH, KBH and NBH wastewater
4.4.2 Optimization of ideal reaction time
4.4.3 Photocatalytic treatment - UV /ZnO
4.4.4 Photocatalytic treatment - solar /ZnO
4.4.5 Comparison of photocatalytic treatment efficiency between ZnO/ UV radiation/Solar
4.4.5.1 Comparison of UV/solar/ ZnO treatment system - KBH
4.4.5.2 Comparison of UV/solar/ ZnO treatment system – CBH
4.4.5.3 Comparison of UV/solar/ ZnO treatment system - NBH
4.4.6 Photocatalytic treatment - UV /TiO₂
4.4.7 Photocatalytic treatment - Solar/TiO₂
4.4.8 Comparisons - photocatalytic treatment system (UV-Solar /TiO₂)
4.4.8.1 Comparison - UV/solar/ TiO₂ treatment system - KBH
4.4.8.2 Comparison of UV/solar/ TiO₂ treatment system - CBH
4.4.8.3 Comparison of UV/solar/ TiO₂ treatment system - NBH

4.5 Physico-chemical characterization - Treated wastewater
4.5.1 pH
4.5.2 Turbidity
4.5.3 Total Organic Compounds (TOC)
4.5.4 Chemical Oxygen Demand (COD) ---------------------------------- 82
4.5.5 Total Suspended Solids (TSS)------------------------------------- 82
4.5.6 Total Dissolved Solids (TDS)-------------------------------------- 83

4.6 Characterization of TiO\textsubscript{2} and ZnO - Surface morphology -------- 83
4.6.1 Laser Induced Breakdown Spectroscopy (LIBS) ----------------------- 83
  4.6.1.1 TiO\textsubscript{2}--------------------------------------------- 83
  4.6.1.2 ZnO--------------------------------------------- 84
4.6.2 Energy Dispersive X-ray Spectroscopy (EDS)------------------------ 85
  4.6.2.1 ZnO--------------------------------------------- 85
  4.6.2.2 (TiO\textsubscript{2})--------------------------------------------- 86
4.6.3 Scanning Electron Microscope (SEM)-------------------------------- 87
  4.6.3.1 TiO\textsubscript{2}--------------------------------------------- 87
  4.6.3.2 ZnO--------------------------------------------- 88
4.6.4 X-Ray Diffractometry (XRD)---------------------------------------- 90
  4.6.4.1 TiO\textsubscript{2}--------------------------------------------- 90
  4.6.4.2 ZnO--------------------------------------------- 91
4.6.5 Brunauer Emmett Teller (BET) – surface area analysis --------------- 92

CHAPTER FIVE --------------------------------------------------------- 93

5 Conclusions and Recommendations -------------------------------- 93
  5.1 Conclusions-------------------------------------------------------- 93
  5.2 Recommendations--------------------------------------------------- 96

REFERENCES ---------------------------------------------------------- 97

APPENDICES ---------------------------------------------------------- 118
LIST OF TABLES

Table 2.1: Bandgap Energies for various semi-conductors at 0 k .................................................25
Table 3.1: Location of sampling sites ..........................................................................................37
Table 3.2: Sampling duration .......................................................................................................38
Table 3.3: Chemicals and reagents ..............................................................................................44
Table 3.4: Equipment ...................................................................................................................45
Table 4.1: Physico-Chemical characterization of tea processing wastewater .........................63
Table 4.2: Macro-molecules in Tea processing wastewater .......................................................66
Table 4.3: Physico-chemical characterization – Treated wastewater ......................................81
Table 4.4: EDS compositional analysis - ZnO .............................................................................85
Table 4.5: EDS compositional analysis - TiO$_2$ ........................................................................86
Table 4.6: Surface area measurements - ZnO and TiO$_2$ ..........................................................92
LIST OF FIGURES

Figure 1.1: Tea growing areas of Kenya.................................................................2
Figure 2.1: Description of Photocatalytic degradation photocatalysis in solutions containing oxidative and reductive species ...........................................15
Figure 2.2: TiO₂ coated tent material.................................................................17
Figure 2.3: TiO₂ coated exterior tiles.................................................................17
Figure 2.4: TiO₂ coated mirror.............................................................................18
Figure 2.5: Principles of Heterogenous Photocatalysis .........................................19
Figure 2.6: Scanning Electron Microscope apparatus ..........................................30
Figure 2.7: X-Ray Diffraction apparatus .............................................................31
Figure 2.8: Energy Dispersive X-ray Spectroscopy .............................................32
Figure 2.9: Laser Induced Breakdown Spectroscopy setup ....................................33
Figure 2.10: UV-Vis Spectrophotometry..............................................................34
Figure 2.11: Atomic Absorption Spectroscopy ...................................................35
Figure 2.12: Gas Chromatography- Mass Spectrometry ......................................36
Figure 3.1: Map - Nandi County ...........................................................................39
Figure 3.2: Map - CBH factory ............................................................................40
Figure 3.3: NBH factory .......................................................................................41
Figure 3.4: KBH factory .......................................................................................42
Figure 3.5: Major river systems in Nandi County ................................................43
Figure 3.6: UV lamps induced photocatalytic reactor ...........................................47
Figure 3.7: Photocatalytic reactor irradiated with Solar light ..................................48
Figure 4.1: Total chemical elements – CBH, KBH and NBH ..................................68
Figure. 4.2: Absorption spectra CBH, KBH and NBH ..........................................69
Figure 4.3: Optimization of reaction time – UV/TiO₂ treatment of KBH sample ....70
Figure 4.4: UV/ZnO photocatalytic treatment of KBH, CBH and NBH wastewater ....71
Figure 4.5: Solar/ZnO photocatalytic treatment of KBH, CBH and NBH wastewater ...72
Figure 4.6: Solar/ZnO and UV/ZnO photocatalytic treatment system of KBH wastewater .........................................................................................................73
Figure 4.7: Solar/ZnO and UV/ZnO photocatalytic treatment system of CBH wastewater. .................................................................................................................74
Figure 4.8: Solar/ZnO and UV/ZnO photocatalytic treatment system of NBH wastewater .................................................................................................................75
Figure 4.9: UV/TiO₂ photocatalytic treatment of KBH, CBH and NBH wastewater .....76
Figure 4.10: Solar/TiO$_2$ Photocatalytic treatment of KBH, CBH and NBH wastewater.

Figure 4.11: Solar/TiO$_2$ and UV/TiO$_2$ photocatalytic treatment system of KBH wastewater.

Figure 4.12: Solar/TiO$_2$ and UV/TiO$_2$ photocatalytic treatment system of CBH wastewater.

Figure 4.13: Solar/TiO$_2$ and UV/TiO$_2$ photocatalytic treatment system of NBH wastewater.

Figure 4.14: LIBS spectrum - TiO$_2$.

Figure 4.15: LIBS spectrum - ZnO.

Figure 4.16: EDS spectrum - ZnO.

Figure 4.17: EDS spectrum - TiO$_2$.

Figure 4.18: TiO$_2$ (500μm- wd 15.01 mm).

Figure 4.19: TiO$_2$ (100μm (wd 15.01 mm).

Figure 4.20: TiO$_2$ (5 μm –wd 15.10 mm).

Figure 4.21: TiO$_2$ (5μm- wd 15.07 mm).

Figure 4.22: TiO$_2$ (2 μm wd 15.09 mm).

Figure 4.23: TiO$_2$ (2μm wd 15.07mm).

Figure 4.24: TiO$_2$ (1 μm – wd 15.09 mm).

Figure 4.25: TiO$_2$ (1 μm – wd 15.07 mm).

Figure 4.26: ZnO (500 μm-wd 15.02 mm).

Figure 4.27: ZnO (2 μm – wd-15.02 mm).

Figure 4.28: ZnO (2 μm-wd-15.12 mm).

Figure 4.29: ZnO (5 μm- wd-15.14 mm).

Figure 4.30: ZnO (2 μm-wd-15.11 mm).

Figure 4.31: ZnO (2 μm- wd-15.14 mm).

Figure 4.32: ZnO (1 μm- wd-15.10 mm).

Figure 4.33: ZnO (1 μm- wd-15.10 mm).

Figure 4.34: X-Ray Diffraction patterns - TiO$_2$.

Figure 4.35: X-Ray Diffraction patterns - ZnO.
LIST OF APPENDICES

Appendix 1: Chromatogram – KBH sample.................................................................118
Appendix 2: (2-butanone, 4-(2, 6, 6-trimethyl-1-yl)- ........................................119
Appendix 3: 1-[2-[3-(2-acetyloxiran-2-yl)-1, 1-dimethylpropyl] cycloprop-2-etyl}
ethanone ....................................................................................................................120
Appendix 4: Tetradecanoic acid ..............................................................................121
Appendix 5: Acetic acid............................................................................................122
Appendix 6: 3, 7, 11, 15-tetramethyl-2-hexadecen-1-ol........................................123
Appendix 7: Caffeine.................................................................................................124
Appendix 8: (n-hexadecanoic acid) ........................................................................125
Appendix 9: Phytol ....................................................................................................126
Appendix 10: 9, 12, 15-octadecatrienoic acid ........................................................127
Appendix 11: Octadecanoic acid ............................................................................128
Appendix 12: Ethyl iso-allocholate ........................................................................129
Appendix 13: 1, 2-benzenedicarboxylic acid ..........................................................130
Appendix 14: 2, 6, 10, 14, 18, 22-tetracosahexane, 2, 6, 10, 15, 23-hexamethyl- ......131
Appendix 15: Chromatogram – CBH sample ..........................................................132
Appendix 16: 7-(1,3-dimethylbuta-1,3-dienyl)-1,6,6-trimethyl-3,8-
dioxatricyclo[5,1,0,0(2,4)]octane .............................................................................133
Appendix 17: Acetic acid.........................................................................................134
Appendix 18: Caffeine .............................................................................................135
Appendix 19: n-hexadecanoic acid .......................................................................136
Appendix 20: Phytol .................................................................................................137
Appendix 21: 9, 12, 15-octadecatrienoic acid ........................................................138
Appendix 22: Octadecanoic acid ............................................................................139
Appendix 23: 1, 2-benzenedicarboxylic acid, diisooctyl ester ..............................140
Appendix 24: Oleic acid, eicosyl ester ..................................................................141
Appendix 25: Chromatogram – sample NBH.......................................................142
Appendix 26: 1-heptatriacotanol .............................................................................143
Appendix 27: Propiollic acid ..................................................................................144
Appendix 28: Caffeine ............................................................................................145
Appendix 29: Phthalic acid .....................................................................................146
Appendix 30: Phytol ...............................................................................................147
Appendix 31: 9, 12, 15-octadecatrienoic acid ........................................................148
Appendix 32: Octadecanoic acid ...........................................................................................................149
Appendix 33: α-Amyrin..........................................................................................................................150
Appendix 34: α-Tocopherol....................................................................................................................151
Appendix 35: 1, 2-benzenedicarboxylic acid.........................................................................................152
Appendix 36: Vitamin E ..........................................................................................................................153
Appendix 37: 2, 2, 4-trimethyl-heptadeca-3, 7, 11, 15-tetraenyl)-cyclohexanol .........................154
Appendix 38: TiO$_2$-Pulse Energy (70 MJ) .........................................................................................155
Appendix 39: TiO$_2$-Pulse Energy (90 MJ) ..........................................................................................155
Appendix 40: TiO$_2$-Pulse Energy (80 MJ) ..........................................................................................156
Appendix 41: ZnO-Pulse Energy (70 MJ) .............................................................................................156
Appendix 42: ZnO-Pulse Energy (90 MJ) .............................................................................................157
Appendix 43: ZnO-Pulse Energy (80 MJ) .............................................................................................157
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>A</td>
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<tr>
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</tr>
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</tr>
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<td>AOP</td>
<td>Advanced Oxidation Processes</td>
</tr>
<tr>
<td>APHA</td>
<td>American Public Health Association</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett Joiner Halenda</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological Oxygen Demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>CW</td>
<td>Constructed Wetlands</td>
</tr>
<tr>
<td>c</td>
<td>Molar concentration (mol.dm(^{-3}))</td>
</tr>
<tr>
<td>CTC</td>
<td>Cut Tear Curl</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbons</td>
</tr>
<tr>
<td>CFU</td>
<td>Continuous Fermentation Unit</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>d</td>
<td>Optical path (cm)</td>
</tr>
<tr>
<td>Eg</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>E(^{-})(_{cb})</td>
<td>Conduction band electron</td>
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<tr>
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</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Diffractive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Molar extinction coefficient</td>
</tr>
<tr>
<td>Eg</td>
<td>Bandgap energy</td>
</tr>
<tr>
<td>EPK</td>
<td>Eastern Produce Kenya</td>
</tr>
<tr>
<td>FAS</td>
<td>Ferrous Ammonium Sulfate</td>
</tr>
<tr>
<td>FAO</td>
<td>Food Agriculture Organization</td>
</tr>
<tr>
<td>GOK</td>
<td>Government of Kenya</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography-Mass Spectrometry</td>
</tr>
<tr>
<td>h(^{+})</td>
<td>(\text{vb valence band hole})</td>
</tr>
<tr>
<td>h(\nu)</td>
<td>the symbol of a photon of a certain energy</td>
</tr>
<tr>
<td>HCFC</td>
<td>Hydrochlorofluorocarbons</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
</tbody>
</table>
IC  Inorganic carbon
ICTP  Institute of Chemical Technology Prague
KTDA  Kenya Tea Devolvement Agency
LIBS  Laser Induced Breaking-Down Spectroscopy
LVEMP  Lake Victoria Environment Management Programme
NEMA  National Environment Management Authority
pzc  point of zero change
PET  Polyethylene Terephthalate
POP  Persistent Organic Pollutant
ppm  parts per million
PAH  Polyaromatic Hydrocarbons
RS  Raw sample
ROS  Relative Oxygen Species
SHE  Standard Hydrogen Electrode
SEM  Scanning Electron Microscope
SP  Stabilization Ponds
TF  Theaflavins
TR  Thearubigins
TOC  Total Organic Carbon
TSS  Total Suspended Solids
TDS  Total Dissolved Solids
T  Transmittance
 t  Time (min)
TOC  Total Organic Carbon
TRI  Tea Research Institute
TUK  Technical University of Kenya
TBK  Tea Board of Kenya
TC  Total carbon
TS  Treated sample
TDK  Tea Directorate of Kenya
UV  Ultra violet
UON  University of Nairobi
UV  Ultra violet
UVA  Ultra Violet A ($\lambda= 315 \text{ nm}-400 \text{ nm}$)
UVB  Ultra Violet B ($\lambda= 280 \text{ nm}-315 \text{ nm}$)

xix
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>UVR</td>
<td>Electromagnetic spectrum of UV radiation</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Carbon</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction Analysis</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength (nm)</td>
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CHAPTER ONE

1 Introduction
1.1 Background

Tea (*Camellia sinensis*) grows in tropical and sub-tropical climates of the world and is enjoyed globally for its aromatic taste and non-alcoholic nature (Seenivasan *et al.*, 2008). As a drink, tea is the most popular beverage after water and is prepared by brewing hot water with processed cured tea leaves. A tea bush can remain productive for up to 100 years and produce between 3-5 kg of dry tea leaves annually.

A few tea bushes were first planted in Kenya around 1903 by the Caine brothers at Mabroukie-Limuru (Paul *et al.*, 1997). Large-scale tea growing spread to other regions of Kenya after 1930. The major tea growing areas in Kenya are mainly to the west and east of the Rift Valley (Owuor, 2011). The tea growing areas have an ideal climate, fertile red volcanic soils and annual rainfall ranging between 1200 mm to 1400 mm.

Currently small-scale tea production in Kenya is managed by the Kenya Tea Development Agency (KTDA). By the year 2017, KTDA owned 66 tea processing factories, serving over 500,000 farmers, cultivating 150,000 ha of tea plantation. This represents over 60% of total tea production. The rest of the production is done by multinational tea companies (Mucheke, 2015). The bulk of tea processed in Kenya is majorly black tea, which is exclusively processed by the CTC (Cut, Tear and Curl) technique.

The KTDA manages 54 tea companies, owning 66 tea processing factories across Kenya, Eastern Produce (EAP) oversees 5 factories in Nandi and Kericho counties and James Finlay's (K) operates 4 factories in Kericho and Bomet counties. Tea production in Kenya reached 473 million kilograms in 2016 (TDK, 2016). The increase in demand for tea processing has consequently led to generation of large volumes of wastewater produced during processing and cleaning stages. The specific volumes of wastewater discharged from individual processing factories is dependent on the production capacity of each factory.
The major tea growing areas in Kenya are shown in Figure 1.1.

Despite the huge volumes of wastewater produced, the majority of tea processing factories in Kenya lack effective wastewater treatment processes. Most factories rely almost entirely on constructed wetlands (CW), Stabilization Ponds (SPs) with vegetation systems and lagoons. The wastewater discharged from these factories is characterized by a persistent distinct brown colour, since the majority of products formed during tea processing are coloured (Roberts, 1958). The characteristic brown colour of wastewater renders it untenable for discharge into the environment. This study proposes the use of suitable select semi-conductor photocatalysts irradiated with Solar/UV light to remedy the challenge posed by the coloured wastewaters on the entire tea sector.
1.2 Tea processing wastewater
1.2.1 Characteristics of tea processing wastewater

Tea processing leads to the generation of large volumes of wastewater that is characterized by high organic matter, high suspended matter, heavy metals, odour, surfactants, and high oxygen demanding parameters. In addition, other wastewater components include: unprocessed tea leaves, detergents, waste grease and oil from machine parts (Tum et al., 2016).

The greatest concern for the tea industry in Kenya, remains the persistent colour problem caused by large volumes of coloured wastewater discharged from their factories into the environment. The coloured wastewater results from the presence of organic macromolecules, that are characterized by conjugated carbon-carbon bonds in their structures formed during tea processing (Graham, 1992; Maghanga et al., 2009; Tum et al., 2016). Flavanols, which are colour pigments are responsible for the colouring of wastewater from tea processing factories. These flavanols that include theaflavins, are brick-red pigments characterized by conjugated aromatic rings (Haddis & Devi, 2008).

Discharge of untreated tea processing wastewater leads to contamination of the eco-system. This contamination leads to disruption of aquatic life by reducing the amount of sunlight penetrating into water bodies. Further contamination affects plants like algae and weeds that are consumed by fish and other aquatic animals thereby disrupting the food chain upwards (Onyatta et al., 2016). Pollution also disrupts the oxygen cycle that sustains living organisms by disturbing the natural balance and affecting the environment in various ways.

1.2.2 Wastewater management- Tea processing wastewater
1.2.2.1 Wetlands

Wetlands are vegetative regeneration zones that allow rainfall to percolate into the ground allowing wastewater regeneration (Lin et al., 2003). These wetlands are composed of vegetation that act as natural sponges (Chung et al., 2008). They absorb particulate matter in wastewater thereby removing the characteristic brick-red colour. The retention ability of wetlands enables them to discharge and recharge surface and ground water respectively. According to (Lin et al., 2003) wetlands cleanse wastewater by purifying it naturally, removing silts and sucking in toxins.
1.2.2.2 Lagoons

Tea processing factories use lagoons to treat their wastewater. These treatment system consists of one or several ponds built to hold wastewater for a certain duration of time. The construction of these ponds involves lining with material such as clay to prevent leaks to the ground water. The wastewater treatment is achieved by biological and chemical processes that occur naturally. The lagoons are designed to use aeration devices that increase oxygen in wastewater. Aeration improves wastewater treatment efficiency, to utilize less land area (Lawson, 2011).

1.2.2.3 Stabilization ponds (SPs)

These are man-made ponds in which tea processing wastewater is treated and discharged safely into river systems. Stabilization ponds are linked in a series that includes several types of ponds that include, (i) anaerobic ponds, (ii) facultative ponds and (iii) aerobic ponds (Arthur, 1983). Aerobic and facultative ponds remove CODs while anaerobic ponds are designed to remove bacteria. Suspended solids are digested at the base of the ponds and aerobic ponds act as final stage treatment. The ponds are generally effective in treatment, however its disadvantage includes the long time it takes to treat wastewater and the large land mass required (Arthur, 1983).

1.2.2.4 Electro-coagulation (EC)

Involves the use of an electrochemical cell where contaminants in wastewater such as heavy metals, organics and inorganics are held together by electric charges. (Gilmore & Renk, 2014). An electric charge is applied on metallic plates inserted in the wastewater while a second charge is applied holding contaminating particles together. These are thereafter separated from the purified water. These particles coagulate forming a mass that is separated by filtration (Rajeshwar & Ibanez, 1995). Iron metal is preferred as the conducting material at both the anode and cathode (Mollah et al., 2001). Electrocoagulation as a wastewater treatment technique has been investigated by several researchers including (Maghanga et al., 2009).
1.3 Pollution of water resources

Water pollution results from natural and man-made activities. Large amounts of polluted wastewater in developing countries (80 - 90%) is discharged directly into surface water bodies with little or minimal treatment (Water, 2008). The pollution of these water resources has led to severe water stress and by the year 2025, it is predicted about two-thirds of the world’s population would lack access to clean and safe water for domestic and industrial use (Clark, 2007).

Severe shortages in treated water, has caused humans and livestock to use water fetched from rivers and lakes that may not be safe for domestic use (Van der Bruggen & Braeken, 2006). In the past, wastes generated from industries, were dumped without treatment into rivers where they were subjected to dilution and self-purification (Karr & Chu, 2006). Large influxes of pollutants results in severe oxygen depletion negatively affecting the aquatic environment causing degradation (Zimmerman, 1993). These environmental problems include eutrophication which results from a decrease in sunlight penetration due to presence of pollutants, reducing the photosynthesis process of aquatic animals and visual pollution (Azad et al., 2014; Guillard et al., 2003). The presence of high colour levels in wastewater affects its aesthetic qualities and reduces light penetration and affecting plant growth and habitat. Organic contaminants discharged in wastewater from various industries, are the major causes of degradation of water resources (Rajaram & Das, 2008).

The majority of rivers and streams in Kenya are heavily polluted. The sources of this pollution, includes domestic wastes and wastewater discharged from industries. Rivers situated near major towns and cities are worst affected as they are heavily contaminated with organic pollutants (Monteith et al., 1995). Colour is a significant indicator of water quality, however the decolourization of industrial wastewater remains a great challenge requiring strict controls i.e. industries should consider new methods of wastewater decolourization and disposal (Monteith et al., 1995). Coloured wastewater from tea processing factories adversely impact on animal and plant life in the environment (Monteith et al., 1995).
1.4 National Environmental Legal Framework in Kenya

The Government of Kenya, through legislation requires all manufacturing industries to treat all wastewater before disposal. This is to regulate and protect surface water resources from adverse impacts. These regulations are enacted in the Water Quality Regulation act, 2006 and the Wetlands and River bank Regulations act, 2006. These regulations prohibit the discharge of any substances into a flowing river, lake or wetland, if the substance would negatively affect Water quality. In addition, the (GOK Environmental Management and Coordination Act, 2009) prohibits the intentional discharge of noxious wastes into water resources.

Other laws that regulate wastewater disposal include; (GOK Water Bill, 2014); (GOK Strategic Assessment, Integrated Impact Assessment and Audit) Regulations, 2017 and GOK Occupational Safety and Health Act, 2007; Act No. 15 of 2007.

1.5 Problem Statement

Individual tea processing factories in Kenya require an average of 70 m$^3$ of fresh water daily during their cleaning and maintenance operations (EPK, 2010). This requirement is in contrast to the available fresh water reserves available in Kenya, which is water-scarce with 647 m$^3$ of freshwater available per capita. The wastewater that is formed after tea processing is largely released into the natural environment without effective treatment. These wastewater is loaded with contaminants such as high organic matter, high suspended matter, heavy metals, odour, surfactants, and high oxygen demanding parameters that make the water unpalatable. Of great concern is the persistent problem of colour and other parameters that cannot and have never been removed through conventional wastewater treatment. Wastewater from Chebut, Kibwari and Nandi tea processing factories located in the Nandi hills catchment, in Nandi County, is discharged into tributaries for rivers Yala and Nyando that feed into Lake Victoria. Pollution load is highest on the Kenyan side of Lake Victoria due to these inflows. Communities living along the course of these tributaries and rivers have had to live with poor water quality as a result of this untreated wastewater from the factories. Women have to walk long distances in search of clean and safe water for domestic use. Water in these rivers leave deposits of sludge and slurry on vegetation and banks, thereby destroying the aquatic life in these waters. Fish stocks in river Nyando and Yala have been steadily declining over the years (Maghanga et al.,
2009). The destruction and loss of wetlands in the Nyando and Yala threatens to increase poverty and to undermine development. A decline in the health of the ecosystem due to pollution that has cut down fish stocks in the lake (Maghanga et al., 2009). Industrial run-off, from the various factories in the catchment area has subsequently led to the invasion of water hyacinth in lake Victoria. Some tea processing factories in Kenya have constructed wetlands (CW), where duckweed (*Lemna spp*) and other plants are grown and used to treat wastewater through phyto-remediation, Stabilization Ponds (SPs) and Lagoons. These methods have however largely been less effective leading to much of the wastewater being discharged into nearby rivers while still coloured.

1.6 Justification and significance of the study

The communities living along rivers that are contaminated by coloured wastewater from tea factories will benefit from clean water for their domestic use. In addition, the continued pollution of rivers flowing into Lake Victoria will be mitigated securing the livelihoods of close to 12 million people by maintaining and enhancing the beneficial services to secure livelihoods, food, water, health and security. The proposed utilization of solar light to treat wastewater will results in a cost-effective technique available to all tea processing factories in Kenya.

1.7 Main Objective

To develop a proto-type efficient treatment system for tea processing wastewater using photocatalysts.

1.7.1 Specific Objectives

The specific objectives were to:-

1) To determine the physical - chemical properties of tea processing wastewater.

2) To characterize Organic macro-molecules in tea effluent.

3) To determine metal species prevalent in tea processing wastewater: i.e. Fe, Al, Mn and Ni.

4) To characterize powder photocatalysts.

5) To develop a prototype batch photocatalytic reactor equipped with immobilized
photocatalysts on glass.
CHAPTER TWO

2 Literature review

2.1 Tea Varieties

Tea is enjoyed as a beverage mainly due to its taste, aroma and health benefits. In most parts of the world, tea is considered as a refreshing beverage proposed for consumption because of its therapeutic potential (Karakaya & El, 2006). It is also consumed for the same reasons as those of coffee (Zhu et al., 2002). It is obtained from processing the leaves of *Camellia sinensis* plant (Li et al., 2007).

According to the procedure that is followed during tea production, tea is categorized into green, black, oolong and white teas. Green tea is non-oxidized tea produced by drying and steaming the fresh leaves to inactivate the enzyme polyphenol oxidase that oxidizes polyphenols found in tea and cause the formation of brick-red colour. Among the four types of tea, black tea is the most processed. The production technique used for black tea ensures that it undergoes total oxidation that leads to the development of its distinct dark brown colour of its leaves (Li et al., 2007). Oolong tea is mainly grown in China, and contains various polyphenols such as epigallocatechin, epigallocatechin gallate, epicatechin and polymerized polyphenol (Han et al., 2007) and its production involves the partial oxidation of tea leaves and subsequent drying to preserve the natural flavors (Lin et al., 2008); (Alcazar et al., 2007). In addition, Oolong tea, undergoes partial fermentation that permits limited levels of enzymatic oxidation throughout preparation and has high anti-oxidative activities (Zhu et al., 2002; Nakahara et al., 1993; Han et al., 1999; Ou et al., 2002). Oolong tea is also broadly consumed in Asia as a result of its polyphenols that are of many biological and pharmaceutical benefits that include anticarcinogenic, antioxidative and hypolipidemic properties (Han et al., 2007); (Kilmartin & Hsu, 2003). The organic structure of the Oolong tea polyphenols have been found to contain conjugated carbon-carbon double bonds (Han et al., 2007).

White tea is produced by harvesting the tea leaves with their buds just before they fully open up when the buds are still covered in fine white hairs (Teixeira et al., 2012). Further production techniques involve the steaming thoroughly of the leaves to activate the enzymes responsible for tea discoloration. The leaves are then subsequently dried in a dryer or the sun (Dufresne & Farnworth, 2001). The quality of tea processed is dependent
on various factors i.e. the geographical locations of the tea plantations, climatic conditions, soil profiles and tea processing technique.

2.2 Tea pigments

Tea consists of several pigments, which include theaflavins that are yellow-brown substances that contributes significantly to the astringency, briskness, brightness and colour of black tea. On average, theaflavins make up 0.3% to 1.8% on dry weight basis of the total black tea composition (Takino et al., 1965). Thearubigins (TR) make up another important group of compounds that are formed during processing of black tea from catechins as well as by oxidative degradation of theaflavins (Lin et al., 2005). They constitute 10% to 20% of dry weight and cause the colour and flavour of the tea (Roberts & Caserio, 1977).

2.2.1 Biochemical constituents of Tea

Tea plucking is either done physically by human tea pluckers or by specialized tea harvesters. It involves the plucking of crop shoots (apical bud and two terminal leaves). The nature of plucked tea leaves influences the biochemical characteristics which in turn influences the quality of the tea (Thomas et al., 2006). Tea constitutes many biochemical components. These include, phenolic components, alkaloids, vitamins, enzymes, crude fiber, proteins, lipids and carbohydrates. Among the biochemical constituents, the phenolic compounds have been found to be prevalent (Ramaswamy, 1993). Polyphenols found in tea, particularly theaflavins and thearubigins determine tea quality. The taste and flavour of the teas is due to the oxidative transformation of phenolic compounds. Enzymes like polyphenol oxidase and peroxidase act upon these phenolic molecules during fermentation in black tea processing (Ramaswamy, 1993). Tea is composed of 30% of polyphenols and catechins on the dry weight basis (Saravanan et al., 2005). Catechins in the green leaf of tea is influenced by seasons and geographical considerations (Couladis et al., 2003).
2.3 Tea processing in Kenya

Tea leaf processing in Kenya, involves Cutting, Tearing and Curling (CTC) technique. The technique mainly involves the reduction of leaf moisture content without any addition of water. The process of tea manufacture leads to the discharge of waste water generated from the process namely Cutting, Tearing and Curling (CTC) machine, Continuous Fermentation Unit (CFU) troughs and the driers (Wasewar et al., 2009). In summary, black tea processing includes the following steps:-

(i) Withering – sun drying of tea leaves under the sun for up 18 hours, to reduce moisture content to 60%.
(ii) Rolling – this takes 1-3 hours, in which tea leaves are crushed to allow enzymatic oxidation of flavanols.
(iii) Fermentation – responsible for the distinct black tea flavour and colour. The fermentation process, is the most critical step and is dependent on oxygen availability, temperature, relative humidity, time and pH. The fermentation process produces dark-colored polymerization products of polyphenols.
(iv) Firing – tea leaves are passed through hot air dryers to prevent enzymatic fermentation
(v) Sorting – physical isolation of tea leaves into quality grades. Flavonoids contents and other polyphenols are affected by different types of processing (Chan et al., 2009).

2.3.1 Coloured wastewater treatment techniques

Conventional wastewater treatment techniques such as flocculation and coagulation have proved ineffective in the treatment of coloured wastewater which have high organic load (Habib et al., 2012). Various researchers in recent years have investigated alternative wastewater treatment methods. These techniques include advanced oxidation processes

(i) Advanced Oxidation Processes (Couladis et al., 2003); H₂O₂/UV photocatalysis (Arslan & Balcioglu, 2001); Photo-Fenton (Lin & Chang, 2000).
(ii) Ozonation (Agustina et al., 2005; Rice et al., 1996).
(iii) Sonolysis (Gogate & Pandit, 2004).
(iv) Gamma–radiolysis (Wojnarovits & Takacs, 2008).
(v) Electro-coagulation (Azarian et al., 2007; Inan et al., 2004).
(vi) Biological and combined anaerobic–photocatalytic treatment (Ndasi et al., 2011; Chan et al., 2009).

To remedy coloured industrial wastewater, various techniques have been proposed. However these methods have serious shortfalls (Chong et al., 2010; Chan et al., 2009). Traditional methods such as adsorption on waste materials, adsorption on activated carbons, precipitation, air stripping, flocculation, reverse osmosis and ultrafiltration have been successfully applied to remedy coloured wastewater. However these methods are merely phase transferring methods and require further treatment for disposal (Akpan & Hameed, 2009).

2.3.1.1 Phytoremediation

This techniques involves the use of select distinct plants for example duckweed to remedy coloured wastewater. The application of plants for coloured wastewater treatment has several advantages that remarkably efficient, cost-effective, driven by natural energy and requires minimal capital to set up. (Parra et al., 2012). The floating plant, Lemna species has been identified as the most effective for use in photoremediation of wastewater. Favourable conditions for the duckweed to grow include, water temperature range of 17°C to 35°C (Iqbal, 1999). Another significant advantage of the duckweed is that they reproduce vegetatively, about 10 times in its lifecycle (Skillicorn et al., 1993).

2.3.1.2 Physico-chemical techniques

These methods comprises precipitation, flocculation, coagulation, ion-exchange, adsorption, membrane separation, sedimentation, bleaching by ozone/chlorine, ion-exchange on synthetic adsorbent resins, reverse osmosis (Cooper, 1993). However physico-chemical methods remove or separate colour physically and require subsequent solid waste disposal that raises costs and is time consuming. Disadvantages of these methods include high sludge formation, handling and disposal problems, and expensive regeneration of adsorbent. (Frølund et al., 1996).

2.3.1.3 Biological techniques

Involves mainly aerobic and anaerobic digestion, whereby colour removal is achieved by adsorption on activated sludge or by biological degradation of molecules. The
disadvantages include slow process, the overall efficiency is dependent on performance of some external factors (pH and salts) and a large mass of land required for the treatment process (Bergamini et al., 2009). Biological treatment of wastewater may be preferred over the physico-chemical methods, however they are time consuming and leads to the formation of large amounts of sludge. This poses a challenge of recycling or disposal (Bergamini et al., 2009). Coloured wastewater discharged from industrial plants including from tea processing factories are highly resistant to biodegradation.

2.3.1.4 Electrochemical techniques

Involves dialysis or ion oxidation that combines oxidation of organic pollutants by electrolytic processes. A final process involves a physical-chemical precipitation of sludge and filtration. Disadvantages of this method includes formation of sludge and high electricity costs (Idota et al., 1997).

2.3.1.5 Electromagnetic radiation

Utilizes light energy in the form of electromagnetic radiation and sensitivity of particles to this energy to achieve eventual mineralization of organic pollutants in wastewater. For wastewater treatment, the removal of colour from coloured wastewater is more important than removal of colourless contaminants present in the wastewater (Hussein & Abass, 2010).

2.3.1.6 Conventional methods

Traditional methods of wastewater treatment combines physical and biological processes to remove organic pollutants from solutions that include wastewater (Hammer, 1996). In conventional wastewater treatment methods, sedimentation is the first step. The settled and floated organic matter is removed. Biological treatment follows next. Then in the tertiary stage, specific chemicals are removed from the partially already purified water before final disinfection.

Depending upon the nature of the pollutant, tertiary treatment can include some of the chemical and physical processes, such as adsorption of nonpolar organic molecules onto activated carbon, removal of phosphate by its precipitation as the calcium salt, heavy metal removal by the addition of hydroxide or sulfide, desalination by reverse osmosis, electro dialysis or ion exchange. The conventional purification of drinking water follows similar
stages of purification as wastewater treatment, but the quality of drinking water must meet much more strict standards compared to wastewater treatment to avoid causing any health problems to water users (Doan et al., 1999).

Aeration is commonly used as the first step in purification of drinking water to get rid of dissolved gases, such as H₂S, organosulphur compounds and other volatile organic compounds (VOCs) (Vinodgopal et al., 1996). After aeration, settling and precipitation of colloidal particles achieved by adding Al³⁺ or Fe²⁺ salts, gelatinous hydroxides form at neutral and alkaline pH values that physically incorporate colloidal components (Doan et al., 1999). To get rid of harmful bacteria and viruses from drinking water, disinfection is applied as a last step of purification. Various disinfection methods includes, chlorination, UVC radiation or Ozonation (De Lasa et al., 2005).

2.3.1.7 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) techniques are dependent on production of powerful oxidizing species that effectively treat wastewater (Parsons, 2004). The subsequent generation of hydroxyl radicals (•OH), which are powerful oxidation species leads to the quick non-selective reaction with the majority of electron-rich sites of organic pollutants (Doan et al., 1999).

With UV light irradiation and appropriate photocatalyst, electron/hole pairs with free electrons are produced in the unfilled conduction band, leaving positively charged holes in the valence band. These electron/hole pairs start a chain of chemical reactions that mineralize organic contaminants into CO₂ and water. The process gradually degrades organic contaminants. This method prevents the formation of sludge and leads to no secondary pollution. Advanced Oxidation Processes (AOPs) have been used to treat and remove organic contaminants in wastewater (Oppenlander, 2003; De Lasa et al., 2003)

Suitable powder photocatalyst including TiO₂ and ZnO act as semi-conductor photocatalysts to degrade organic and inorganic pollutants into H₂O and CO₂ (Habib et al., 2012; Mahmood et al., 2003). This process involves the cleavage of the conjugated carbon–carbon double bonds found in polyphenols by (•OH) radicals that causes decolorization of coloured wastewater and mineralization to CO₂ and H₂O.

It has been established that TiO₂/ZnO powder photocatalysts, with UV irradiation mineralizes organic pollutants present in wastewaters into harmless products such as CO₂, and H₂O (Singh et al., 2013). Photocatalytic reactions readily eliminate from wastewater all organic impurities. Its applications in slurry type suspensions is limited due to the
challenge caused by catalyst separation after photocatalytic treatment (Mehrvar et al., 2001; Khezrianjoo & Revanasiddappa, 2012). The development of knowledge in semiconductor electrochemistry has led to tremendous growth in the field of photocatalysis (Heller, 1981). The application of photocatalytic degradation to remove cyanide in wastewater has been investigated by Frank & Bard, 1977). The authors accurately predicted great developments in the field of environmental purification that led to extensive efforts to build up knowledge in the field of photocatalysis (Ollis & Ekabi-Al, 1993; Fox & Dulay, 1993; Akira Fujishima et al., 1999; Akira Fujishima & Rao, 1997). (Mathews, 1988) conducted studies to investigate the viability of using TiO₂ and ZnO to degrade by photosensitized oxidation aromatic hydrocarbons containing phosphorus, sulphur, nitrogen and halogen. The end products were CO₂, H₂O, PO₄³⁻ and SO₄²⁻. Photocatalytic degradation experiments have been applied as a remedial technique to remove organic pollutants in wastewater (Gaya & Abdullah, 2008).

Photocatalysis as a novel wastewater treatment technique involves a light induced process that results in the oxidation of organic compounds by oxidation-reduction reactions activated by electron–hole pairs that form on the surface of powder catalysts (Chen et al., 2011).

### 2.4 Photocatalytic degradation mechanism

![Photocatalysis mechanism](image)

Figure 2.1: Description of photocatalytic degradation photocatalysis in solutions containing oxidative and reductive species

Source: (Rajeshwar & Ibanez, 1995).
The photogenerated holes formed after the excitation of electrons migrate from the valence band to conduction band. The holes possess extreme oxidizing potential and the photogenerated electrons are reduced to form superoxides from Dioxygens (Akira Fujishima et al., 2000). (Akira Fujishima & Honda, 1972) promoted extensively the study of photocatalysis. They described the “Honda-Fujishima effect” where they explained the photochemical splitting of H_{2}O into H_{2} and O_{2} using titanium dioxide. Photocatalysis was described as cost effective, simple and promising method to achieve complete mineralization of organic molecules in waste water into CO_{2} and H_{2}O. This new process of wastewater treatment was referred to as the Advanced Oxidation Process (AOPs) (Khataee et al., 2009).

2.4.1 Applications of Photocatalytic degradation

2.4.1.1 Destruction of organics

Photocatalytic degradation has been used to mineralize organic compounds in particular alcohols, carboxylic acids, chlorinated aromatics, phenolic derivatives into harmless end products e.g. CO_{2} and water (Bhatkhande et al., 2002; Pirkanniemi & Sillanpaa, 2002). Another application of photocatalytic degradation is the treatment of wastewater streams contaminated with oil (Grzechulska et al., 2000).

2.4.1.2 Water disinfections

Heterogeneous photocatalytic reactions are applicable in reactions to eliminate bacteria and viruses that may include streptococcus natuss, Streptococcus mutans, Streptococcus cricetus, Escherichia coli, Saccharomyces cerevisias, Lactobacillus acidophilus and Poliovirus 1 (Mills & Le Hunte, 1997). Microcystin toxins have been successfully photocatalytically degraded by immobilized TiO_{2} catalyst (Shephard et al., 2002). Cholera Vulgaris which has a thick cell wall, can be eliminated from wastewater streams by photo disinfection sensitized by TiO_{2} (Shephard et al., 2002). Several authors have reported TiO_{2} as a microbiocide effective at photokilling Lactobacillus acidophilus, Saccharomyces cerevisiae and Escherichia coli. (Matsunaga et al., 1985; Fujishima et al., 1986) reported using TiO_{2} to photokill tumor cells (Hela cells). (Sonawane et al., 2004) concludes that Fe^{2+} doped TiO_{2} films could decolourize 95% of methyl orange dye in solar light illumination for a duration of 3-4 hrs. Highly hydrophilic TiO_{2} surfaces with excellent
anti-fogging and self-cleaning properties have been developed (Wang et al., 1997). The examples below illustrate a few applications of photocatalysis.

Figure 2.2: TiO$_2$ coated tent material
Source: (Fujishima et al., 2000)

In Figure 2.2 TiO$_2$ is used as a coat on building materials. The TiO$_2$ films possess self-cleaning qualities as a result of strong oxidizing properties.

Figure 2.3: TiO$_2$ coated exterior tiles
Source: (Fujishima et al., 2000)

In Figure 2.3 the sections labelled A and B represent:-
A. Tiles coated photocatalytic super hydrophilic layer
B. Ordinary painted wall tiles
In Figure 2.4 with ordinary mirrors, when fog comes into contact with glass, droplets of water are formed fogging the glass. In glass coated with TiO$_2$, the water forms a continuous flat sheet preventing fogging.

### 2.4.1.3 Photocatalytic treatment of natural organic matter

The use of humic acid has been investigated by (Al-Rasheed & Cardin, 2003) as a model substance to decrease organic content using Advanced Oxidation Processes (AOPs). During the process no toxic byproducts or sludge were created. The findings indicate that after 1 hr. of UV light irradiation and 1g/L of TiO$_2$, about 40% of Total Organic Carbon (TOC) and 75% of colour was eliminated at $\lambda = 400$ nm (Bekbölet & Özkösemen, 1996). In other work related to Humic Acid, 80% of commercial humic acid was eliminated by UV light illumination with TiO$_2$ (Minero et al., 1999). An aqueous solution of TiO$_2$ illuminated by UV light showed high photocatalytic activity within the lowering of Humic Acid (HA) concentrations (approximately 50% elimination was achieved in 10 minutes (Eggins et al., 1997). To raise the rates of photocatalytic degradation of organic substances including humic acid, photocatalytic degradation has been applied along with other physical methods sono-photocatalysis, Ozonation photocatalysis (Davydov et al., 2001; Kerc et al., 2003).
2.4.1.4 Seawater treatment

An investigation into sea water reveals that it could be decomposed under UV light irradiation by TiO$_2$ using an artificial light source (Ziolli & Jardim, 2002).

2.4.2 Principles of semi-conductor photocatalysis

![Principles of heterogenous photocatalysis](image)

Figure 2.5: principles of heterogenous photocatalysis
Source: (Ajmal et al., 2014)

An important feature of photocatalytic reactions is conduction and valence band are on different energy levels. All photochemical reactions are characterized by an activation energy related to the absorption of at least one photon by a molecule. The range of wavelengths generally used in photochemistry lies in UV/Vis spectrum $\lambda = 200$ nm to 700 nm (Turro et al., 2009).

Semi-conductors are characterized by certain non-stoichiometry, unlike oxides such as MgO or Al$_2$O$_3$, which are insulators. These oxides have their valence bands filled with electrons and their conduction bands empty. Semi-conductors e.g. ZnO/TiO$_2$ have their valence and conduction bands on different energy levels (Demkov & Posadas, 2014).

The principle of photocatalytic degradation is dependent on UV light, in the form of a photon, with energy equal or greater than the band gap energy ($E_g$) falling on the surface of a catalyst causing the promotion of electrons from the valency band to conduction band.
This leads to the formation of electron/hole (e⁻/h⁺) pairs with free electrons in the empty conduction band leaving an electron vacancy/hole in the valence band. The formation of these holes allows adsorbed water to be oxidized to strong (•OH) radicals whose strong oxidative species (2.8 V vs. SHE) oxidize most organic compounds (Guan et al., 2008). The organic intermediates formed are oxidized by O₂ or (•OH) radicals and mineralized to CO₂ and H₂O. Hydroxyl radicals (•OH) are strong oxidants that rapidly react most electron-rich sites of organic pollutants (Zimbron & Reardon, 2009).

2.4.2.1 Photocatalytic oxidation

Photocatalytic processes are initiated by the absorption of UV light (λ<400 nm) in a semiconductor generating electrons and holes in the valency and conduction bands. The photogenerated holes that avoid recombination move to the semi-conductor surface and react with adsorbed (•OH) or H₂O forming trapped holes. Trapped holes are usually shown as surface-bound or adsorbed (•OH). Hydroxyl radicals generated at the surface of a semiconductors leaves the surface into the bulk solution to forming free (•OH). In oxygen rich environments, oxidative species, such as H₂O₂ are formed in their reduction sites (Konstantinou & Albanis, 2004).

2.4.2.2 Photosensitized oxidation

Photosensitized oxidation represents photocatalytic degradation reactions induced by visible light (λ>400 nm) irradiation. Organic pollutants absorb light (λ>400 nm and inject an electron on to the conduction band of the powder photocatalyst. Excited organic molecules convert to cationic radicals (organic+c⁻) and the photocatalyst leads to the formation of oxidation species O₂⁻, HO₂ or HO⁻ that drive the mineralization process (Konstantinou & Albanis, 2004).

2.4.3 Heterogenous photocatalytic degradation

Heterogeneous photocatalysis is a powerful technique for the total mineralization of almost all the organic pollutants (Mahmoodi et al., 2006). In this mechanism a metal oxide is selected as a semi-conductor, a source of UV light identified to drive the photodegradation process. Not all metal oxides can act as a semi-conductor. Research has
shown that some metal oxides like ZnO, WO₃ and SrTiO₃ have also proven to be photoactive like TiO₂ (Ullah & Dutta, 2008).

2.4.4 Homogenous photocatalytic degradation (Photo-Fenton Reaction)

The Photo-Fenton process, an example of Advanced Oxidation Processes (AOPs), is a technique used to effectively treat wastewater (Lopez-Alvarez et al., 2012; Lucas et al., 2013). The Photo-Fenton oxidation process depends on the oxidation potentials of (•OH) radicals. The radicals are formed by the decomposition of H₂O₂ catalyzed by Fe²⁺ ion (Fenton reaction) and the photo-reduction of Fe³⁺ (Photo-Fenton reaction) (Lucas et al., 2013). The Hydroxyl radicals (•OH) formed in aqueous mediums oxidize and degrade organic pollutants.

The Photo-Fenton reactions can be summarized as follows;

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + (\text{OH}•) + \text{OH}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HOО}• + \text{H}^+
\end{align*}
\]

(Wadley & Waite, 2004)

**Reaction 1:** (Fenton reaction) - Decomposition of H₂O₂ catalyzed by Fe²⁺ and leads to the oxidation of Fe²⁺ to Fe³⁺ producing (•OH) radicals in acidified aqueous mediums.

**Reaction 2:** (Photo-reduction) of Fe³⁺ by UV/Vis light generates (•OH) radicals that enables the photo-Fenton catalytic cycle process, where Fe is interchanged between the (+2) and (+3) oxidation states. (Wang, 2008).

2.5 Solar induced photocatalytic degradation

UV light irradiation is responsible for the excitation of electrons from valency to conduction band of a selected semi-conductor. The UV component in solar irradiation comprises only 5% of the incident solar radiation. This means only 5% is made available to TiO₂ and ZnO photocatalytic degradation of organic pollutants (Thiruvenkatachari et al., 2008; Anpo & Takeuchi, 2003). Solar light mediated heterogenous photocatalytic degradation is promising process for environmental remediation. Practically its effectiveness is dependent on efficient photocatalysts (Ajmal et al., 2014; Muruganandham et al., 2014; Tachibana et al., 2012; Bizani et al., 2006; Kubacka et al., 2011; Galian & Perez-Prieto, 2010). Zinc oxide (ZnO) as a potential semi-conductor under
solar light irradiation, demonstrates great efficiencies in the degradation of organic contaminants (Strunk et al., 2009). Considering various photocatalysts, ZnO and TiO$_2$ remain the most practical because of high photosensitivity, nontoxicity and low cost. This is despite their utilization of a tiny fraction of solar radiation (3% – 5%) in the UV region as a result of their large bandgap energies (Palaez et al., 2012; Chong et al., 2010; Chen et al., 2011; Cho et al., 2011).

2.5.1 Solar Ultra-violet radiation (UVR)

The composition of UV light radiation in solar light is about 5%. The UV component of solar irradiation from the sun at midday comprises 95% UVA and 5% UVB. In addition to direct solar rays, reflections of solar light from certain ground surfaces contributes in large proportions to the total amount of scattered UVR (Moseley, 1988). Levels of Solar UV radiation is influenced by the following factors. (i) Time of the day. (ii) Season – variance in terrestrial UV irradiance is less significant near the equator (Diffey, 1991) (iii) Geographic latitude – yearly UVR exposure dose diminishes with increasing distance from the equator (Diffey, 1991) (iv) Altitude – it is estimated that each 300 metre increase in altitude increases sunburning of solar light by 4% (Diffey, 1991) (v) Clouds – cloud cover interferes with the amount of irradiation through reflection, refraction, absorption. Total cloud cover may prevent about 50% of UVR energy from reaching the surface of the Earth (Diffey, 1991).

2.5.2 Advantages of Solar induced photocatalytic degradation

The advantages include, cost-effective, no sludge formation like other methods such as adsorption, coagulation and flocculation. It’s also environmentally friendly. It is extremely an energy self-sufficient process as it can work under solar radiation. Finally the method does not generate any other secondary pollutant like other methods as the final products are CO$_2$ and H$_2$O (Sharma & Bhattacharya, 2017). The selected catalyst possess no toxicity to human health, have wide applications especially to molecular structured complex contaminants and the energy at $\lambda < 365$ nm comprising at least 5% of solar light illuminating the surface of the earth (Tang et al., 2014).


2.5.3 Limitations of Solar induced photocatalytic degradation

Lack of consistency and reliability in solar light availability caused by erratic weather patterns is a significant drawback in solar induced photocatalytic treatment (Moseley, 1988). Solar systems rely on the steady absorption of sunlight. Factors such as latitude and cloud cover affect the overall availability of solar radiation reaching the earth (Gokmen et al., 2013).

2.6 Zinc oxide and Titanium dioxide photocatalysts - (Semi-conductors)

Among several semi-conductors, TiO$_2$ and ZnO have been extensively investigated as potentially efficient photocatalysts. In particular, ZnO is a potential alternative to TiO$_2$, considering band gap energy and greater photoactivity that has been reported for ZnO compared to TiO$_2$ (Cho et al., 2010; Hayashi et al., 2007; Huang et al., 2008). ZnO and TiO$_2$ photocatalysts have shown tremendous potential to eliminate toxic organic contaminants in wastewater streams (Akpan & Hameed, 2009).

Various factors such as the surface area and defects of metal semi-conductor oxides such as ZnO and TiO$_2$ are important factors that enhance photocatalysis (Mahmood & Dutta, 2012; Tipton & Slack, 2005). Zinc oxide has shown great potential in the field of nanotechnology, ZnO has a large band gap and excitation binding energy (Staszkiewicz, 2004; Dai et al., 2003). The form of TiO$_2$ and ZnO nanoparticles catalysts immobilized on suitable substrates e.g. glass and stainless steel affects the efficiency of photocatalytic systems (Ali & Hassan, 2008; Baruah & Dutta, 2009).

2.6.1 Theory of semi-conductors

Most of the photocatalytic degradation studies have been tested at wavelengths between 320 nm – 400 nm (Thiruvenkatachari et al., 2008). These wavelengths are related to the band gap energies of TiO$_2$ and ZnO (Robel et al., 2007). Therefore the light source that supplies optimum radiation can be selected i.e. UV light or solar light. In most typical photocatalytic reactors, UV light irradiation is supplied by fluorescent low-pressure and medium mercury lamps emitting low and high intensity UV light respectively (Thiruvenkatachari et al., 2008). Various types of photocatalytic degradation systems have
been investigated for wastewater treatment. These include TiO$_2$, ZnO, ZrO$_2$, CdS, and WO$_3$ (Kim et al., 2010; Mohabansi et al., 2011). Several metal oxides are known to have their band-gap energies in the UV region. Thus their band gap energies are $\geq 3.36$ e.V. at $\lambda = 390$ nm (Thiruvenkatachari et al., 2008). These catalysts support photocatalytic degradation processes under UV light illumination (Sung-Suh et al., 2004).

2.7 Suspension photocatalysis

Suspension photocatalysis has several advantages and disadvantages. It ensures a larger surface area, improving higher efficiency, due to uniform photocatalyst distribution. Catalyst fouling is minimized because the catalyst is continuously removed. The greatest disadvantage is the requirement of a filter to separate the catalyst which increases the unit costs. The method is expensive after scaling-up because catalyst particle recovery is difficult and expensive (Angeles et al., 2014).

2.8 Thin film photocatalysis

Thin film photocatalysis describes the immobilization of powder photocatalysts onto a suitable substrate or support. These substrates include (i) glass (ii) fibers (iii) stainless steel (iv) inorganic materials (v) sand (vi) activated carbons (ACs). The immobilized catalysts on suitable substrates allow for re-use for reactions taking place at room temperature and reduces the drawbacks of photolysis reactions because organic contaminants are oxidized to harmless compounds such as CO$_2$ and H$_2$O (Aramendia et al., 2008; Malabo et al., 2003). Immobilized catalysts on thin films is a continuous process and not requiring a separation step after the reaction. Compared to suspension photocatalysis, it is less effective because the surface area available for reactions are lower compared to the suspension technique. A more suitable alternative is the immobilization of powder catalysts onto various particulate layers or catalytic supports without reducing photocatalytic activity (Staszkiewicz, 2004; Al-Rasheed, 2005; Mok, 2009).
2.8.1 Ideal Photocatalysts

Suitable photocatalytic materials should possess the following characteristics (i) active photocatalytic activity (ii) biochemical inertness, (iii) photocorrosion resistance (v) UV/Vis light absorption ability (vi) affordable (vi) non-toxic

Table 2.1 shows a list of various types of semi-conductors and their band-gap energies at 0 K.

Table 2.1: Bandgap energies for various semi-conductors at 0 K

<table>
<thead>
<tr>
<th>Semi-conductors</th>
<th>Bandgap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.32</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.37</td>
</tr>
<tr>
<td>Diamond</td>
<td>5.4</td>
</tr>
<tr>
<td>CdS</td>
<td>2.42</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.6</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>3.54</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>2.76</td>
</tr>
<tr>
<td>Si</td>
<td>1.17</td>
</tr>
<tr>
<td>Ge</td>
<td>0.744</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>3.87</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>2.172</td>
</tr>
</tbody>
</table>

Source: (Thiruvenkatachari et al., 2008)

2.8.1.1 Nano – photocatalysts

Due to surface area considerations, nano-scale powder photocatalysts show a greater photocatalytic activity than the normal scale powder photocatalysts. The nano-particles have larger surface area available for contact between reactants. Smaller particle sizes reduces the time needed for the carrier diffusing out of the photocatalyst pores to the photocatalysts surface (Mehrvar et al., 2001).
2.8.1.2 Titanium dioxide photocatalyst

Significant amounts of research on TiO$_2$ as a suitable photocatalyst have been carried out over the last five decades (Akira Fujishima et al., 2000). TiO$_2$ has been investigated as an ideal photocatalyst but is limited by certain characteristics such as poor absorption of visible light radiation and a fast recombination of photogenerated electron/hole pairs. Extensive research shows that TiO$_2$ is a highly efficient photocatalyst due to its high photoactivity and photochemical stability. TiO$_2$ has found applications in photocatalytic treatment of wastewater, pesticide degradation and water splitting by TiO$_2$ to generate H$_2$ (Mor et al., 2006; Thomson & Yates, 2006; Chen & Mao, 2007). The TiO$_2$ driven photocatalytic degradation of coloured wastewater maybe achieved through excitation of the coloured organic compounds onto semiconductor surfaces under a visible light mediation in a process referred to as photosensitized photocatalysis (Vinodgopal et al., 1996). Some drawbacks for example, include a band gap of 3.32 e.V that corresponds to 388 nm and thus does not absorb visible light (Carp et al., 2004). This means it only absorbs solar light in the UV region of solar light. Solar spectrum comprises about 40% of the visible region (400 nm to 700 nm) and characterized by rapid recombination rates of photogenerated electron–hole pairs which lowers degradation rates (Ajmal et al., 2014). The equations below indicate the reactions that take place when TiO$_2$ acts as a semi-conductor.

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow e_{\text{CB}}^- + h_{\text{VB}}^+ \\
\text{O}_2 + e_{\text{CB}}^- & \rightarrow \text{O}_2^- \\
\text{H}_2\text{O} + h_{\text{VB}}^+ & \rightarrow \text{OH}^- + \text{H}^+
\end{align*}
\]

TiO$_2$ exists in several crystalline modifications, the significant ones being anatase and rutile. Anatase form is the most practical and can be applied in many photocatalytic applications, since it’s biologically and chemically inert (Pal & Dutta, 2002; Souther & Alspaugh, 1957). TiO$_2$ has been applied to remove organic contaminants in wastewater (Sakthivel & Kisch, 2003; Akyol et al., 2004; Inan et al., 2004). Sakthivel demonstrated that TiO$_2$ is a superior photocatalyst compared to other semi-conductors e.g. WO$_3$, $\alpha$-Fe$_2$O$_3$, SnO$_2$ and ZrO$_2$ under similar experimentation conditions (Ameta & Ameta, 2016). Another investigator, Augugliaro concluded that TiO$_2$ displays superior photochemical stability compared to ZnO. However, ZnO is photochemically more active compared to TiO$_2$ despite its lower surface to volume ratio (Augugliaro et al., 1988).
2.8.1.3 Zinc oxide photocatalyst

Several researchers have indicated that ZnO photocatalyst demonstrates high photocatalytic efficiencies for the mineralization of organic contaminants (Strunk et al., 2009; Gilmore & Renk, 2014; Ullah & Dutta, 2008; Huang et al., 2012). ZnO as a select photocatalyst has been studied to achieve complete mineralisation of organic pollutants in the environment (Kansal et al., 2007; Gaya & Abdullah, 2008; Nirmala et al., 2010). ZnO has been studied as an excellent photocatalytic material applied to remedy wastewater such as printing and dyeing wastes, dairy and food wastewater, drugs and pesticides wastewater, textile wastewater, papermaking wastewater e.t.c. (Rizzo, 2011).

The photocatalytic efficiency of ZnO is better than most photocatalysts (Georgekutty et al., 2008). It has extensively been used to as a remedy for environmental pollution, ZnO as a semi-conductor photocatalyst has received attention from many researchers (Li et al., 2007). Zinc oxide nanoparticles have been widely utilized for opt-electronics, antimicrobial activity because of its excellent properties in UV absorption and reflective properties. ZnO has further been used widely in semiconductors, cosmetics, sunscreens, plastic additives, and pigments among a wide range of other applications (Wu et al., 2010; Li et al., 2013). As a photocatalyst the band gap energy of ZnO is similar to that of TiO₂. The band gap energy of ZnO is approximately (3.2 e.V) making it a suitable semi-conductor catalyst (Garcia and Semancik, 2007). In some applications ZnO has shown a greater tendency towards photodegradation and mineralisation of organic or inorganic pollutants compared to TiO₂ (Gouvea et al., 2000; Hayashi et al., 2007; Huang et al., 2008). If ZnO absorbs a photon of energy equal to or greater than its band gap width (3.2 e.V), an electron may be excited from the valency band to the conduction band leaving behind an electron vacancy or hole in the valency band.

\[ \text{ZnO} + \text{UV} \rightarrow \text{electron (e−) + positive hole (h+)} \] (formation of electron–hole pair) \hspace{1cm} (6)

ZnO photocatalytic characteristics is dependent on its morphology, crystal size, density and structure, and crystallographic orientation (Garcia & Semancik, 2007; Wang, 2004). Zinc oxide has been seen as an efficient semi-conductor catalyst used for water treatment, organic pollutant decontamination and various types of photolysis because it generates hydrogen peroxide (H₂O₂) more proficiently (Carraway et al., 1994). Reactions with ZnO have shown high levels of mineralization and reaction rates as a result of more active sites (Akyol et al., 2004). Zinc oxide photocatalyst is affordable and exhibits high photochemical sensitivity, utilizing solar energy (Yang et al., 2004). Application of ZnO
nanoparticles as a potential photocatalyst material to decompose environmental contaminants have been widely investigated (Li et al., 2008). It has been suggested that for better photocatalytic efficiency in various applications, ZnO should absorb UV radiation in addition to visible light (Li et al., 2012). As a semi-conductor ZnO has been used to develop surface coatings for a variety of engineering applications because of its wide band gap energy, these applications include, synthesis of advanced ceramics, binding energy (60 e.V) and natural synthesis of nanocrystalline materials (Li et al., 2007). Zinc oxide powder has been shown to be the most effective practical material for photocatalytic degradation reactions as a photocatalyst promotes the generation of Reactive Oxygen Species (ROS) under illumination with energy at or above its band gap energy 3.37 e.V (equivalent to 368 nm wavelength) (Ma et al., 2011).

ZnO absorbs UV light radiation at wavelengths equal or less than 385 nm (Nirmala et al., 2010). To enable ZnO absorb visible light, its band gap can be narrowed or divided into several band gaps (Wang et al., 2013; Kim & Park, 2009). ZnO has been identified as a suitable replacement for TiO$_2$, since their photodegradation mechanisms have been proven to be similar (Gouvea et al., 2000; Krishnakumar et al., 2010). Zinc oxide absorbs a large amount of UV radiation at a corresponding wavelength of 425 nm (Behnajady et al., 2006), this makes ZnO a better photocatalyst especially under the visible light excitation. Investigations show that ZnO is an effective photocatalyst in the treatment of some organic pollutants in aqueous systems (Gouvea et al., 2000; Krishnakumar et al., 2010). The cost of ZnO is affordable compared to TiO$_2$ especially for large-scale treatment systems (Daneshvar et al., 2004). ZnO can replace TiO$_2$ as a catalyst, since their photocatalytic treatment mechanisms are identical (Krishnakumar et al., 2010; Wu et al., 2010; Pirkanniemi & Sillanpää, 2002). The reactions below explain the photocatalytic reaction taking place with ZnO as a photocatalyst.

\[
\begin{align*}
\text{ZnO} + \text{hv} & \rightarrow \text{h}^+ + \text{e}^- \\
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \cdot\text{OH} \\
\text{H}^+ + \text{OH}^- & \rightarrow \text{HO}_2 \cdot \\
\text{H}^+ + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \cdot\text{OH} \\
\text{e}^- + \text{O}_2 & \rightarrow \cdot\text{O}_2 \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2 \cdot \\
2\text{HO}_2 \cdot & \rightarrow \cdot\text{O}_2 + \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \cdot\text{O}_2^- & \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2
\end{align*}
\]

(7) (8) (Mehrvar et al., 2001)
2.8.2 Influence of TiO$_2$ and ZnO Structural and morphological character on wastewater photocatalytic treatment

The photocatalytic activity of a particular photocatalyst is affected by its structural and morphological characterization. The parameters that relate a photocatalyst and its efficiency include: (i) light absorbing properties (ii) rate of reduction and oxidation of the molecule by photogenerated holes (iii) rate of electron hole recombination.

The particle and crystal size of individual catalyst powders affect photocatalytic treatment efficiency. Surface area measurements are calculated by the Brunauer Emmett Teller (BET) method. X-ray Diffraction (XRD) determines catalyst particle size and another technique used to estimate crystal size is Scanning Electron Microscope (SEM) technique, from which crystal sizes can be estimated by observing the scanned images.

2.8.2.1 Structural and Morphological characterization – ZnO/TiO$_2$

2.8.2.1.1 Scanning Electron Microscope (SEM)/ Brunauer Emmett Teller (BET)

The number of photon striking the photocatalyst controls the rate of reaction which signifies that the reaction takes place only in the absorbed phase of the photocatalyst availability of active sites where oxidative reactions can take place (Wang, 2004). The amount of the surface-adsorbed water and hydroxyl groups is related to the crystallite form and surface area. A large surface positively influences certain photodegradation reactions, as a large amount of adsorbed molecules promotes the reaction rate. (Cernigoj et al., 2007).
2.8.2.1.2 X-Ray Diffraction (XRD)

Surface morphology such as particle size and agglomerate size, is an important factor to be considered in photocatalytic degradation process because there is a direct relationship between organic compounds and surface coverage of the photocatalyst (Yang, 2004). Particle size is an important parameter for photocatalytic efficiency, since the predominant way of electron/hole recombination may be different depending on the particle size (Cernigoj et al., 2007). When the crystallite dimension of a semiconductor particle falls below a critical radius of approximately 10 nm, the charge carriers appear to behave quantum mechanically (Hoffmann et al., 1995). A perfect balance between surface area and crystallinity must be found in order to obtain the highest photoactivity.
The crystal size of TiO$_2$ and ZnO powder is calculated using Scherrer’s equation;

$$D = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (9)

D Diameter of the grain,
K Scherrer constant (0.9) which depends on crystal shape, how width is determined, and the size distribution,
\(\lambda\) wavelength of X-rays in nanometers (\(\lambda = 0.15418\) nm or 1.54Å),
\(\beta\) angle between the incident and diffracted beams in degrees (Full Width at Half Maximum, FWHM) in radians obtained by using the formula,
$$\beta = 2(\theta_2 - \theta_1)$$ \hspace{1cm} (10)

\(\theta\) Bragg’s angle.
2.8.2.1.3 Energy Dispersive X-Ray Spectrometry (EDS)

Energy Dispersive X-Ray spectroscopy is a technique that analyses and characterizes samples to determine their elemental and chemical composition (Russ, 1984). This method relies on investigating the interactions between x-ray magnetic radiation and matter. It analyses the X-rays emitted by the matter after bombardment with charged particles. Each element has a distinct unique atomic structure (Russ, 1984). The number and energy of the X-rays emitted from the samples is measured by use of an Energy Dispersive Spectrometer. The energy of the X-rays is characteristic of the difference in energy between two energy levels of the element from which they are emitted. This allows the elemental composition of the samples to be determined (Russ, 1984). The EDS experimental system comprises the following components.

i. X-Ray detector – detects and converts X-rays into electronic signals
ii. Pulse processor – measures the electronic signals to determine energy of each X-ray detected
iii. Multiple channel analyzer – displays and interprets X-ray data

Figure 2.8 Energy Dispersive X-Ray Spectroscopy
Source: (Russ, 1984)
2.8.2.1.4 Laser Induced Break-down Spectroscopy (LIBS)

The LIBS system is used to analyse the elemental identification of chemical substances on the basis of atomic emission spectroscopy. The intense laser beam interacts with the samples and create a signal which is collected and transmitted to camera equipped with a delay generator.

The recorded emission spectrum represents the signature of various elements present in the samples (Gondal et al., 2016). Ultra Violet and visible emission from the plasma can be resolved spectrally and recorded for quantitative and qualitative sample analysis.

It is important to optimize the experimental set-up, factors such as the delay time between excitation and data acquisition and laser influence on LIBS signal intensity. The wavelength of light provides information on the identity of elemental composition and the intensities indicate relative abundance (Gondal et al., 2016).

Figure 2.9 Laser Induced Breakdown Spectroscopy setup

Source: (Gondal et al., 2016)
2.8.2.1.5 Ultra-violet / Visible spectrophotometry (UV/Vis)

The spectrophotometer measures the absorbance of a liquid sample in the UV (200 nm-400 nm) and Vis (400 nm-800 nm) regions of light spectrum. In coloured wastewater samples, treatment that leads to decolourization is measured as the decrease in colour intensity at a specific wavelength on the basis of the experimental measurements (Ajmal et al., 2014). Colour as a water quality parameter is optimally monitored in the visible region. The Lambert-beer law gives the relationship between wastewater concentration and absorbance (Akyol et al., 2004). To measure accurate changes in colour, accurate readings of light absorbance at different wavelengths in and near the visible part of the spectrum must be made.

\[ A = \varepsilon cd \]

Where \( A \) is absorbance measured using spectrophotometer
\( c \) is concentration (mol.dm\(^{-3}\))
\( \varepsilon \) is the molar extinction coefficient (dm\(^3\) mol\(^{-1}\) cm\(^{-1}\))
\( d \) is the optical length (cm)

Figure 2.10  UV-Vis spectrophometry
Source: (Akyol et al., 2004)
2.8.2.1.6 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy is an analytical method that quantifies/qualifies elements. The method supports procedures that determine the absorbance of radiation at a specific wavelength by vapour composed of ground state atoms. The concentrations of chemical elements present in a liquid sample based on energy absorbed from certain wavelengths of light (200 nm - 900 nm) measured in mg/l. An AAS instrument consists of a primary source that produces the spectrum of the element under detection, a monochromator and photon detector (Sharma and Bhattachrya, 2017). The persistent challenge caused by the brown colour of tea processing wastewater required the investigation of the levels of Al, Mn, Ni and Fe which are colour impactors and heavily present in tea infusions.

![Diagram of Atomic Absorption Spectroscopy](image)

Figure 2.11 Atomic Absorption Spectroscopy
Source: (Sharma and Bhattachrya, 2017)
2.8.2.1.7 Gas Chromatography – Mass Spectroscopy (GC-MS)

GC-MS is an analytical technique that identifies unknown macromolecules present in a sample. The advantage of the GC-MS technique comes from the fact that not only are components of a mixture separated and detected quantitatively, but the detector provides information about the structure of each of the components identified. Compounds are identified by comparing the retention time to a standard and its mass spectrum. Unknown components are identified solely on its mass spectrum eliminating the need to run standards for retention time data. The column used in GC-MS is composed of a capillary column. Different columns may have bonded phases of different characteristics depending on the type of separation to be carried out (Lin et al., 2013).

The formed components are ionized by electron impact. Various ions will have different amounts of internal energy. A parent ion has the same mass in atomic mass units as the neutral molecule. It reflects the highest mass peak in the spectrum. By using the same energy electrons to ionize the components, the mass spectra become highly reproducible. In this way, libraries of mass spectral data have been generated and an unknown compound can be identified by searching through and matching the mass spectra (Lin et al., 2013).

![Gas Chromatography- Mass Spectrometry](image)

**Figure 2.12** Gas Chromatography- Mass Spectrometry

Source: (Lin et al., 2013).
3  Materials and methods

3.1  Sample collection

Five litres wastewater samples were collected every week, in the 3 factories for a duration of 8 months. The samples were collected in two 2.5 litre glass amber coloured bottles, placed in a cooler box at refrigeration 4°C. A total of 48 samples, 16 from each factory were collected.

3.1.1  Sampling sites

Three black tea processing factories found in Nandi County that include Chebut (CBH), Kibwari (KBH), and Nandi (NBH) were investigated were sampled for processing wastewater out of a total of 19 factories found in the whole county. The 19 factories process 600,000 Kgs green leaf daily. The altitudes and locational coordinates are indicated in Table 3.1 below.

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>Altitude (metres)</th>
<th>Longitude</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBH</td>
<td>1980</td>
<td>0°12’14”N</td>
<td>35°6’18”E</td>
</tr>
<tr>
<td>KBH</td>
<td>2114</td>
<td>0°5’32”N</td>
<td>35°11’20”E</td>
</tr>
<tr>
<td>NBH</td>
<td>2147</td>
<td>0°5’32”N</td>
<td>35°11’20”E</td>
</tr>
</tbody>
</table>

As shown in Table 3.1, the terrain in Nandi County is hilly and therefore suitable for black tea plantations.
3.1.2 Sampling period and atmospheric temperature

The average atmospheric temperature in Nandi County and the sampling duration recorded in Table 3.2 below.

Table 3.2 Sampling duration

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>Sampling duration</th>
<th>Mean wastewater temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBH</td>
<td>27/9/2015 – 29/11/2015</td>
<td>24.6°C</td>
</tr>
<tr>
<td>KBH</td>
<td>6/12/2015 – 28/2/2016</td>
<td>25.2°C</td>
</tr>
<tr>
<td>NBH</td>
<td>13/3/2016 – 29/5/2016</td>
<td>25.6°C</td>
</tr>
</tbody>
</table>

As shown in Table 3.2 the average atmospheric temperature in Nandi County during the entire duration of study was 25.1°C. Samples were collected over a duration of 8 months. The climatic conditions in Nandi County that lies in the Western Kenya highlands, are generally cool, humid and wet with an average annual rainfall of 2000 mm.
3.1.2.1 Map - Nandi County

Figure 3.1 shows an administrative map of Nandi County.

Figure 3.1: Map - Nandi County

Nandi County is one of the tea growing areas in the western Kenya highlands and also a major catchment area for rivers flowing into Lake Victoria. Chebut, Kibwari and Nandi tea processing factories are located around Nandi hills that forms a major catchment area for tributaries flowing into Yala and Nyando rivers. In 2017, production of green leaf stood at 71.4 Million Kgs, earning kshs. 21.4 billion.
3.1.2.2 Map - CBH factory

The location of the factory is shown in Figure 3.2 below.

Figure 3.2 Map - CBH factory

CBH factory processes an average of 20 million Kgs annually through the CTC method. The large volumes of wastewater generated require effective treatment before eventual discharge into the environment.
3.1.2.3 Map - NBH factory

The location of the factory is shown in Figure 3.3 below.

Figure 3.3 NBH factory

NBH factory processes 6 million Kgs of green leaf annually using the CTC technique. The subsequently generated wastewater is treated using a system of lagoons and stabilization ponds (SPs) found within the vicinity of the factory.
3.1.2.4  Map - KBH factory

Figure 3.4 below shows the location of KBH factory.

Figure 3.4 KBH factory

The factory is located near Nandi Hills town and has an annual processing capacity of 4 million Kgs using the CTC processing technique. The wastewater that forms after processing is diverted to a nearby constructed wetland (CW).
3.1.2.5 Rivers in Nandi County

Figure 3.5 shows the major rivers in Nandi County.

Figure 3.5: Major river systems in Nandi County

The rivers in Nandi County eventually flow into the Yala before eventually discharging into Lake Victoria. The rivers in Figure 3.5 flow from east to west.
### 3.2 Chemicals and Reagents

The chemicals and reagents used in the study are listed in Table 3.3 below.

**Table 3.3 chemicals and reagents**

<table>
<thead>
<tr>
<th>Item No.</th>
<th>Chemical</th>
<th>Concentration</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc oxide</td>
<td>500 g</td>
<td>ACME chemicals Ltd</td>
</tr>
<tr>
<td>2</td>
<td>Titanium dioxide</td>
<td>500 g</td>
<td>Degussa</td>
</tr>
<tr>
<td>3</td>
<td>Cellulose binder</td>
<td>2 g</td>
<td>ACME chemicals Ltd</td>
</tr>
<tr>
<td>4</td>
<td>Potassium dichromate</td>
<td>0.0042 M</td>
<td>Vishnu chemicals Ltd</td>
</tr>
<tr>
<td>5</td>
<td>Sulfuric acid</td>
<td>0.042 M</td>
<td>Sigma Ltd</td>
</tr>
<tr>
<td>6</td>
<td>Silver (II) sulfate</td>
<td>0.4 g</td>
<td>Okmar chemicals Ltd</td>
</tr>
<tr>
<td>7</td>
<td>Ferrous (II) Sulphate</td>
<td>0.695 g</td>
<td>Vishnu chemicals Ltd</td>
</tr>
<tr>
<td>8</td>
<td>Mercuric sulphate</td>
<td>0.4 g</td>
<td>Vishnu chemicals Ltd</td>
</tr>
<tr>
<td>9</td>
<td>Sulphamic acid</td>
<td>100 ml</td>
<td>E.T Monks Ltd</td>
</tr>
<tr>
<td>10</td>
<td>Buffer solutions</td>
<td></td>
<td>Sigma-Aldrich Ltd</td>
</tr>
<tr>
<td>11</td>
<td>Ferrion indicator</td>
<td>2-3 drops</td>
<td>Sigma-Aldrich Ltd</td>
</tr>
<tr>
<td>12</td>
<td>Ferrous ammonium sulphate</td>
<td>0.25 M</td>
<td>Choice organochem Ltd</td>
</tr>
<tr>
<td>13</td>
<td>1,10-phenanthroline</td>
<td>1.485 g</td>
<td>Kobian Kenya Ltd</td>
</tr>
<tr>
<td>14</td>
<td>Cyclohexane</td>
<td>250 cm$^3$</td>
<td>E.T Monks Ltd</td>
</tr>
<tr>
<td>15</td>
<td>Ethyl acetate</td>
<td>300 cm$^3$</td>
<td>Kobian Kenya Ltd</td>
</tr>
<tr>
<td>16</td>
<td>Anhydrous sodium sulfate</td>
<td>60 g</td>
<td>Muby chemicals Ltd</td>
</tr>
<tr>
<td>17</td>
<td>Dichloromethane</td>
<td>500 cm$^3$</td>
<td>Sigma Ltd</td>
</tr>
<tr>
<td>18</td>
<td>Hexane</td>
<td>300 cm$^3$</td>
<td>Sigma Ltd</td>
</tr>
<tr>
<td>19</td>
<td>Acetone</td>
<td>200 cm$^3$</td>
<td>Kobian Kenya Ltd</td>
</tr>
</tbody>
</table>

The glass used to fabricate photoreactor was purchased from Eldoret Glazers. Reusable glassware such as (test tubes, conical flasks, measuring cylinders, beakers, volumetric, round bottomed flasks etc.), washed in hot soapy water before being rinsed in distilled water. They were then dried in an electric oven at 105°C for 1 hour and allowed to cool at room temperature before use.
### 3.3 Instruments

Table 3.4 below shows the list of equipment used in the study.

<table>
<thead>
<tr>
<th>Item No.</th>
<th>Equipment</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X-Ray Diffractometer</td>
<td>Philips X’pert MPD</td>
</tr>
<tr>
<td>2</td>
<td>UVP – radiometer Light intensity meter</td>
<td>UVA-365</td>
</tr>
<tr>
<td>3</td>
<td>UV/Vis spectrophotometer</td>
<td>Cecil 2041</td>
</tr>
<tr>
<td>4</td>
<td>Turbidity Meter La Motte</td>
<td>TC-3000</td>
</tr>
<tr>
<td>5</td>
<td>Atomic Absorption Spectrophotometer</td>
<td>AA 500</td>
</tr>
<tr>
<td>6</td>
<td>Gas Chromatography – Liquid Spectrometry</td>
<td>Agilent technologies 6890N</td>
</tr>
<tr>
<td>7</td>
<td>Laser Induced Breakdown Spectroscopy</td>
<td>Ocean Optics 2500</td>
</tr>
<tr>
<td>8</td>
<td>Scanning Electron Microscope</td>
<td>Tescan VEGA3</td>
</tr>
<tr>
<td>9</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
<td>Oxford xMaxN</td>
</tr>
<tr>
<td>10</td>
<td>Pyranometer (Actinometer)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Centrifuge</td>
<td>Mikro 200R Hettich</td>
</tr>
<tr>
<td>12</td>
<td>Oven</td>
<td>Fischer Scientific A-160</td>
</tr>
<tr>
<td>13</td>
<td>TOC-VE</td>
<td>Shimadzu</td>
</tr>
<tr>
<td>14</td>
<td>Pelletizer</td>
<td>NSP 001</td>
</tr>
<tr>
<td>15</td>
<td>Magnetic stirrer</td>
<td>LMS-1003</td>
</tr>
<tr>
<td>16</td>
<td>Artificial UV lamps – 15W Black light fluorescent lamps</td>
<td>Sylvania</td>
</tr>
<tr>
<td>17</td>
<td>Weight balance</td>
<td>Memmert UM 400</td>
</tr>
<tr>
<td>18</td>
<td>Calciner</td>
<td>classic Clare 4.0</td>
</tr>
<tr>
<td>19</td>
<td>Heating mantle</td>
<td>Labtech Ltd</td>
</tr>
<tr>
<td>20</td>
<td>Homogenizer</td>
<td>Model – UP 2005</td>
</tr>
<tr>
<td>21</td>
<td>Carbon analyzer</td>
<td>TCA-08</td>
</tr>
<tr>
<td>22</td>
<td>300-mm double surface condenser</td>
<td>Liebig, Friedrichs, West</td>
</tr>
<tr>
<td>23</td>
<td>Nephelometric turbid meter</td>
<td>2100P</td>
</tr>
<tr>
<td>24</td>
<td>pH meter</td>
<td>Japan Ltd</td>
</tr>
</tbody>
</table>
3.3.1 UV light source (UV lamps)

The first set of experiments required UV light irradiation from 2 UV lamps 15 W and 18 cm long fitted 10 cm above the wastewater solution in the reactor proto-type. The lamps emitted light of wavelengths between 320 nm - 400 nm. All the UV light induced photocatalytic degradation reactions took place at room temperature.

3.3.2 Solar light

A second set of experiments mediated by solar light was repeated following the procedure described in (section 3.3.1). The solar mediated photocatalytic treatment reactions were done between 11 am and 3 pm to maximize on the sunshine hours available.

3.3.3 Preparation of ZnO and TiO₂ surface layers

Several TiO₂ and ZnO surface layers of dimensions (18 cm × 13 cm) were prepared on clean and degreased borosilicate glass plates by immobilization from sediments of their aqueous suspensions \( c = (10 \text{ gL}^{-1}) \) in a rounded-bottomed flask of volume 250 cm³. An ultra-sonic homogenizer was used to break-down any agglomerates that may be present in the aqueous suspension making suspension uniform. A 10 cm³ syringe of was used to immobilize 28.8 cm³ of the prepared suspension onto the glass layers ensuring an optimum catalyst loading of 0.5 mg/cm². The surface layers were left to dry in ambient air for about 2 hours and further dried in an oven at a temperature \( t = 50 \, ^\circ\text{C} \). In order to fixate the catalyst suspension on the glass layer, the surface layers were finally annealed at 300°C for 1 hour.

3.3.4 Preparation of ZnO and TiO₂ pellets

Small pellets comprising ZnO and TiO₂ powder catalysts were prepared using a pelletizer by measuring an amount of 0.5 g of the powder catalyst and 0.1 g of a cellulose binder. The mixture was then mixed uniformly before being pressed together to from the pellets.
3.3.5 Fabrication of photocatalytic reactors

3.3.5.1 Photocatalytic reactor fitted with UV lamps

A reactor prototype of dimensions (20 cm×15 cm×10 cm) fitted with 2 UV lamps was fabricated from borosilicate glass as depicted in Fig. 3.6. The reactor was fitted with two 15 W UV lamps emitting UV light of irradiation flux intensity (I=3.0 mW/cm²) and a magnetic stirrer. A volume of 500 cm³ of filtered wastewater sample was put into the photoreactor to a height of approximately 2 cm. The base of the photoreactor was fitted with the surface layer containing ZnO or TiO₂ powder photocatalyst prepared in (Section 3.3.3) above. The UV lamps were fitted at a height of cca. 10 cm above the wastewater samples in the reactor. To monitor progress in photocatalytic treatment, 3 cm³ of the samples were removed after every 15 minutes and its absorbance measured at λ = 410 nm by a UV/Vis spectrophotometer. The wastewater samples were treated for a duration of 180 mins.

Figure 3.6: UV lamps induced photocatalytic reactor
3.3.5.2 Photocatalytic reactor irradiated by solar light

A second set of experiments similar to the reactions described in section (3.3.5.1) were repeated mediated by solar light as shown in Fig. 3.7. The average irradiation flux intensity was measured and determined to be 1.45 mW/cm$^2$. To monitor photocatalytic degradation of wastewater samples, 3 cm$^3$ were drawn every 15 minutes using a pipette and its absorbance determined by a UV/Vis spectrophotometer at $\lambda = 410$ nm. The photocatalytic treatment reactions were done for a maximum irradiation time of 180 minutes. The solar mediated treatment reactions were done between 11 am and 3 pm to maximize on the sunshine hours available.

![Figure 3.7: Photocatalytic reactor irradiated with solar light](image-url)
3.3.6 Experimental design

A volume of 500 cm$^3$ of wastewater was sampled and filtered under gravity into 250 cm$^3$ Erlenmeyer flasks and placed into 500 cm$^3$ beakers. The filtered solution was then put into photocatalytic reactors described in sections whose base was coated with a layer of ZnO or TiO$_2$ catalyst powders as described in Sections (3.3.5.1) and section (3.3.5.2). The wastewater sample in the photoreactor was at a height of cca 2 cm from bottom bed. The photoreactor was placed on top of a magnetic stirrer to ensure sample homogeneity during the photocatalytic degradation reactions. The photoreactor was illuminated using 2 UV lamps producing irradiation at wavelength $\lambda = 365$ nm of intensity 3.0 mW/cm$^2$ for a maximum duration of 180 mins. A second set of experiments were repeated as above with solar light irradiation of intensity ($I = 1.45$ mW/cm$^2$). The degradation of colour intensity of the wastewater sample was measured using a UV/Vis spectrophotometer at $\lambda = 410$ nm. Samples of 5cm$^3$ were drawn every 15 minutes and absorbance measured for a duration of 180 minutes.

3.4 Methods

3.4.1 Measuring light intensity

3.4.1.1 UV lamps

The intensity (amount of UV energy on the wastewater per unit area expressed in (mW/cm$^2$) of the UV lamps was measured by a radiometer (UVA-365) to measure the maximum irradiation flux density. The radiometer was placed at a height (10 cm) similar to distance between the UV lamps and wastewater sample. The UV metre directly faced the UV lamps emitting radiation. The readings were taken as a grid i.e. from right, left and centre to determine the homogeneity of the result. The intensity is measured as energy output in mW/cm$^2$ in the range between 200 nm - 400 nm. The results show spectra irradiance i.e. intensity at each wavelength.

3.4.1.2 Solar light

A Pyranometer was used to measure solar irradiance on a planar surface. The solar light irradiance were recorded at a meteorological station in Nandi County.
3.5 Physico-Chemical characterization of Raw and Treated wastewater

Wastewater was analysed to determine their physico-chemical properties i.e. colour, pH, Turbidity, Total Organic Compounds, Chemical Oxygen Demand, Total Suspended Solids and Total Dissolved solids.

3.5.1 pH

The digital pH meter was switched on and allowed to stand for some time and then calibrated using appropriate standards supplied by the manufacturer.

- 30 cm$^3$ of the sample was poured into a beaker
- The probe was then thoroughly rinsed with distilled water and the pH mode switched on.
- The probe was then immersed into the sample
- Homogeneity between the probe and the sample was insured by stirring the sample using a stirring bar to establish equilibrium.
- The pH reading was read and recorded
- The electrode was then rinsed thoroughly with distilled water
- After use, the electrode was placed in the beaker containing distilled water

3.5.2 Turbidity

The operating mode of the turbid meter was selected at “auto” mode.

- Three clean matched sample cells were used.
- The turbid meter was switched on and calibrated according to the manufacturer supplied operating manual and supplied standards.
- A sample cell was rinsed and cleaned with distilled water and the wastewater sample.
- The wastewater samples were rapidly poured into the sample cell avoiding touching the cell walls.
- Any condensation that forms on the walls of the sample cell was wiped using a clean lenses tissue.
• The sample cells containing the samples were inserted into the cell holder and digital turbidity readings recorded.
• The procedure was repeated at least twice using fresh samples until sequential readings fall within ± 10 percent and recorded in Nephelometric Turbidity Units (N.T.U) units.

3.5.3 Total Organic Carbon – Direct method

The direct method involved wastewater samples being oxidized to carbon dioxide by persulfate digestion. The carbon dioxide that is formed then diffuses into a coloured pH indicator solution where converted to carbonic acid was. The resulting colour change is directly proportional to the concentration of carbon present in the samples. The procedure proceeded as follows.
• A volume of 10cm³ of the sample was added to a persulfate solution placed in a digestion tube. The persulfate and digestion reagent oxidised the carbon in the wastewater sample to carbon dioxide.
• An opened ampule of pH indicator reagent was inserted into the digestion tube.
• The tube was then securely sealed
• The assembled unit was digested at 105°C for a duration of 2 hours. The carbon dioxide formed diffuses into the inner ampule and forms carbonic acid. The acid converts the pH of the indicator and colour. The change in colour (indicator) is related to the initial amount of organic carbon present in the wastewater sample. The amount of carbon present in the wastewater sample is equal to the concentration of carbonaceous material in the wastewater.
• After cooling, the complete unit was placed into a suitable photometer for colour measurements.

3.5.4 Chemical Oxygen Demand (COD) (mg/L) – closed reflux titrimetric method

The dichromate technique was used to determine COD of the wastewater samples. The excess chromate was determined through back titration with ferrous ammonium sulphate using the ferrion indicator to detect the end point. The chemicals required to measure the COD of wastewater samples included;
1) 0.042 M Sulfuric acid
2) standard potassium dichromate solution (made by dissolving 12.3 g of K$_2$Cr$_2$O$_7$ primary standard grade, dried at 103 °C for 2 hours, in distilled water and diluted to 1 litre);
3) 0.0042 M dilute standard potassium dichromate solution (made by diluting 100 ml of the standard potassium dichromate solution to 1 litre);
4) 0.25 M of standard ferrous ammonium sulphate solution (made by dissolving 98 g of Fe(NH$_4$)$_2$ (SO$_4$)$_2$ .6H$_2$O analytical grade crystals in distilled water added to 20 ml of H$_2$SO$_4$ and diluted to 1 litre)
5) 0.025 M dilute standard ferrous ammonium sulphate solution (made by diluting 100 ml of the standard ferrous ammonium sulphate solution to 1 litre ), standardized against the 0.0042 M dilute standard potassium dichromate;
6) 0.4 g silver sulphate, reagent powder directly in powder form;
7) mercuric (II) sulphate, analytical grade crystals;
8) ferroin indicator solution 0.695 g of ferrous sulphate, FeSO$_4$.7H$_2$O dissolved in H$_2$O to which 1.485 g of 1,10-phenanthroline monohydrate was added , swirling until the solution is dissolved and then diluted to 100 cm$^3$,
9) Sulphamic acid, analytical grade to eliminate interference of nitrites (APHA, 2005).

**Procedure**

20 cm$^3$ of the sample and 10 cm$^3$ of standard dichromate solution were transferred into a 250 cm$^3$ Erlenmeyer flask. 0.4 g of Mercuric (II) Sulphate and 30 cm$^3$ of the concentrated, sulphuric acid was carefully poured into the solution and thoroughly mixed until a uniform solution was appeared. The flask containing the solution was covered with a clean cover glass and allowed to stand for at least 30 minutes in a boiling water bath. The solution in the flask was topped up to 75 cm$^3$ with distilled water. 2-3 drops of ferrion indicator was added and solution titrated with ferrous ammonium sulphate. The solution changed from yellow-orange to blue-green. At end point, the solution turns reddish brown and the results tabulated. A reagent blank was also prepared using 20 cm$^3$ of distilled water (APHA, 2005).

**3.5.5 Total Suspended Solids (TSS)**

Total suspended solids (TSS) in the samples were determined by the following steps:-
3 dry filtration papers were weighed to measure their weights (mg)
3 samples each of volume 1 L were filtered into 1000 cm³ flat-bottomed flasks.
The 3 filter papers containing residue from filtration were dried in an oven at a temperature of 105°C
The filter paper was removed from the oven and its weight measured every 60 minutes until there was little or no change in its weight.
The TSS of the samples in (mg/L) was determined by the averages in the differences between the weight of dry filter papers and final weight of the oven dried filter papers.

3.5.6 Total Dissolved Solids (TDS)

100 cm³ wastewater filtered in (3.4.6) above was used to determine Total Dissolved Solids (TDS). The procedure included:-
- The weights of 3 empty 50 cm³ beakers (g) was determined
- 100 cm³ of the wastewater is transferred into each of the 3 beakers
- The beakers are placed into an oven heated to a temperature of t = 105°C for a duration of 2 hours.
- After 2 hours the beakers are taken out of the oven and weighed
- The average differences in weights between the beakers before and after heating is the TDS of the samples in (mg/L).

3.6 Decolourization of wastewater
3.6.1 Colour measurement by UV/Vis spectrophotometer

Colour of the wastewater samples were analysed by measuring their absorbance using a UV/Vis Spectrophotometer. Quartz cuvettes were used in the analysis. A cuvette containing distilled water (blank) was placed in the sample compartment with the transparent sides facing the light source and the sample compartment lid was closed. The transparent sides of the cuvette were kept dry and clean.
- The auto zero button was pressed to set zero absorbance
- The distilled water was discarded and a cuvette containing the wastewater sample was placed in measuring position.
- The sample compartment lid was closed and the “start button” pressed to start colour measurement
The absorbance units obtained were recorded and reported as colour units.

### 3.6.2 Spectral analysis of wastewater

Decolourization of the wastewater was measured as a decrease in colour intensity using a UV-Vis spectrophotometer.

- A volume of 20 cm$^3$ of CBH, NBH and KBH samples were filtered into a 50 cm$^3$ beaker
- One quartz cuvette was cleaned and dried using distilled water and linen tissue to ensure the transparent side remained clear.
- UV-Vis spectrophotometer was switched on
- A cuvette (optical length 1 cm) containing distilled water (blank) was placed in the sample compartment with the transparent sides facing the light source and the sample compartment lid was closed.
- The auto zero button was pressed to set zero absorbance
- A full UV-Vis scan of CBH, KBH and NBH samples was done at wavelengths between 350 nm-520 nm.

### 3.6.3 Photocatalytic decolourization of wastewater

Changes in colour intensity with increase photocatalytic treatment time was measured by a UV-Vis spectrophotometer. Reduced absorbance values with increased solar-UV light irradiation light showed increased wastewater decolourization efficiency.

To determine changes in absorbance, mixing and irradiation of the wastewater is interrupted every 15 mins. After which 3 cm$^3$ of the sample is removed from the reactor and put into a cuvette of optical length 1 cm and its absorbance measured at 410 nm. After absorbance measurements, the sample is placed back into the reactor and irradiation resumed. The photocatalytic treatment proceed for a reaction time of 180 mins. Confirmatory reactions time indicates minimal changes in absorbance beyond 3 hrs of treatment.

The decolourization efficiency for the samples was calculated as follows;

$$\text{Decolourization (%) } = \frac{C_o - C}{C_o} \times 100 = \frac{A_o - A}{A_o} \times 100$$  \hspace{1cm} (11)

Where $C_o$ is the initial concentration

$c$ variable concentration
Ao is the initial absorbance
A variable absorbance

In addition to colour intensity, the final Total Organic Carbon and Chemical Oxygen Demand parameters of the samples are useful to estimate progress in photocatalytic treatment.

3.6.4 UV-ZnO film decolourization system

A description of the photoreactor set-up is described in section (3.3.5.1) and equipped with two 15W UV lamps. In addition, a ZnO surface layer prepared as described in section (3.3.3) and fitted at the base of the photoreactor. 500 cm$^3$ of wastewater sample was put into the reactor and irradiated by UV lamps whose irradiation flux intensity (W/cm$^2$) was measured by a digital UVP meter. A stirrer was used to ensure uniform mixing in the photoreactor.

3.6.5 Solar-ZnO film decolourization system

The photoreactor set-up is described in section (3.3.5.2). The experimental conditions are similar to those described in section (3.5.4) apart from solar light that supplied irradiation for photocatalytic treatment. The solar irradiation flux density (mW/cm$^2$) was measured over a period of 6 months using a solar intensity meter during sunny days between 11am to 3pm.

3.6.6 UV/TiO$_2$ film – decolourization system

The photoreactor set-up for the reactions is described in section (3.3.5.1). A TiO$_2$ Surface layer is inserted at the base of the photoreactor fitted with two 15W UV lamps that irradiated 500 cm$^3$ of wastewater. The intensity of the UV lamps (W/cm$^2$) was measured using a digital UVP meter.

3.6.7 Solar /TiO$_2$ film – decolourization system

This experimental procedure was similar to section (3.6.5). TiO$_2$ was immobilized on a glass surface layer
3.7 Macro-molecules in tea processing wastewater

3.7.1 Gas Chromatography – Mass Spectrometry

1) A volume of 50 cm$^3$ of wastewater was mixed with anhydrous sodium sulphate (20 g) and transferred into an Erlenmeyer flask with a mixture of 100 cm$^3$ hexane, acetone (60:40, v/v) and dichloromethane.

2) The flask containing the solution, was put into an ultrasonic bath for 30 minutes. The extract was then filtered through another layer of anhydrous sodium sulphate.

3) The filtrate obtained after solvent evaporation was dissolved in 5 cm$^3$ solution mixture of cyclohexane: ethyl acetate (50:50, v/v) and filtered through the polytetrafluoroethylene (PTFE) filter with a pore size of 1 µm.

4) The step of PAHs isolation cleanup procedure was carried out by gel permeation chromatography (GPC) and column TSK Gel G1000HXL (300 mm x 7.8 mm, 5 µm).

5) Chromatographic separation was performed by isocratic method with mixture cyclohexane: ethyl acetate (50:50, v/v) used as mobile phase. Samples were eluted at a flow rate of mobile phase of 0.8 cm$^3$/min.

6) The purified extract of PAHs was subjected to concentration, then dissolved in toluene and analysed by GC-MS solution software was used for data processing, and Shimadzu GC-MS Metabolites spectral Database and NIST 2008 mass spectral library were used as the mass spectral libraries.

3.8 Chemical elements in tea processing wastewater

3.8.1 Atomic Absorption Spectroscopy

Wastewater samples were collected using new PET bottles and transported to the laboratory for analysis in a cooler box at temperatures below 4°C. The samples were stored under refrigeration in the laboratory. The following steps were followed to determine the chemical elements in wastewater:

The process of atomic absorption spectroscopy involves two steps;

a) Atomization of the wastewater

b) Absorption of radiation from a light source to free atoms
Preparation of standard solutions

Standard solutions of Aluminum (Al), Manganese (Mn), Nickel (Ni) and Iron (Fe) metal concentrations in water were prepared in water. The standards were prepared within the working range of the method and stored under refrigeration at 4°C.

For the procedure involving air-acetylene flame:

1) Installation of the hollow cathode lamp for the specific metal being analysed at roughly at the desired wavelength
2) The slit-width and lamp current is set and the instrument allowed to warm up until stability is achieved.
3) The wavelengths were adjusted until optimum energy is gained. The lamp was thereafter aligned according to manufacturer’s instructions.
4) The air-acetylene burner was installed and the burner head position adjusted. Turn on air and adjust flow rates to give maximum sensitivity for the metal being measured. Acetylene was then turned and adjusted to ignite flame.
5) A standard solution of the desired metal was aspirated and adjusted. The aspiration rate of the nebulizer was also adjusted to ensure maximum sensitivity. A standard solution was aspirated near the middle of the linear working range and the burner adjusted vertically and horizontally to obtain maximum response. The instrument was then ready for use.
6) On completion the flame is extinguished by turning off the acetylene first and then followed by air.

For determination involving nitrous oxide acetylene, the process proceeds as in (1) to (3) above followed by:

4) The nitrous oxide-acetylene burner was installed and its burner head adjusted to position. The acetylene was turned on without igniting the flame and its flow rate adjusted to the specified value. The nitrous oxide was then turned on. After ignition the burner was allowed to come to thermal equilibrium before analysis is started.
5) A standard solution of the desired metal was aspirated and the aspiration rate of the nebulizer adjusted to achieve maximum sensitivity. A standard solution was aspirated near the middle of the linear working range and the burner adjusted vertically and horizontally to achieve maximum response.
6) The instrument was then ready for analysis
Further measurements involve:

1.) Filtration of the sample when necessary to avoid clogging the atomizer burner
2.) Each sample and standard was atomized, scale reading observed and recorded.
3.) The process in (2) above is repeated and an average of the two values recorded
4.) The concentrations (mg/L) of the chemical elements in the sample was obtained from a plot of scale readings of standards. A working curve from each set of samples was determined.

3.9 Surface morphology characterization of TiO$_2$ and ZnO

Particles of the catalyst powders were characterized to determine their particle size, surface area and chemical composition by Scanning Electron Microscope (SEM), X-Ray diffraction (XRD), Brunauer Emmett-Teller (BET) and Laser Induced Breakdown Spectroscopy (LIBS).

3.9.1 Laser Induced Breakdown Spectroscopy (LIBS)

The samples were prepared into pellet form by binding with cellulose as described in section (3.3.4). A compact ocean optics spectrometer controlled by a computer installed with Oolibs software was used.

1) The experimental set-up was switched on and the laser allowed to warm up for about 30 minutes.
2) The icon was clicked to start-up the spectrometer program.
3) On the main screen of the Oolibs program the integration time box was located. Then an appropriate integration time of 500 milliseconds was selected. The integration time is the time the detector spends collecting photons. Long integration times means more intense peaks.
4) The averaging box was set at 1 to enable the spectrometer to respond faster. However after the integration time was checked to be satisfactory, the averaging was increased to 7 in order to improve the quality of recorded spectra
5) The ZnO and TiO$_2$ were alternatively affixed onto sample discs using a double-sided tape
6) The sample disc was then placed back into the vacuum chamber and then closed
7) The start button was pressed on the Q-switch control section of the laser control panel
From the fourth harmonic of Nd: YAG laser, 500 mm spectrograph and gated ICCD camera with in-built delay generator.

8) Make the laser hit the samples and save the generated spectra in the computer
9) Optimize by varying the number of shots, ablations, incident laser energy, and gate time delay time.

### 3.9.2 Energy-Dispersive X-ray spectroscopy (EDS)

An Oxford xMaxN EDS measuring instrument was used to determine the elemental composition of the samples.

1) The crystalline phase was determined using an Analytical Empyrean X-Ray Diffractometer (XRD), employing a scanning rate of 0.12 °C/min in a 2θ range from 20° to 70° with Cu Kα radiation (λ = 1.5418 Å).
2) The working distance was set at 14 mm and the acceleration voltage adjusted to 20 KV.
3) The detector was moved down to 45 mm by turning the knob located below the detector
4) The sample (ZnO/TiO₂) was focused
5) On the computer screen, the X-ray setup icon was clicked-on and enabled for a live time of about 200 seconds
6) The X-ray icon was activated and the cursor placed on the spectrum window and the total number of counts read per second and the dead time (DT) at the spectrum window noted.
7) The dead time (DT) was adjusted to between 25-30% by manipulating the spot size.
8) The current spectrum was erased and a new X-ray spectrum measured
   a. To identify the peaks, possible existing elements in the samples were checked with the periodic table to determine whether the peaks were matching
9) The spectrums were saved in the computer
3.9.3 Scanning Electron Microscope (SEM) – Crystal size

A Tescan VEGA3 Scanning Electron Microscope (SEM) equipped by a field emission source (FESEM) which was preferred over regular SEM with Lanthanum hexaboride, LaB6, filament as a high voltage source for morphological characterization due to its high resolution and brightness at low accelerating voltages.

1) Prior to SEM analysis, the samples were first mounted on an aluminum stub using a double sided carbon tape, and then coated with a thin layer (10 nm - 30 nm) of 60/40 gold-palladium alloy by means of vacuum sputtering coating using a Denton Desk 1 Sputter-Coater under a 70 mtorr vacuum.

Other conditions:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM HV</td>
<td>20.0 kV</td>
</tr>
<tr>
<td>View field</td>
<td>6.36 μm</td>
</tr>
<tr>
<td>SEM mag</td>
<td>30.0 kx</td>
</tr>
</tbody>
</table>

2) The two samples were inscribed for identification
3) The samples were dried at an oven 60°C for 3 hours
4) The samples were loaded into the SEM holder and the valves of the nitrogen gas tanks are opened and the vent button located at the display panel of the microscope table pressed. The sample holder were set at their mounting holes and tightened effectively.
5) When the vacuum reaches an optimum level the filaments light went on and the key switch put on and the monitor lit up.
6) The acceleration voltage was set at 20 KV, lowest magnification (30X) and TV mode scan selected.
7) The coarse focus was switched on and the focus knob adjusted to a safe working distance of 14 mm.
8) The focus was switched to slow scan mode and magnification increased. The samples stage was brought up slowly by pressing z-axis UP key. The variable button was opened up to open a small variable window on the screen. The image was focused within the small screen using outer focus ring and inner focus ring until indicator light reaches the middle.
9) The image was previewed and adjusted to contrast and the image set-up window closed. The image acquire icon was clicked to record the image formed and the image saved.

3.9.4 X-Ray Diffractometry (XRD) – Crystallite size

X-Ray diffraction (XRD) measurements were done:
- at ambient temperature at an angle 2θ set for the range 5° - 90° at a rate of 0.5°/min using a diffractometer fitted with Ni-filtered Cu Kα radiation (λ=1.5406Å).
- Finely ground crystalline powder were placed in the path of monochromatic x-ray beam, diffraction occurred from planes in those crystallites which happen to be oriented at the correct angle to fulfill the Bragg condition.

1) The enclosure doors were opened and the samples loaded
2) The slide doors were carefully and gently pressed together until they interlocked
3) On the computer the XRD commander was expanded and the following working parameters included
   4) Scan parameters: start and end 2q limits 0 - 130 - 2q
   5) Step size 0.5 - 0.1 – 2q
   6) Step time (1 sec)
   7) Start scan
   8) When scan was completed the file was saved

Particle sizes are calculated by XRD using the Scherer’s equation \( l = \frac{k\lambda}{\beta \cos \theta} \).
Where \( \lambda \) is the wavelength of rays, \( k \) is a constant taken to be 0.9 (assuming no crystal distortions in the lattice), \( \beta \) is the full width at half maximum of the radians corrected for the instrumental broadening and \( \theta \) is the diffraction angle in degrees

3.9.5 Brunauer Emmett Teller (BET) – surface area analysis

The BET surface area was measured through a multipoint method utilizing adsorption data in the relative pressure (P/Po) in the range 0.005-0.3 using nitrogen (99.99%) physico-sorption at 200°C.
1) The system used liquid nitrogen in a 500 cm³ Dewar flask placed on the stage of the instrument.

2) Sample housing and samples holder were cleaned using a damp wipe

3) Stubs were screwed into a specimen holder

4) ZnO and TiO₂ were first evacuated for 2 hours at 150°C to eliminate adsorbed water

5) The specimen chamber was evacuated and specimen holder set onto specimen stage

6) The HT icon was pressed after the samples were loaded and the ACB, AF and AS icons clicked to observe the images formed.

7) The image qualities were adjusted using the contrast, brightness, focus and stig X, stig Y buttons.

8) To observe at high magnification, the focus was set at low magnification first and then magnification was raised gradually

9) The resolution of the images formed were set at 80 seconds

10) SEM Data Display tab displayed selected SEM data on the image. The photo button was selected and the samples scanned and saved.

11) The SEM image list tab showed a list of the images taken
CHAPTER FOUR

4 Results and Discussion

4.1 Physico-Chemical Characterization - untreated wastewater

Table 4.1 below summarizes the physico-chemical characteristics of untreated tea processing wastewater from CBH, KBH and NBH tea factories.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>TOC [mg/l]</th>
<th>COD [mg/l]</th>
<th>TSS [mg/l]</th>
<th>TDS [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBH</td>
<td>6.1</td>
<td>62.3</td>
<td>210</td>
<td>547.34</td>
<td>312</td>
<td>1326.37</td>
</tr>
<tr>
<td>KBH</td>
<td>5.6</td>
<td>65.9</td>
<td>236</td>
<td>562.31</td>
<td>327</td>
<td>1368.52</td>
</tr>
<tr>
<td>NBH</td>
<td>5.9</td>
<td>64.0</td>
<td>213</td>
<td>553.06</td>
<td>319</td>
<td>1338.13</td>
</tr>
</tbody>
</table>

The physico-chemical characteristics of wastewater as outlined in Table 4.1 are summarized in Sections (4.1.1 – 4.1.6) below.

4.1.1 pH

Table 4.1 shows averaged pH for wastewater samples. The pH of untreated wastewater are recorded in Table 4.1 above. The pH values of aqueous systems is an important parameter for photocatalytic degradation reactions because it affects the adsorption pollutants that takes place on the surface of selected photocatalysts. The generation of •OH is dependent on the pH of wastewater. The pH values of CBH, KBH and NBH samples were measured at 6.1, 5.6 and 5.9 respectively. The untreated samples were slightly acidic, while CBH sample was noted to be less acidic in comparison to KBH and NBH samples. The pH influences the surface properties of selected photocatalysts. Greater photocatalytic treatment is normally observed at neutral pH. This is due to the point of zero change (pzc) of the photocatalysts. The pH values measured are a factor of climatic conditions, soil types and the compositional macro-molecules in the initial tea varieties. In strongly acidic wastewater systems, the • OH radicals generated are quickly discarded that there is little time to react with the pollutants.
4.1.2 Turbidity

The turbidity of the wastewater samples were measured according to the procedure described in section (3.5.2) and the values recorded in Table 4.1 above. The values were found to be 62.3 N.T.U, 65.9 N.T.U and 64.0 N.T.U for CBH, KBH and NBH respectively. The results indicate greatest turbidity in KBH sample and least turbidity in CBH sample. These findings are consistent with Total Suspended Solids findings recorded in Section (4.1.5) and Total Dissolved Solids in Section (4.1.6) Turbidity as a water quality parameter is influenced by TSS and TDS. Higher TSS and TDS values increase the turbidity of wastewater solutions. KBH sample showed high Turbidity, TSS and TDS values compared to samples form CBH or NBH.

4.1.3 Total Organic Compounds (TOC)

The Total Organic Carbon (TOC) level for the wastewater samples were analysed according to the procedure in section (3.5.3). According to Table 4.1, the TOC of CBH, KBH and NBH was analysed to be 210 mg/L, 236 mg/L and 213 mg/L respectively. The greatest levels of TOC were observed in KBH and the least levels in CBH sample. This results show that the greatest contamination was present in KBH sample and the least in CBH.

4.1.4 Chemical Oxygen Demand (COD)

The COD for the wastewater samples was determined according to the procedure in section (3.5.4). The findings in Table 4.1 indicate that, CBH, KBH and NBH samples showed COD values of 547 mg/L, 562.31 mg/L and 553.06 mg/L. The greatest levels of COD were observed in KBH sample and the least in CBH. There exists a direct correlation between COD and TOC of wastewater systems. From the values indicated in Table 4.1, Section (4.1.4) and (4.1.5) KBH sample showed the greatest TOC and COD values and CBH sample the least. The volatility of the organic components present in the wastewater influenced the relationship between TOC and COD of the wastewater. In Section (4.4.1), GC-MS analysis of wastewater showed the macro-molecules present in wastewater as follows; CBH = 9, KBH= 14 and NBH= 12 respectively. These values show that is KBH sample the oxygen demand is highest due to the total number of compounds identified. Sample CBH had least number of compounds identified.
4.1.5 Total Suspended Solids (TSS)

The values of the Total Suspended Solids are presented in Table 4.1 and measured at 312, 327 and 319 mg/l for CBH, KBH and NBH. These values were determined as per the procedure described in section (3.5.5). Sample KBH had the highest amounts of suspended matter and sample CBH had the least. The levels of suspended matter present in the wastewater affected its turbidity. The values correlate with the Turbidity values as shown in section (4.1.2).

4.1.6 Total Dissolved Solids (TDS)

The TDS for the samples were determined as per the procedure in section (3.5.6) and the values obtained for the 3 sample recorded as CBH=1326.37 mg/L, KBH= 1368.52 mg/L and NBH= 1338.13 mg/L. The levels of dissolved solids influenced the turbidity of the samples as discussed in section (4.1.2). The results show that the KBH sample had the greatest amounts of dissolved solids that also elevated its turbidity and sample CBH the least dissolved solids and turbidity.
4.2 Analysis of macro-molecules in tea processing wastewater

4.2.1 Gas Chromatography – Mass Spectrometry (GC-MS)

Table 4.2 Macro-molecules in tea processing wastewater

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Times (mins)</th>
<th>Molecular formula</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2-Butanone, 4-(2, 6, 6-trimethyl-1-yl)-</td>
<td>9.054</td>
<td>C_{13}H_{22}O</td>
<td>194</td>
</tr>
<tr>
<td>1-[2-[3-(2-Acetyloxiran-2-yl)-1,1-dimethylpropyl] cycloprop-2-enyl] ethanone</td>
<td>9.280</td>
<td>C_{14}H_{20}O_{3}</td>
<td>236</td>
</tr>
<tr>
<td>Tetradecanoic acid</td>
<td>10.023</td>
<td>C_{14}H_{38}O_{2}</td>
<td>228</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>10.286</td>
<td>C_{14}H_{22}O_{3}</td>
<td>238</td>
</tr>
<tr>
<td>3, 7, 11, 15-Tetramethyl-2-hexadecen-1-ol</td>
<td>10.872</td>
<td>C_{20}H_{40}O</td>
<td>296</td>
</tr>
<tr>
<td>Caffeine</td>
<td>11.677</td>
<td>C_{8}H_{10}N_{4}O_{2}</td>
<td>194</td>
</tr>
<tr>
<td>n-Hexadecanoic acid</td>
<td>13.604</td>
<td>C_{16}H_{32}O_{2}</td>
<td>256</td>
</tr>
<tr>
<td>Phytol</td>
<td>17.138</td>
<td>C_{20}H_{40}O</td>
<td>296</td>
</tr>
<tr>
<td>9, 12, 15-Octadecatrienoic acid</td>
<td>19.164</td>
<td>C_{18}H_{30}O_{2}</td>
<td>278</td>
</tr>
<tr>
<td>Octadecanoic acid</td>
<td>19.470</td>
<td>C_{18}H_{36}O_{2}</td>
<td>284</td>
</tr>
<tr>
<td>Ethyl iso-allocholate</td>
<td>21.320</td>
<td>C_{26}H_{44}O_{5}</td>
<td>436</td>
</tr>
<tr>
<td>1, 2-Benzenedicarboxylic acid</td>
<td>24.030</td>
<td>C_{24}H_{38}O_{4}</td>
<td>390</td>
</tr>
<tr>
<td>2, 6, 10, 14, 18, 22-Tetracosahexane, 2, 6, 10, 15, 23-hexamethyl-</td>
<td>27.595</td>
<td>C_{30}H_{50}</td>
<td>410</td>
</tr>
<tr>
<td>7-(1,3-Dimethylbuta-1,3-dienyl)-1,6,6-trimethyl-3,8-dioxatricyclo[5,1,0,(2,4)]octane</td>
<td>9.057</td>
<td>C_{15}H_{22}O_{2}</td>
<td>234</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>10.307</td>
<td>C_{14}H_{22}O_{3}</td>
<td>238</td>
</tr>
<tr>
<td>Caffeine</td>
<td>11.705</td>
<td>C_{8}H_{10}N_{4}O_{2}</td>
<td>194</td>
</tr>
<tr>
<td>n-Hexadecanoic acid</td>
<td>13.991</td>
<td>C_{16}H_{32}O_{2}</td>
<td>256</td>
</tr>
<tr>
<td>Phytol</td>
<td>17.284</td>
<td>C_{20}H_{40}O</td>
<td>296</td>
</tr>
<tr>
<td>9, 12, 15-octadecatrienoic acid</td>
<td>19.432</td>
<td>C_{18}H_{30}O_{2}</td>
<td>278</td>
</tr>
<tr>
<td>Molecule</td>
<td>Molecular Weight</td>
<td>Molecular Formula</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>------------------</td>
<td>-------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>octadecanoic acid</td>
<td>19.750</td>
<td>C_{18}H_{36}O_2</td>
<td>284</td>
</tr>
<tr>
<td>1, 2-Benzene dicarboxylic acid, diisooctyl ester</td>
<td>24.138</td>
<td>C_{24}H_{38}O_4</td>
<td>390</td>
</tr>
<tr>
<td>Oleic acid, eicosyl ester</td>
<td>26.703</td>
<td>C_{38}H_{74}O_2</td>
<td>562</td>
</tr>
<tr>
<td>1-Heptatriacotanol</td>
<td>9.038</td>
<td>C_{37}H_{76}O</td>
<td>536</td>
</tr>
<tr>
<td>Ppropiolic acid</td>
<td>10.237</td>
<td>C_{13}H_{20}O_3</td>
<td>224</td>
</tr>
<tr>
<td>Caffeine</td>
<td>11.262</td>
<td>C_{8}H_{10}N_{4}O_{2}</td>
<td>194</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>12.829</td>
<td>C_{26}H_{42}O_4</td>
<td>418</td>
</tr>
<tr>
<td>Phytol</td>
<td>17.089</td>
<td>C_{20}H_{40}O</td>
<td>296</td>
</tr>
<tr>
<td>9, 12, 15-octadecatrienoic acid</td>
<td>18.976</td>
<td>C_{18}H_{36}O_2</td>
<td>278</td>
</tr>
<tr>
<td>Octadecanoic acid</td>
<td>19.364</td>
<td>C_{18}H_{36}O_2</td>
<td>284</td>
</tr>
<tr>
<td>α-Amyrin</td>
<td>20.891</td>
<td>C_{30}H_{50}O</td>
<td>426</td>
</tr>
<tr>
<td>γ-Tocopherol</td>
<td>21.456</td>
<td>C_{28}H_{48}O_4</td>
<td>416</td>
</tr>
<tr>
<td>1, 2-Benzene dicarboxylic acid</td>
<td>24.028</td>
<td>C_{24}H_{38}O_4</td>
<td>390</td>
</tr>
<tr>
<td>Vitamin E</td>
<td>25.933</td>
<td>C_{29}H_{50}O_2</td>
<td>430</td>
</tr>
<tr>
<td>2, 2, 4-Trimethyl-heptadeca-3, 7, 11, 15-tetraenyl)-cyclohexanol</td>
<td>26.587</td>
<td>C_{30}H_{52}O</td>
<td>428</td>
</tr>
<tr>
<td>Hexadecanoic acid</td>
<td>13.442</td>
<td>C_{16}H_{32}O_2</td>
<td>256</td>
</tr>
</tbody>
</table>

Table 4.2 presents molecules found in tea processing wastewater from CBH, KBH and NBH factories. The macro-molecules present included carboxylic acids, alcohols, caffeine among others. The presence of this molecules in the wastewater was responsible for its acidity and characteristic brown colour as described in (section 1.7) indicating that some of the identified compounds were chromophores. In addition the retention times for the identified compounds ranged from (9.038 – 27.595 minutes). The molecular weights of the compounds ranged from 194 – 562 g/mol. The findings suggest that the molecules identified were large.
4.3  **Total chemical elements in tea processing wastewater**

Figure 4.1 below indicates the total chemical Fe, Mn, Ni & Al elements in wastewater

![Total chemical elements in tea processing wastewater](image)

Figure 4.1  Total chemical elements – CBH, KBH and NBH

**4.3.1  Total Chemical element – Ni**

From the data presented in Figure 4.1, Ni is the least prevalent chemical element in the wastewater compared to Fe, Mn & Al. The Ni present in KBH was 0.258 mg/l. In CBH and NBH the amount of Ni present was 0.347 mg/l.

**4.3.2  Total Chemical element – Al**

Aluminum element was shown to be the most prevalent in all the 3 samples namely CBH, KBH and NBH. In NBH sample the Al present was determined to be 18.889 mg/l. In CBH the Al levels was measured as 10.667 mg/l and in KBH 7.444 mg/l.
4.3.3 Total Chemical element – Mn

The total Mn chemical element was measured as follows; KBH=1.63 mg/L, NBH= 0.258 mg/L and CBH= 1.617 mg/L. The greatest levels of Mn were measured in KBH and least in NBH.

4.3.4 Total Chemical element – Fe

The greatest levels of Fe element was observed in CBH = 1.628 mg/L. NBH = 1.393 mg/L showed lowest levels. The levels in KBH was 1.393 mg/L.

4.4 Photocatalytic treatment of tea processing wastewater
4.4.1 Spectral analysis of untreated CBH, KBH and NBH wastewater

Figure 4.2 below shows a UV/Vis spectral analysis of wastewater at wavelengths between (350 nm – 500 nm).

Several investigators observed a similar UV/Vis spectral profile of tea processing wastewater. The spectral profile reveals that the wastewater samples absorb light actively in the visible region of light spectrum \( \lambda = (400 \text{ nm} – 800 \text{ nm}) \). From the spectra in Figure 4.2 we observe that CBH sample showed significantly lower absorbance compared to
KBH and CBH samples which showed almost similar absorbance levels. For Environmental and aesthetic concerns, the decolourization of the tea processing wastewater was more necessary than the removal of other colourless organic compounds. Semi-conductors photocatalysts i.e. ZnO or TiO$_2$ generally absorb different colour light depending on band-gap energy. The absorbance was measured at 410 nm to monitor the changes in the characteristic brown colour of the wastewater. The wavelength lies in the visible region of the electromagnetic spectrum.

### 4.4.2 Optimization of ideal reaction time

Figure 4.3 below shows the optimization of reaction conditions to determine optimum UV/ZnO irradiation reaction time.

![Optimization of reaction time](image)

**Figure 4.3** optimization of reaction time – UV/TiO$_2$ treatment of KBH sample

To determine the optimum reaction time required to treat wastewater, an experiment was done for 5 hours using KBH sample and a UV/TiO$_2$ treatment system. It was observed that after 3 hours of treatment, there was very little change in sample decolourization. In all the subsequent treatment experiments, the reaction time was set as 180 minutes for all UV/Solar light mediated reactions.
4.4.3 Photocatalytic treatment - UV /ZnO

Figure 4.4 below represents the results of photocatalytic treatment of CBH, KBH and NBH samples by UV light /ZnO treatment system.

Figure 4.4: UV/ZnO photocatalytic treatment of KBH, CBH and NBH wastewater

The findings indicate that the treatment of the wastewater using ZnO/UV light system proved very effective. The results indicate that after 1 hour of treatment 64.9% of CBH, 55.5% of NBH and 52.4% of KBH colour had been degraded. After 3 hours of treatment an average of 80% of the persistent colour had been degraded from all the 3 samples. This results suggest that the coexistence of a suitable semi-conductor and light exposure is necessary for photocatalytic degradation of tea processing wastewater.
4.4.4 Photocatalytic treatment - solar/ZnO

The results in Figure 4.5 show the results obtained after KBH, CBH and NBH wastewater samples were treated using solar/ZnO treatment system.

![Graph showing % decolourization over irradiation time](image)

Figure 4.5: Solar/ZnO photocatalytic treatment of KBH, CBH and NBH wastewater

The findings indicate that after 1 hour, 65.5% of CBH, 62.7% of NBH and 55.4% of KBH colour had been removed. After 3 hrs. 87% of CBH, 84.2% of NBH and 78.7% of KBH colour had been degraded. From fig.4.5 the efficiency of colour removal was higher in CBH and least in KBH. ZnO absorbed visible light in addition to UV light results also indicate that solar light provided a viable source of energy to decolourize tea processing wastewater in the presence of ZnO.
4.4.5 Comparison of photocatalytic treatment efficiency between ZnO/ UV radiation/Solar

The findings shown in Figure 4.6, 4.7 and 4.8 relates Solar/ZnO and UV/ZnO wastewater treatment system to determine the effect of UV/Solar light source on photocatalytic treatment.

4.4.5.1 Comparison of UV/solar/ ZnO treatment system - KBH

Fig. 4.6 below represents results obtained between Solar/ZnO and UV/ZnO treatment system of KBH wastewater.

![Graph of decolourization vs irradiation time](image)

**Figure 4.6:** Solar/ZnO and UV/ZnO photocatalytic treatment system of KBH wastewater

After 1 hour of photocatalytic treatment 55.4% of solar/ZnO and 52.4% of UV/ZnO decolourization was achieved. After 3 hours of treatment 78.7% of solar/ZnO and 77.5% of UV/ZnO decolourization was achieved. The results were achieved despite the irradiation flux intensity for solar light (I=1.49 mW/cm²) and UV lamp (I=3.0 mW/cm²). These results were observed despite the UV irradiation from solar light being almost 50% lower than UV light. ZnO was determined as an effective photocatalyst that absorbed solar
light irradiation in addition to UV light. Solar light irradiation is a reliable and cost-effective because of its abundance.

4.4.5.2 Comparison of UV/solar/ ZnO treatment system – CBH

Figure 4.7 below represents findings obtained between Solar/ZnO and UV/ZnO treatment system of CBH wastewater.

![Graph showing decolorization of CBH wastewater with Solar/ZnO and UV/ZnO treatments over time.](image)

Figure 4.7: Solar/ZnO and UV/ZnO photocatalytic treatment system of CBH wastewater

After 1 hour of photocatalytic treatment 65.5% of solar/ZnO and UV/ZnO decolorization was achieved. After 3 hours of treatment 78.7% of solar/ZnO and 77.5% of UV/ZnO decolorization was achieved. The results were achieved despite the irradiation flux intensity for solar light being (I=1.49 mW/cm²) and UV lamp (I= 3.0 mW/cm²). These results were observed despite the UV irradiation from solar light being almost 50% lower than UV light. ZnO absorbed a wider range of light spectrum irradiation and is more applicable for solar mediated photocatalytic treatment. ZnO showed high electron mobility.
4.4.5.3 Comparison of UV/solar/ ZnO treatment system - NBH

Figure 4.8 below shows the results obtained between Solar/ZnO and UV/ZnO treatment system of NBH wastewater.

Figure 4.8: Solar/ZnO and UV/ZnO photocatalytic treatment system of NBH wastewater

After 1 hour of photocatalytic treatment 62.7% of solar/ZnO and 55.6% of UV/ZnO decolourization was achieved. After 3 hours of treatment 84.2% of solar/ZnO and 81.0% of UV/ZnO decolourization was achieved. The results were achieved despite the irradiation flux intensity for solar light being \( I = 1.49 \text{ mW/cm}^2 \) and UV lamp \( I = 3.0 \text{ mW/cm}^2 \). These results were observed despite the UV irradiation from solar light being almost 50% lower than UV light. ZnO was determined as an effective photocatalyst that absorbed solar light irradiation in addition to UV light. Solar light irradiation is a reliable and cost-effective because of its abundance. Solar light also provided a good source of energy to degrade tea processing wastewater in the presence of ZnO.
4.4.6 Photocatalytic treatment - UV/TiO$_2$

Figure 4.9 below represents the results of photocatalytic treatment of CBH, KBH and NBH samples by UV light /TiO$_2$ treatment system.

![Graph showing % decolourization vs. Irradiation time for KBH, CBH, and NBH samples treated with UV/TiO$_2$.]

Figure 4.9: UV/TiO$_2$ photocatalytic treatment of KBH, CBH and NBH wastewater

The findings indicate that the treatment of the wastewater using ZnO/ artificial UV light system proved very effective. The results indicate that after 1 hour of treatment 60.03% of CBH, 52.4% of NBH and 50.6% of KBH colour had been degraded. After 3 hours of treatment an average of 73.3% of the persistent colour had been degraded from all the 3 samples. This results suggest that the coexistence of a suitable semi-conductor and light exposure is necessary for photocatalytic degradation of tea processing wastewater. The investigations indicate that the coexistence of TiO$_2$ photocatalyst and light exposure is necessary for the decolourization of tea processing wastewater.
4.4.7 Photocatalytic treatment - Solar/TiO₂

Figure 4.10 below represents the results of photocatalytic treatment of CBH, KBH and NBH samples by solar /TiO₂ treatment system.

![Graph showing decolorization efficiency over irradiation time for CBH+Solar+TiO₂, KBH+Solar+TiO₂, and NBH+Solar+TiO₂ samples.]

Figure 4.10: Solar/TiO₂ photocatalytic treatment of KBH, CBH and NBH wastewater

The findings indicate that after 1 hour, 65.4% of CBH, 58.3% of NBH and 55.6% of KBH colour had been removed. From fig.4.3 the efficiency of colour removal was higher in CBH and least in KBH. After 3 hours of treatment, an average of 75.6% of decolourization was achieved. The results indicate that solar light provided a viable source of energy to decolourize tea processing wastewater mediated by TiO₂. The findings indicate that solar irradiation could be used as a substitute cost effective light source because of its abundance.
4.4.8 Comparisons - photocatalytic treatment system (UV-Solar /TiO$_2$)

The results shown in Figure 4.11, 4.12 and 4.13 relates the Solar/TiO$_2$ and UV/TiO$_2$ wastewater treatment systems to determine the effect of UV/Solar light source on photocatalytic treatment.

4.4.8.1 Comparison - UV/solar/ TiO$_2$ treatment system - KBH

Figure 4.11 below represents results obtained between Solar/TiO$_2$ and UV/TiO$_2$ treatment system of KBH wastewater.

![Graph showing decolorization over time for KBH+UV lamp+TiO$_2$ and KBH+Solar+TiO$_2$ treatments.]

Figure 4.11: Solar/TiO$_2$ and UV/TiO$_2$ photocatalytic treatment system of KBH wastewater

After 1 hour of photocatalytic treatment 55.6% of solar/ZnO and 50.6% of UV/ZnO decolourization was achieved. After 3 hours of treatment 78.7% of solar/ZnO and 77.5% of UV/ZnO decolourization was achieved. The results were achieved despite the irradiation flux intensity for solar light being $I=1.49$ mW/cm$^2$ and UV lamp= 3.0 mW/cm$^2$. These results were observed despite the UV irradiation from solar light being almost 50% lower than UV light. Solar light irradiation is a reliable and cost-effective because of its abundance.
4.4.8.2 Comparison of UV/solar/ TiO\textsubscript{2} treatment system - CBH

Figure 4.12 below represents findings obtained between Solar/TiO\textsubscript{2} and UV/TiO\textsubscript{2} treatment system of CBH wastewater.

![Graph showing decolourization over irradiation time for CBH+UV lamp+TiO\textsubscript{2} and CBH+Solar+TiO\textsubscript{2}](image)

Figure 4.12: Solar/TiO\textsubscript{2} and UV/TiO\textsubscript{2} photocatalytic treatment system of CBH wastewater

The findings show that after 1 hour of photocatalytic treatment, 65.4\% decolourization was achieved for solar/TiO\textsubscript{2} and 60.1\% for UV/TiO\textsubscript{2} treatment systems. After 3 hours of treatment 78.7\% of solar/TiO\textsubscript{2} and 77.5\% of UV/TiO\textsubscript{2} decolourization was achieved. The results were achieved despite the irradiation flux intensity for solar light being I=1.49 mW/cm\textsuperscript{2} and UV lamp= 3.0 mW/cm\textsuperscript{2}. These results were observed despite the UV irradiation from solar light being almost 50\% lower than UV light.
4.4.8.3 Comparison of UV/solar/ TiO$_2$ treatment system - NBH

Figure 4.13 below shows the results obtained between Solar/TiO$_2$ and UV/TiO$_2$ treatment system of NBH wastewater.

![Graph showing decolourization vs irradiation time for NBH+UV lamp+TiO$_2$ and NBH+Solar+TiO$_2$](image_url)

Figure 4.13: Solar/TiO$_2$ and UV/TiO$_2$ photocatalytic treatment system of NBH wastewater

After 1 hour of photocatalytic treatment 58.3% of solar/ZnO and 52.5% of UV/ZnO decolourization was achieved. After 3 hours of treatment 84.2% of solar/ZnO and 81.0% of UV/ZnO decolourization was achieved. The results were achieved despite the irradiation flux intensity for solar light being $I=1.49$ mW/cm$^2$ and UV lamp= 3.0 mW/cm$^2$. These results were observed despite the UV irradiation from solar light being almost 50% lower than UV light. Solar light irradiation is a reliable and cost-effective because of its abundance and provided a good source of energy to degrade tea processing wastewater in the presence of TiO$_2$. 

80
4.5 Physico-chemical characterization - Treated wastewater

The physico-chemical characteristics of treated wastewater are indicated in Table 4.3 below.

Table 4.3 Physico-chemical characterization – treated wastewater

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>TOC [mg/l]</th>
<th>COD [mg/l]</th>
<th>TSS [mg/l]</th>
<th>TDS [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBH</td>
<td>6.8</td>
<td>34.8±0.37</td>
<td>48.8±0.71</td>
<td>224.27±0.78</td>
<td>129±0.13</td>
<td>785.4±0.6</td>
</tr>
<tr>
<td>KBH</td>
<td>6.6</td>
<td>35.6±0.44</td>
<td>63.7±0.16</td>
<td>239.29±0.23</td>
<td>132±0.39</td>
<td>801.6±0.2</td>
</tr>
<tr>
<td>NBH</td>
<td>6.7</td>
<td>35.2±0.24</td>
<td>51.3±0.39</td>
<td>226.96±0.57</td>
<td>130±0.08</td>
<td>788.7±0.09</td>
</tr>
</tbody>
</table>

The physico-chemical characterization of treated wastewater is discussed in sections (4.5.1 - 4.5.6) below.

4.5.1 pH

Table 4.3 above shows that photocatalytic treatment of wastewater led to a shift in pH from acidity to neutrality. Table 4.1 showed the pH of untreated wastewater samples which was measured as; (CBH=6.1, KBH=5.6 and NBH=5.9). After 180 minutes of treatment, the readings were as follows; (CBH=6.8, KBH=6.6, NBH=6.7). This corresponds to the following (%) change; (CBH=10.29%, KBH=15.15% and NBH=11.94% respectively. The average shift in pH for the 3 samples was measured at 12.46%. The greatest shift was measured in KBH sample at 15.15%.

4.5.2 Turbidity

Table 4.3 shows that photocatalytic treatment resulted in significant turbidity reduction for the 3 samples. Table 4.1 shows the turbidity of untreated wastewater measured as; (CBH=62.3 NTU, KBH=65.9 NTU and NBH=64.0 NTU).

Photocatalytic treatment resulted in significant reductions in turbidity levels which were measured as; (CBH=34.8 NTU, KBH=35.6 NTU, NBH=35.2 NTU). This shift corresponded to the following shift (%); (CBH=44.14%, KBH=45.97% and NBH=45.0%). The average shift for the 3 samples was determined at 45.03%. The greatest shift was measured in KBH sample at 45.97%.
4.5.3  **Total Organic Compounds (TOC)**

In Table 4.3 above shows that photocatalytic treatment resulted in the TOC of the 3 samples reducing significantly. The TOC of untreated wastewater was shown in Table 4.1 as follows; (CBH=210 mg/L, KBH=236 mg/L and NBH= 213 mg/L). The TOC readings for treated wastewater samples were shown as; (CBH=48.78 mg/L, KBH=63.7 mg/L, NBH=51.26 mg/L). This corresponded to the following shift as follows; (CBH=76.77%, KBH= 73.1% and NBH= 75.93% shift in TOC respectively. The average TOC shift for the 3 samples was 75.27%. The greatest shift was measured in CBH sample at 76.77%.

4.5.4  **Chemical Oxygen Demand (COD)**

From Table 4.3 the results show that photocatalytic treatment lowered COD significantly. Table 4.1 showed COD measurements of untreated wastewater as follows; (CBH=547.34 mg/L, KBH= 562.31 mg/L and NBH= 553.06 mg/L). The change in COD after photocatalytic treatment in Table 4.3 was measured as follows; (CBH= 224.27 mg/L, KBH= 239.29 mg/L, NBH= 226.96 mg/L). This represented; (CBH= 59.02%, KBH= 57.45% and NBH= 58.96% respectively. The average COD shift for the 3 samples was measured at 58.48% and the greatest shift was measured in sample CBH at 59.02%.

4.5.5  **Total Suspended Solids (TSS)**

Table 4.3 shows that photocatalytic treatment lowered TSS for the 3 samples. Table 4.1 showed the TSS for untreated wastewater as follows; (CBH=312 mg/L, KBH= 327 mg/L and NBH= 319 mg/L). The shift in TSS after photocatalytic treatment was represented in Table 4.3 as follows; (CBH= 129.09 mg/L, KBH= 132.28 mg/L, NBH= 130.54 mg/L). This shift was determined as; (CBH= 58.63%, KBH= 59.54% and NBH= 59.07 %). The average shift for the 3 samples was measured at 59.08%. The greatest shift was measured in sample CBH at 59.54%.
4.5.6 Total Dissolved Solids (TDS)

From Table 4.3 the results show that photocatalytic treatment lowered TSS of the 3 samples. Table 4.1 showed TSS measurements for untreated wastewater as follows; (CBH=1326.37 mg/L, KBH= 1368.52 mg/L and NBH= 1338.13 mg/L). Changes in TSS for the 3 samples after photocatalytic treatment was has been reported in Table 4.3 as follows; (CBH= 785.36, KBH= 801.56, NBH= 788.69). This change represented the following shift; (CBH= 40.79%, KBH= 41.43% and NBH= 41.1 %). The average shift for the 3 samples was measured at 40.12% and the greatest shift measured in sample KBH at 41.43%.

4.6 Characterization of TiO$_2$ and ZnO - Surface morphology

4.6.1 Laser Induced Breakdown Spectroscopy (LIBS)

4.6.1.1 TiO$_2$

The elemental composition of TiO$_2$ using LIBS at pulse energy (100 MJ) is shown in Figure 4.14 below.

Figure 4.14. LIBS spectra for TiO$_2$
Fig. 4.14 indicates the LIBS spectra for TiO$_2$ (99.5% - purity; 100MJ - pulse energy). The LIBS spectrum depicted was recorded in the 350 nm - 500 nm wavelength spectral range. Pronounced peaks were recorded indicating the following elements; (Ti=375 nm, 400 nm, 463 nm); (O= 407 nm, 444 nm, 465 nm, 469 nm); (Fe= 480 nm). Detection at this wavelengths signaled their elemental signature. This wavelength is within the active UV/Vis light range of 200 nm - 800 nm. Spectra measured at various pulse energies (70 MJ, 80 MJ and 90 MJ) are recorded in the appendix section.

4.6.1.2 ZnO

The LIBS spectra shown in Figure 4.15 analyses ZnO to determine its elemental composition at pulse energy - (100 MJ).

![LIBS spectrum - ZnO](image)

Figure 4.15: LIBS spectrum - ZnO

Fig. 4.15 indicates the libs spectra for TiO$_2$ (99.5% purity). The LIBS spectrum depicted was recorded in the 350 nm–500 nm wavelength spectral range. Pronounced peaks were recorded indicating the following elements ; (Zn= 370 nm, 375 nm, 400 nm, 440 nm, 444 nm and 454 nm) ; (O= 353 nm, 417 nm); (Na= 446 nm); (Ca= 407 nm, 434 nm); (Si= 460, 470 nm). Detection at this wavelengths signaled their elemental signature. This wavelength is within the active UV/Vis light range of 200 nm - 800 nm. Spectra measured at various pulse energies (70 MJ, 80 MJ and 90 MJ) are recorded in the appendix section.
4.6.2 Energy Dispersive X-ray Spectroscopy (EDS)

4.6.2.1 ZnO

Analysis of ZnO by EDS to determine its elemental composition (wt. %) is represented in Figure 4.16 below.

![EDS spectrum - ZnO](image)

Figure 4.16  EDS spectrum - ZnO

The EDS spectrum indicates the presence of five peaks which were identified as zinc, oxygen, sodium, silicon and calcium. The most prevalent element was Zn- 61.5 wt.% , O -21.4 wt.%, Na – 16.3 wt.%, Si – 0.5 wt.% and Ca – 0.3 wt.%.

In Table 4.4 below, the elemental composition of ZnO is indicated.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Experimental results (Atomic wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>61.5</td>
</tr>
<tr>
<td>O</td>
<td>21.4</td>
</tr>
<tr>
<td>Na</td>
<td>16.3</td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca</td>
<td>0.3</td>
</tr>
</tbody>
</table>
4.6.2.2 (TiO$_2$)

Analysis of ZnO by EDS to determine its elemental composition (wt. %) is represented in Figure 4.17 below.

![EDS spectrum - TiO$_2$](image)

EDS spectrum indicates two peaks which were identified as Ti – 60 wt. % and O – 40 wt. %.

In Table 4.5 below, the elemental composition of TiO$_2$ is shown.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Experimental results (Atomic wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>60.0</td>
</tr>
<tr>
<td>O</td>
<td>40.0</td>
</tr>
</tbody>
</table>
4.6.3 Scanning Electron Microscope (SEM)

4.6.3.1 TiO$_2$

Figure 4.18, 4.19, 4.20, 4.21, 4.22, 4.23, 4.24 and 4.25 show SEM images of TiO$_2$ powders used in this study. The images represent TiO$_2$ surface morphology and particle size. The catalyst particle size and morphology affects its photocatalytic efficiency. A crystalline structure promotes photocatalytic activity. The amount of the surface-adsorbed water and hydroxyl groups is related to the crystallite form and surface area. Particle size is an important parameter for photocatalytic efficiency, since the predominant way of electron/hole recombination may be different depending on the particle size.

Figure 4.18: TiO$_2$ (500μm- WD 15.01 mm)

Figure 4.19: TiO$_2$ 100μm (WD 15.01 mm)

Figure 4.20: TiO$_2$ (5 μm–WD 15.10 mm)

Figure 4.21: TiO$_2$ (5μm- WD 15.07 mm)
The SEM images show that individual particle sizes to be approximately 16 nm and spherical in shape. This particle size observed is similar to the figure calculated from X-Ray Diffraction measurements in section 4.6.4.1.

The significance of particle size is significant because smaller sizes promote the recombination of photogenerated electrons and holes in the powder catalysts, leading to poor photocatalytic activity. This is observed because smaller particle size reduces the time needed for the carrier gas diffusing out of the photocatalyst pores to the photocatalysts surface.

4.6.3.2 ZnO

Figure 4.26, 4.27, 4.28, 4.29, 4.30, 4.31, 4.32 and 4.33 show SEM images of ZnO powder as used in the study. The images were characterized to determine particle size and morphology which affects its photocatalytic efficiency. A large surface area can be determining factor in certain photodegradation reactions, as a large amount of adsorbed molecules promotes the reaction rate.
From the SEM images, the particle size were estimated to be approximately 16 nm and hexagonal shape. This value is very close to the figure calculated from X-Ray Diffraction measurements in section 4.6.4.2.
The SEM images show that ZnO has an open porous structure that improves photocatalytic activity by providing adsorption sites for organic molecules on catalyst surface during photocatalytic treatment.

4.6.4 X-Ray Diffractometry (XRD)

4.6.4.1 TiO₂

Figure 4.34 shows an XRD analysis of TiO₂ to determine its crystallinity and particle size.

![XRD Diagram](image)

Figure 4.34: X-ray Diffraction patterns - TiO₂

The average crystallite size of TiO₂ was obtained from the most intense diffraction peak of anatase TiO₂ at 25.28°. The crystallite size was calculated at 16 nm.

Figure 4.34 shows a series of diffraction peaks at 2θ=25.28° (101), 37.69° (104, 112), 47.88° (200), 55.20° (105, 211), 62.28° (204, 211), 69.32° (116) and 74.54° (215).

From the XRD spectra in Figure 4.34 the crystal structure of TiO₂ has been revealed as amorphous. This provides more of active sites with high specific surface photoactivity.
Small variations in particle diameters often leads to great modifications in the surface/bulk ratio, thus modifying the significance of volume and surface electron-hole recombination.

### 4.6.4.2 ZnO

Figure 4.35 shows an XRD analysis of ZnO to determine its crystallinity and particle size.

![X-ray Diffraction patterns - ZnO](image)

The average crystallite size of ZnO was obtained from the most intense diffraction peak of ZnO at 36.20° (84539).

The crystallite size was calculated at 16.21 nm. Fig.4.35 shows a series of diffraction peaks at 2θ= 31.74° (46467), 34.38° (39405), 36.20° (84539), 47.52° (17962), 56.54°(26625), 62.8° (23470), 67.93° (19051) and 69.06° (9272).

The sharp and intense peaks seen in Fig. 4.35 indicate high crystallinity in ZnO which affected its electronic and photocatalytic properties. It can absorb wider range of spectrum of radiation. When the crystallite dimension of a semiconductor particle falls below a
critical radius of approximately 10 nm, the charge carriers appear to behave quantum mechanically. It is well known that in the nanometer-size range, physical and chemical properties of particles including semiconductors are modified compared with bulk. Increased crystallinity leads to better catalyst photocatalytic activity.

4.6.5 Brunauer Emmett Teller (BET) – surface area analysis

In Table 4.6 below, the surface area measurements for ZnO and TiO₂ are indicated.

**Table 4.6: surface area measurements - ZnO and TiO₂**

<table>
<thead>
<tr>
<th>Powder photocatalyst</th>
<th>Surface area Uncalcined (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>31.76</td>
</tr>
<tr>
<td>ZnO</td>
<td>40.14</td>
</tr>
</tbody>
</table>

The results from Table 4.6 indicates that the surface area for TiO₂ and ZnO was 31.76 m²/g and 40.14 m²/g. The results in this work show that treatment by Solar/Ultraviolet/ZnO system, indicated a 9.7% greater efficiency compared to Solar/Ultraviolet/TiO₂ system. This results indicate that ZnO is a better catalyst because of its morphology and increased surface area. The combination of surface area and particle size are important determining factors in photocatalytic treatment reactions because large surface areas lead to effective contact with organic pollutant molecules and this promotes higher reaction rates because more active sites are available for reactions to take place. Despite smaller crystals having larger inner surface areas, smaller catalyst particles can also promote the recombination of photogenerated electrons and holes, which in turn leads to poor photoactivity. A balance between surface area and particle size must be found in order to find the optimum photocatalytic activity.
CHAPTER FIVE

5 Conclusions and Recommendations

5.1 Conclusions

Nandi is one of the tea growing Counties in Kenya, in addition to being a catchment area for rivers flowing into Lake Victoria. Wastewater from 3 black tea processing factories that include Chebut (CBH), Kibwari (KBH), and Nandi (NBH) were investigated, out of a total of 19 factories located in Nandi County. The annual processing capacities of black tea in the 3 factories was found to be CBH= 20 million kgs, KBH= 4 million kgs and NBH= 6 million kgs. This corresponds to CBH=11.142 m$^3$, KBH= 3.342 m$^3$ and NBH=2.228 m$^3$ respectively of wastewater. This data indicates production per annum, on average 1 kg of tea subsequently generates 0.557 litres of wastewater.

A total of 16 wastewater samples were collected from each individual factory, making a total of 48 samples over a period of 6 months. The samples were characterized by their physico-chemical parameters, macro-molecules and heavy metals. The results show that, CBH (pH= 6.1, Turbidity= 62.3 N.T.U, Total Organic Carbon= 201 mgL$^{-1}$, Chemical Oxygen Demand= 547.34 mgL$^{-1}$, Total Suspended Solids =312 mgL$^{-1}$; Total Dissolved Solids= 1326.37 mgL$^{-1}$, Total metals; Fe=1.63 mgL$^{-1}$, Mn=1.62 mgL$^{-1}$, Al=10.67 mgL$^{-1}$ and Ni=0.35 mgL$^{-1}$). KBH (pH= 5.6, Turbidity= 65.9 N.T.U, Total Organic Carbon= 236 mgL$^{-1}$, Chemical Oxygen Demand= 562.31 mgL$^{-1}$, Total Suspended Solids =327 mgL$^{-1}$; Total Dissolved Solids= 1368.52 mgL$^{-1}$), Metals Fe=1.39 mgL$^{-1}$, Mn=1.63 mgL$^{-1}$, Al= 7.44 mgL$^{-1}$ and Ni=0.26 mgL$^{-1}$). NBH (pH=5.9 Turbidity= 64.0 N.T.U, Total Organic Carbon= 213.0 mgL$^{-1}$, Chemical Oxygen Demand= 553.06 mgL$^{-1}$, Total Suspended Solids =319 mgL$^{-1}$; Total Dissolved Solids= 1338.13 mgL$^{-1}$) Fe= 1.35 mgL$^{-1}$, Mn=0.26 mgL$^{-1}$, Al=18.89 mgL$^{-1}$ and Ni= 0.35 mg/L$^{-1}$.

The wastewater samples were spectrophotometrically analysed to determine the wavelength of absorption for the 3 samples, CBH, KBH and NBH. The absorption wavelength was determined at $\lambda$= 410 nm.

Two powders used in photocatalytic treatment and colour removal; TiO$_2$ and ZnO were characterized by Laser Induced Breaking down spectroscopy (LIBS), Brunauer Emmett
Teller (BET), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), Laser Induced Breaking Down Spectroscopy (LIBS) and X-Ray Diffraction (XRD). The obtained values were; (TiO\textsubscript{2} = Laser Induced Breakdown Spectroscopy, indicating Ti spectral peak at $\lambda = 400$ nm, Brunauer Emmett Teller surface area of TiO\textsubscript{2} -31.76 m\textsuperscript{2}/g, X-Ray Diffraction and Scanning Electron Microscope showed particle sizes of TiO\textsubscript{2} (16 nm ± 2 nm) and Spherical morphology, Energy Dispersive X-ray Spectroscopy indicated the degree of Titanium (Ti) in TiO\textsubscript{2} as 60%. (ZnO=Laser Induced Breakdown Spectroscopy indicating Zn spectral peaks at $\lambda = 400$ nm, Brunauer Emmett Teller surface area of ZnO 40.14 m\textsuperscript{2}/g, X-Ray Diffraction and Scanning Electron Microscope analysis showed particle sizes of ZnO = (16.21 nm ± 2 nm) and hexagonal morphological shape. Energy Dispersive X-ray Spectroscopy indicated the degree of zinc (Zn) in ZnO as 61.5%.

A prototype batch photocatalytic reactor of dimensions (20 cm×15 cm×10 cm) constructed from borosilicate glass was placed onto a magnetic stirrer and illuminated with either UV lamps ( $I=3.0$ mW/cm\textsuperscript{2}) or solar light (I= 1.49 mW/cm\textsuperscript{2}).

Physico-chemical parameters of treated wastewater indicated; (CBH pH= 6.8, Turbidity= 34.8 N.T.U, Total Organic Carbon= 48.78 mg/l, Chemical Oxygen Demand= 224.27 mg/l, Total Suspended Solids = 129.09 mg/l; Total Dissolved Solids=785.36mg/l); (KBH - pH= 6.6, Turbidity= 35.6 N.T.U, Total Organic Carbon= 63.7 mg/l, Chemical Oxygen Demand= 239.29 mg/l, Total Suspended Solids = 132.28 mg/l; Total Dissolved Solids= 801.56 mg/l); (NBH - pH= 6.7, Turbidity= 35.2 N.T.U, Total Organic Carbon= 51.26 mg/l, Chemical Oxygen Demand= 226.96 mg/l, Total Suspended Solids = 130.54 mg/l; Total Dissolved Solids= 788.69 mg/l).

The photocatalytic treatment was found to minimize, Total Organic Carbon, Chemical Oxygen Demand, Turbidity, Total Suspended Solids and Total Dissolved Solids by 74.8 %, 58.5 %, 45.1 %, 59.07 % and 41.53 % respectively, and shifted pH from acidity to neutrality by 12.5 % from 5.6 to 6.8 after 180 minutes. A GC-MS analysis of untreated wastewater samples indicated the presence of organic macromolecules that were identifiable and quantifiable. The number of molecules were as follows; (CBH= 9, KBH=14 and NBH= 12) respectively.
Photocatalytic treatment led to the following results; (TiO$_2$/UV lamps - CBH = 76.22%, KBH = 70.32% and NBH = 73.27%); ZnO/UV lamp - CBH = 82.05%, KBH = 77.5% and NBH = 80.73%); (TiO$_2$/solar - CBH = 78.47%, KBH = 72.25% and NBH = 76.05%); (ZnO/solar - CBH = 87.0%, KBH = 78.67% and NBH = 84.18%).

A UV/TiO$_2$ treatment system achieved an efficiency of 73.27% colour removal in 180 min compared to a solar/TiO$_2$ treatment system where, 75.59% of colour was eliminated. In addition a ZnO/UV lamp system achieved 80.09% colour removal efficiency in 180 min compared to 83.2% colour removal in a ZnO/solar light system.

The solar/TiO$_2$ treatment system, proved efficient compared to UV/TiO$_2$ by 2.3% and the solar/ZnO treatment system, proved more efficient compared to UV/ZnO treatment system by 3%, despite the solar radiation intensity ($I=1.49$ mW/cm$^2$) applied, being less than half that of UV lamp ($I=3.0$ mW/cm$^2$). From the results solar light provided an efficient supply of UV photons to drive the photocatalytic treatment reactions.

The UV/ZnO treatment system, was found to be more efficient, compared to UV/TiO$_2$ by 6.8% and ZnO/solar light treatment system, more efficient compared to solar/TiO$_2$ by 7.6%. ZnO is therefore a more effective photocatalyst compared to TiO$_2$. The experimental results indicate that for the effective treatment and colour removal of tea processing wastewater, a Solar/ZnO photocatalyst prototype would be effective.
5.2 Recommendations

- A large scale continuous flow photocatalytic reactor based on ZnO/solar light system be piloted for large scale wastewater treatment.
- The role of visible light in solar mediated photocatalytic treatment be investigated in relation to the 5% UV light present.
- Focus for the development of more reliable photocatalysts which can absorb visible and solar radiation or both.
REFERENCES


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APPENDICES

Appendix I

GC-MS analysis – KBH Sample

Appendix 1 Chromatogram – KBH sample
Appendix 2

(2-Butanone, 4-(2, 6, 6-trimethyl-1-yl)-)
Appendix 3

1-\{2-[3-(2-Acetyloxiran-2-yl)-1, 1-dimethylpropyl] cycloprop-2-enyl\} ethanone
Appendix 4  Tetradecanoic acid
Appendix 5  Acetic acid
Appendix 6

3, 7, 11, 15-Tetramethyl-2-hexadecen-1-ol
Appendix 8  (n-Hexadecanoic acid)
Appendix 10

9, 12, 15-Octadecatrienoic acid
Appendix 12  Ethyl iso-allocholate
Appendix 13

1, 2-Benzenedicarboylic acid
Appendix 14

2, 6, 10, 14, 18, 22-Tetracosahexane, 2, 6, 10, 15, 23-hexamethyl-

[Diagram of molecular structure]

Name: 2, 6, 10, 14, 18, 22-Tetracosahexane, 2, 6, 10, 15, 23-hexamethyl-, (all-E)-

Mw: 410 CAS#: 111-02-4 NIST#: 290752 DE#: 30560 DG: mainlib

10 Long Period Peaks:
52 2698 | 85 844 | 41 284 | 98 155 | 89 134 | 121 121 | 137 121 | 135 116 | 53 106 | 67 107 |

[Other diagrams and data]

Page 1 of 2
Appendix II

GC-MS analysis – CBH sample

Appendix 15 Chromatogram – CBH sample
Appendix 16  7-(1,3-Dimethylbuta-1,3-dienyl)-1,6,6-trimethyl-3,8-dioxatricyclo[5,1,0,0(2,4)]octane
Appendix 17

Acetic acid
Appendix 19

n-Hexadecanoic acid
Appendix 21

9, 12, 15-octadecatrienoic acid
Appendix III

GC-MS analysis – NBH sample

Appendix 25 Chromatogram – sample NBH
Appendix 26

1-Heptatriacotanol

![Graph of 1-Heptatriacotanol]

**1-Heptatriacotanol**

**CAS:** 10570458-60-1

**Molecular Formula:** C37H78O2

**Molecular Weight:** 550.14

**Density:** 0.94

**Boiling Point:** 327.2°C

**Melting Point:** 81.5°C

**Molar Refractivity:** 8853.7

**Heat of Formation:** 67.7 kcal/mol

**Heat of Combustion:** 66.5 kcal/mol

**Heat of Vaporization:** 92.2 kcal/mol

**Heat of Sublimation:** 91.4 kcal/mol

**Unknown; m/z 324**

![Graph of Unknown; m/z 324]

**Average of 0.092 to 0.067 min.: 2011-05-19 07:00:00**

**Molar Refractivity:** 8853.7

**Molar Refraction:** 8853.7

**Heat of Combustion:** 83.3 kcal/mol

**Heat of Sublimation:** 81.3 kcal/mol

**Heat of Vaporization:** 80.3 kcal/mol

**Heat of Formation:** 95.3 kcal/mol

**Heat of Vaporization:** 93.3 kcal/mol

**Heat of Combustion:** 90.3 kcal/mol

**Heat of Sublimation:** 89.3 kcal/mol

**Heat of Formation:** 88.3 kcal/mol

**Heat of Vaporization:** 87.3 kcal/mol

**Heat of Sublimation:** 86.3 kcal/mol

**Heat of Combustion:** 85.3 kcal/mol

**Heat of Sublimation:** 84.3 kcal/mol

**Heat of Formation:** 83.3 kcal/mol

**Heat of Vaporization:** 82.3 kcal/mol

**Heat of Sublimation:** 81.3 kcal/mol

**Heat of Combustion:** 80.3 kcal/mol

**Heat of Sublimation:** 79.3 kcal/mol

**Heat of Formation:** 78.3 kcal/mol

**Heat of Vaporization:** 77.3 kcal/mol

**Heat of Sublimation:** 76.3 kcal/mol

**Heat of Formation:** 75.3 kcal/mol

**Heat of Vaporization:** 74.3 kcal/mol

**Heat of Sublimation:** 73.3 kcal/mol

**Heat of Formation:** 72.3 kcal/mol

**Heat of Vaporization:** 71.3 kcal/mol

**Heat of Sublimation:** 70.3 kcal/mol

**Heat of Formation:** 69.3 kcal/mol

**Heat of Vaporization:** 68.3 kcal/mol

**Heat of Sublimation:** 67.3 kcal/mol

**Heat of Formation:** 66.3 kcal/mol

**Heat of Vaporization:** 65.3 kcal/mol

**Heat of Sublimation:** 64.3 kcal/mol

**Heat of Formation:** 63.3 kcal/mol

**Heat of Vaporization:** 62.3 kcal/mol

**Heat of Sublimation:** 61.3 kcal/mol

**Heat of Formation:** 60.3 kcal/mol

**Heat of Vaporization:** 59.3 kcal/mol

**Heat of Sublimation:** 58.3 kcal/mol

**Heat of Formation:** 57.3 kcal/mol

**Heat of Vaporization:** 56.3 kcal/mol

**Heat of Sublimation:** 55.3 kcal/mol

**Heat of Formation:** 54.3 kcal/mol

**Heat of Vaporization:** 53.3 kcal/mol

**Heat of Sublimation:** 52.3 kcal/mol

**Heat of Formation:** 51.3 kcal/mol

**Heat of Vaporization:** 50.3 kcal/mol

**Heat of Sublimation:** 49.3 kcal/mol

**Heat of Formation:** 48.3 kcal/mol

**Heat of Vaporization:** 47.3 kcal/mol

**Heat of Sublimation:** 46.3 kcal/mol

**Heat of Formation:** 45.3 kcal/mol

**Heat of Vaporization:** 44.3 kcal/mol

**Heat of Sublimation:** 43.3 kcal/mol

**Heat of Formation:** 42.3 kcal/mol

**Heat of Vaporization:** 41.3 kcal/mol

**Heat of Sublimation:** 40.3 kcal/mol

**Heat of Formation:** 39.3 kcal/mol

**Heat of Vaporization:** 38.3 kcal/mol

**Heat of Sublimation:** 37.3 kcal/mol

**Heat of Formation:** 36.3 kcal/mol

**Heat of Vaporization:** 35.3 kcal/mol

**Heat of Sublimation:** 34.3 kcal/mol

**Heat of Formation:** 33.3 kcal/mol

**Heat of Vaporization:** 32.3 kcal/mol

**Heat of Sublimation:** 31.3 kcal/mol

**Heat of Formation:** 30.3 kcal/mol

**Heat of Vaporization:** 29.3 kcal/mol

**Heat of Sublimation:** 28.3 kcal/mol

**Heat of Formation:** 27.3 kcal/mol

**Heat of Vaporization:** 26.3 kcal/mol

**Heat of Sublimation:** 25.3 kcal/mol

**Heat of Formation:** 24.3 kcal/mol

**Heat of Vaporization:** 23.3 kcal/mol

**Heat of Sublimation:** 22.3 kcal/mol

**Heat of Formation:** 21.3 kcal/mol

**Heat of Vaporization:** 20.3 kcal/mol

**Heat of Sublimation:** 19.3 kcal/mol

**Heat of Formation:** 18.3 kcal/mol

**Heat of Vaporization:** 17.3 kcal/mol

**Heat of Sublimation:** 16.3 kcal/mol

**Heat of Formation:** 15.3 kcal/mol

**Heat of Vaporization:** 14.3 kcal/mol

**Heat of Sublimation:** 13.3 kcal/mol

**Heat of Formation:** 12.3 kcal/mol

**Heat of Vaporization:** 11.3 kcal/mol

**Heat of Sublimation:** 10.3 kcal/mol

**Heat of Formation:** 9.3 kcal/mol

**Heat of Vaporization:** 8.3 kcal/mol

**Heat of Sublimation:** 7.3 kcal/mol

**Heat of Formation:** 6.3 kcal/mol

**Heat of Vaporization:** 5.3 kcal/mol

**Heat of Sublimation:** 4.3 kcal/mol

**Heat of Formation:** 3.3 kcal/mol

**Heat of Vaporization:** 2.3 kcal/mol

**Heat of Sublimation:** 1.3 kcal/mol

**Heat of Formation:** 0.3 kcal/mol

**Heat of Vaporization:** 0.3 kcal/mol

**Heat of Sublimation:** 0.3 kcal/mol

**Heat of Formation:** 0.3 kcal/mol
Appendix 29  Phthalic acid
Appendix 30  Phytol

Name: Phytol
Formula: C₂₀H₄₀O
MW: 296  CAS: 150-90-7  NIST#: 105727  IUPAC: 6051 DD: no
Other Use: None

Phytol, Phytol, Phytol, Phytol, Phytol
15 largest peaks:
71 550  45 291  67 224  41 379  99 289  99 299  81 323  68 198  123 184  98 190

Page 2 of 2
Appendix 31

9, 12, 15-octadecatrienoic acid
Appendix 32

Octadecanoic acid

Name: Octadecanoic acid
Formula: C18H36O2
MW: 284 CAS#: 87-11-4 NIST: 219000 IDE: 5451 DB: emulif
10 largest peaks:
43,950 | 73,042 | 151,661 | 207,675 | 56,837 | 41,888 | 139,800 | 88,432 | 71,429 | 83,517

Page 2 of 2

Unknown: m/z=223

Name: Averages of 10.330 to 10.440 min.; 21MAY2017-57.D/1.txt ma
MW: N/A IDE: TEMA IDR: Test File
Comment: N/A
10 largest peaks:
88,888 | 73,051 | 57,755 | 60,714 | 50,620 | 294,593 | 129,549 | 71,492 | 67,473 | 83,639

Page 1 of 2
Appendix 33

\( \alpha \)-Amyrin

\[ \text{Formula: C}_{30}H_{50}O \]

\[ \text{MW: 450, CAS: 528-38-9, INN: RHO} \]

10 largest peaks:

\[
\begin{align*}
218 & \quad 996 \quad 44 \quad 331 \quad 219 \quad 190 \quad 43 \quad 157 \quad 55 \quad 154 \quad 363 \quad 148 \quad 69 \quad 137 \quad 436 \quad 138 \quad 188 \quad 130 \quad 193 \quad 118
\end{align*}
\]

Unknown; InLib=218

\[ \text{Average of 20.053 to 21.056 min., 21MAY2017-57.D ata.m s} \]

10 largest peaks:

\[
\begin{align*}
218 & \quad 996 \quad 203 \quad 473 \quad 86 \quad 228 \quad 69 \quad 197 \quad 96 \quad 189 \quad 210 \quad 187 \quad 81 \quad 175 \quad 57 \quad 155 \quad 70 \quad 146 \quad 67 \quad 139
\end{align*}
\]
Appendix 35

1, 2-Benzenedicarboxylic acid

[Chemical structure diagram]
Appendix 37

2, 2, 4-Trimethyl-heptadeca-3, 7, 11, 15-tetraenyl)-cyclohexanol
APPENDIX IV

LIBS Spectra (TiO$_2$)

Appendix 38  TiO$_2$ -pulse energy (70MJ)

Appendix 39  TiO$_2$-pulse energy (90MJ)
APPENDIX V

LIBS Spectra – (ZnO)

Appendix 41  ZnO-pulse energy (70MJ)