

University of Fort Hare

Faculty of Science and Agriculture

DEVELOPMENT OF A VISIBLE LIGHT ACTIVE, PHOTO-CATALYTIC, AND ANTIMICROBIAL NANOCOMPOSITE OF TITANIUM DIOXIDE AND SILICON DIOXIDE FOR WATER TREATMENT

By

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**A thesis submitted to the University of Fort Hare in fulfilment of the
requirements for the award of the degree of Master of Science in
Chemistry**

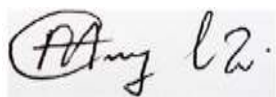


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Declaration

I declare that this thesis entitled “Development of a visible-light active, photo-catalytic, and antimicrobial Nano-composite of $\text{TiO}_2\text{-SiO}_2$ for water treatment,” is the result of my own research except as cited in the references. The study methodology has adopted the same procedure used by the research group as reported in Nyamukamba *et.al*, 2012. The dissertation has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.



Signature :

Name : HENRY HEROE MUNGONDORI.....

Date : 30-04-2012.....

Dedication

This work is dedicated to the Mungondori family and my fiancé Tawanda Mataruse for their unconditional love and support.

Acknowledgements

I thank the Lord for the gift of life and keeping me in good health throughout my studies.

I thank my supervisor Dr L. Tichagwa for her support and guidance. May the dear Lord bless her abundantly for her kindness.

I also thank Dr E. Green who assisted in the antimicrobial section of this project, I greatly appreciate his effort, and may the Lord bless him abundantly for his kindness.

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Abstract

The aim of this study was to prepare composite materials based on titanium dioxide (TiO_2) and silicon dioxide (SiO_2), and to evaluate their photo-catalytic and antimicrobial properties. Carbon and nitrogen doped TiO_2 nano-particles were prepared via a sol gel synthesis, which is a simple hydrolysis and condensation technique. In situ doping was carried out using glucose and urea as carbon and nitrogen sources respectively. Doping increased the spectral response of titanium dioxide photo-catalyst, allowing it to utilise the visible region which is much wider than the UV region (about 40 % of the solar spectrum), thus making it a more efficient photo-catalyst. The carbon and nitrogen doped TiO_2 - SiO_2 nano-particles were immobilized on glass support material to allow for easy separation of the spent photo-catalyst after the photo-degradation process. Tetraethyl orthosilicate (TEOS) was employed as both a binder and precursor for silicon dioxide. A mixture of TiO_2 and TEOS in a 1:1 ratio was allowed to polymerize on a glass support which had been treated with hydrofluoric acid to introduce OH groups. The prepared photo-catalytic material was characterized by FT-IR, XRD, DRS, TEM, EDX, and BET analyses.

Carbon was found to be more effective as a dopant than nitrogen. It brought about a band gap reduction of 0.30 eV and a BET surface area of $95.4 \text{ m}^2\text{g}^{-1}$ on the photo-catalyst as compared to a gap reduction of 0.2 eV and surface area of $52.2 \text{ m}^2\text{g}^{-1}$ for nitrogen doped TiO_2 . On the other hand, introduction of SiO_2 allowed utilization of visible light by the TiO_2 - SiO_2 nano-composite leading to an improved rate of photo-degradation of both methyl orange and phenol red. However, the immobilization of TiO_2 on support material made it less effective towards inactivation of *E. coli* ATCC 25922 bacterial cells when compared to powdered TiO_2 which was able to inactivate about 98 % of the bacterial cells within an hour of treatment.

Table of contents

Declaration	ii
Dedication	iii
Acknowledgements	iv
Abstract	v
Table of contents	vi
List of tables	ix
List of figures	x
List of abbreviations.....	xii
CHAPTER 1	1
1. Introduction	1
1.1 General background.....	1
1.2 Study introduction and motivation	2
1.3 Problem statement	5
1.4 Hypothesis	5
1.5 Aims and objectives.....	5
1.6 Scope of study	6
1.7 Dissertation outline.....	7
Bibliography	8
CHAPTER 2	10
2. Literature review	10
2.1 Photo-catalysis.....	10
2.2 Attributes of titanium dioxide.....	11
2.3 Mechanism of photo-catalysis and generation of oxidative species.....	12
2.4 Antimicrobial properties of TiO ₂	13
2.5 Contaminants that can be removed by TiO ₂	16

2.6 Methods of TiO ₂ synthesis	20
2.7 Modification of TiO ₂	22
2.8 Support material for titanium dioxide	27
Bibliography	30
CHAPTER 3	36
3. Experimental: Materials and general procedures	36
3.1 Introduction	36
3.2 Materials and chemical reagents.....	36
3.3 Characterization techniques.....	38
Bibliography	45
CHAPTER 4	47
4. Preparation and characterization of carbon or nitrogen doped titanium dioxide and its immobilization on glass support material	47
4.1 Introduction	47
4.2 Experimental.....	48
4.3 Characterization techniques.....	52
4.4 Results and discussion	54
Bibliography	71
CHAPTER 5	72
5. Evaluation of the photo-catalytic activity of carbon/ nitrogen doped TiO ₂ -SiO ₂ immobilized on glass substrate.....	72
5.1 Introduction	72
5.2 Photo-catalytic activity measurements	72
5.3 Results and discussion	75
Bibliography	84
CHAPTER 6	86

6. Evaluation of antimicrobial activity of carbon or nitrogen doped TiO ₂ -SiO ₂ immobilized on glass support.....	86
6.1 Introduction	86
6.2 Methodology.....	86
6.3 Results and discussion	88
Bibliography	92
CHAPTER 7	93
7. Conclusions and recommendations	93
7.1 Conclusions	93
7.2 Recommendations	95

List of tables

Table 1: Chemical names, formulae, molecular structures and molecular masses of reagents	37
Table 2: Scherrer particle sizes of prepared photo-catalysts determined from XRD analysis	57
Table 3: BET surface area analysis results for photo-catalysts	58
Table 4: Band gap energies of photo-catalysts	60
Table 5: Scherrer particle size of N-TiO ₂ , N-TiO ₂ -SiO ₂ , & TiO ₂ -SiO ₂	64
Table 6: BET surface area analysis results for nitrogen doped photo-catalyst.....	64
Table 7: Band gap energies of N-TiO ₂ , N-TiO ₂ -SiO ₂ , TiO ₂ -SiO ₂ & DP25 TiO ₂	67
Table 8: TEM particle sizes of TiO ₂ -SiO ₂ , C-TiO ₂ -SiO ₂ , & N-TiO ₂ -SiO ₂	69
Table 9: McFarland standards for visual/ spectrophotometric comparisons of bacterial densities in saline or liquid growth medium	87

List of figures

Figure 1.1: Cubic structure of titanium dioxide.....	1
Figure 2.1: Mechanism of photo-degradation of organic pollutants.....	13
Figure 2.2: Cross-section of <i>Escherichia coli</i> bacterium.....	18
Figure 2.3: Sol-gel processing options.....	22
Figure 2.4: Activation mechanism of TiO ₂ in the presence of silicon.....	26
Figure 3.1: Schematic diagram of DRS instrument.....	40
Figure 4.1: A schematic diagram to represent the Sol gel process using TiCl ₄ precursor.....	48
Figure 4.2: Programmable muffle furnace for calcination.....	50
Figure 4.3: Glass surface after the etching process.....	51
Figure 4.4: Polymerization of TiO ₂ with SiO ₂ on glass substrate	52
Figure 4.5: FT-IR spectra of C-TiO ₂ , C-TiO ₂ -SiO ₂ , and TiO ₂ -SiO ₂	55
Figure 4.6: XRD diffractograms of C-TiO ₂ , C-TiO ₂ -SiO ₂ & TiO ₂ -SiO ₂	56
Figure 4.7: DRS spectra & derivatives of C-TiO ₂ , C-TiO ₂ -SiO ₂ , TiO ₂ -SiO ₂ , & DP25 TiO ₂ -SiO ₂	59
Figure 4.8: FT-IR spectra of N-TiO ₂ , N-TiO ₂ -SiO ₂ , & TiO ₂ -SiO ₂	62
Figure 4.9: XRD diffractograms of N-TiO ₂ , N-TiO ₂ -SiO ₂ & TiO ₂ -SiO ₂	63
Figure 4.10: DRS spectra of N-TiO ₂ , N-TiO ₂ -SiO ₂ , TiO ₂ -SiO ₂ , & DP25 TiO ₂	66
Figure 4.11: TEM images of TiO ₂ -SiO ₂ (A), C-TiO ₂ -SiO ₂ (B), & N-TiO ₂ -SiO ₂ (C)	68
Figure 4.12: EDX spectra of C-TiO ₂ and N-TiO ₂	70
Figure 5.1: Photo-oxidation reactor setup.....	73
Figure 5.2: Calibration curve for methyl orange	74

Figure 5.3: Calibration curve for phenol red	75
Figure 5.4: Photo-degradation profiles of MeO using $\text{TiO}_2\text{-SiO}_2$ photo-catalyst under UV lamp (366 nm) and visible light	76
Figure 5.5: Photo-degradation profiles of MeO using C- $\text{TiO}_2\text{-SiO}_2$, N- $\text{TiO}_2\text{-SiO}_2$, & $\text{TiO}_2\text{-SiO}_2$ as photo-catalysts	78
Figure 5.6: Photo-degradation profiles of MeO using powder and immobilized TiO_2 as photo-catalysts under strict UV light.....	79
Figure 5.7: Photo-degradation profiles of PRed using $\text{TiO}_2\text{-SiO}_2$ under UV and visible light	81
Figure 5.8: Photo-degradation profiles of PRed using $\text{TiO}_2\text{-SiO}_2$, C- $\text{TiO}_2\text{-SiO}_2$, & N- $\text{TiO}_2\text{-SiO}_2$	83
Figure 6.1: Images of E. coli ATCC 25922 treated with immobilized photo-catalyst C- $\text{TiO}_2\text{-SiO}_2$ (A), N- $\text{TiO}_2\text{-SiO}_2$ (B), $\text{TiO}_2\text{-SiO}_2$ (C), & control (D).....	90
Figure 6.2: Images of E. coli ATCC 25922 treated with non-immobilized DP25 TiO_2 (E)	90

List of abbreviations

BET	Brunauer Emmet Teller surface area analysis
C.B	Conduction band
EHA	Environmental health agency
EHEC	Enterohaemorrhagic Escherichia coli
ETEC	Enterotoxigenic Escherichia coli
FAO	Food and Agriculture Organization of the United Nations
FT-IR	Fourier transform infrared spectroscopy
HUS	Haemolytic uremic syndrome
NO _x	Nitric oxide
ROS	Reactive oxygen species
STEC	Shiga toxin producing Escherichia coli
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
THM	Trihalomethane
TTP	Thrombotic thrombocytopenic purpura
UNICEF	United Nations Children's Fund
UV/VIS	Ultraviolet/ visible light spectroscopy
V.B	Valence band
VOC	Volatile organic compound
WHO	World health organization
XRD	X-ray diffraction

CHAPTER 1

1. Introduction

1.1 General background

Titanium dioxide, also known as titania, is the naturally occurring oxide of titanium, with chemical formula TiO_2 and cubic structure illustrated in Figure 1.1 (Mattesini *et.al*, 2004). When used as a pigment, it is called titanium white. It has a wide range of applications such as in paint sunscreen and food colouring. Titanium dioxide occurs in nature as the minerals rutile, anatase and brookite. The most common form is rutile, which is also the most stable. Anatase and brookite both convert to rutile upon heating. Rutile, anatase and brookite all contain six coordinated titanium (El Goresy *et.al*, 2001).

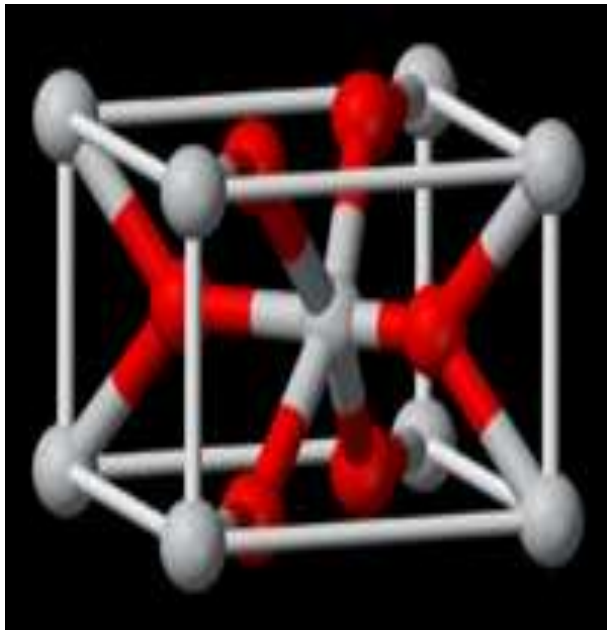


Figure 1.1: Cubic structure of titanium dioxide (wikipedia.org, 2011)

Titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index ($n = 2.7$), in which it is surpassed only by a few other materials. TiO_2 is also an effective opacifier in powder form, where it is employed as a pigment to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods, medicines (i.e. pills and tablets) and toothpastes. Opacity is improved by optimal sizing of the titanium dioxide particles. Titanium dioxide has also been used to whiten skimmed milk to increase the milk's palatability (Phillips and Barbano, 2011).

Titanium dioxide, particularly in the anatase form, is a photo-catalyst under ultraviolet (UV) light. The strong oxidative potential of the positive holes created in the conduction band of TiO_2 after excitation oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for its sterilizing, deodorizing and anti-fouling properties and is used as a hydrolysis catalyst. It is also used in dye-sensitized solar cells, which are a type of chemical solar cell (also known as a Graetzel cell). The photo-catalytic properties of titanium dioxide were discovered by Akira Fujishima in 1967 and published in 1972. The process on the surface of the titanium dioxide was called the *Honda-Fujishima effect*.

1.2 Study introduction and motivation

Due to population growth, rapid urbanization, increased farming activity, and changes in climate, the world is facing a severe shortage of water especially in developing economies. According to the Blue planet network 1.2 billion people in the world do not have access to safe drinking water, and about 2.2 million people in developing countries, most of them children, die every year from

preventable diseases related to lack of access to safe drinking water, inadequate sanitation, and poor hygiene. Unfortunately, despite a growing recognition that more must be done to help those without clean water or adequate sanitation, a report by the Pacific Institute estimates that over 34 million people might perish in the next 20 years from water-related diseases even if the United Nations “Millennium Development Goals,” which aim to cut the proportion of those without safe access by half, are met (WHO/UNICEF, 2005).

Various microbes that may be found in contaminated water bodies pose a great risk to human health if consumed. The main microbes causing disease are bacteria, viruses, fungi and protozoa. *Escherichia coli* O157:H7 is a microorganism that causes diarrhoea ranging from mild, non-bloody stools to those that are virtually mainly blood (Jiang *et.al*, 2002). *Escherichia coli* O157:H7 produces a toxin that damages the lining of the intestines resulting in haemorrhagic colitis (Hunter, 2003). This organism has a very low infectious dose and is thought to cause over 90% of all cases of diarrhoea-associated haemolytic uremic syndrome (HUS), a condition that causes acute renal failure, especially in young children in North America. Waterborne transmission occurs from contaminated drinking water and from swimming in contaminated waters (EHA, 2011). Shigellosis, leptospirosis, giardiasis, hepatitis A, etc. are some of the waterborne diseases that pose risk to human health if contaminated water or fruits and vegetables irrigated with contaminated water are consumed.

Every day an increasing amount of pollution seeps into rivers and lakes making them toxic to humans and other forms of life which depend on water for their existence (Arlington Institute, 2005). Water has been called the universal solvent because so many substances will dissolve in it

and it can also carry many materials in suspension. Unfortunately, water is not particularly selective which compounds become dissolved or suspended. Trihalomethanes (THMs) are a class of organic compounds that are important because their formation and presence in drinking water are a direct result of the most common and economical process used to kill harmful pathogens; that is through chlorination. Such compounds are formed when the chlorine that is added to water interacts with organic material. Distillation is probably the oldest method of water purification, but organics such as herbicides and pesticides, with boiling points lower than 100 °C cannot be removed efficiently and can actually become concentrated in the product water. Carbon absorption is a widely used method of home water filter treatment because of its ability to improve water by removing undesirable tastes and odours, including objectionable chlorine, but it can also generate carbon fines (particles released from granular activated carbon filters) which become a problem in drinking water (Water education, 2011).

There is no single treatment method that can remove all contaminants and often a combination of treatment processes are required to effectively treat water. Regardless of which method of treatment is considered, water is generally tested first to determine what substances are present. It is very important to know what contaminants are present and their concentrations prior to selecting the method of treatment because this helps to choose the best and most effective method. In this study the main focus is photo-catalysis as a way to effect water treatment. Titanium dioxide offers great potential as an industrial material for detoxification or remediation of wastewater due to several factors: photo-catalysis can occur under ambient conditions although very slowly, and direct UV light exposure increases the rate of reaction to complete

oxidation of substrates to CO_2 and H_2O . Titanium dioxide which can be supported on many suitable reactor substrates has high chemical and photo- stability. It is also relatively cheap.

1.3 Problem statement

Commercial titanium dioxide powders are small particles that are often difficult to recover by filtration or centrifugation after use in water. They sometimes have a tendency to agglomerate in aqueous applications resulting in a decreased photo-catalytic activity. The amount of catalyst that can be used is limited at high concentration because titanium dioxide particles could aggregate, reducing the surface area for photo-catalytic breakdown. There is also need for continuous stirring to distribute the catalyst. It is of great interest to find ways of immobilizing titanium dioxide nano-particles for easy recovery and also presenting a larger surface area for photo-catalysis.

1.4 Hypothesis

Titanium dioxide will be immobilized on glass substrate using a coupling agent tetraethyl orthosilicate (TEOS) to abate the problems associated with the use of powdered photo-catalyst for water treatment.

1.5 Aims and objectives

1.5.1 Main aim

The main aim of this study was to develop a nano-composite containing titanium dioxide and silicon dioxide with carbon and nitrogen doping. The nano-composite should show photo-

catalytic activity in the visible light spectrum for degradation of organic pollutants as well as display antimicrobial activity for water treatment.

1.5.2 Specific objectives

- Synthesis and characterization of carbon and nitrogen doped titanium dioxide using the sol gel method
- Immobilization of the synthesized carbon and nitrogen doped titanium dioxide using tetraethyl orthosilicate binder
- Evaluation of the photo-catalytic activity of the support coated catalysts using methyl orange and phenol red as model organic contaminants
- Evaluation of the antimicrobial activity of the support coated catalysts on water contaminated with *Escherichia coli*.

1.6 Scope of study

This study focuses on the preparation of carbon and nitrogen doped titanium dioxide nanoparticles via the sol gel method, using optimum conditions that had been established in the research group (Nyamukamba *et.al*, 2012). The main focus of the study was to establish suitable conditions for the immobilization of the photo-catalytic material on glass support to allow easy removal of spent titanium dioxide photo-catalyst from water.

1.7 Dissertation outline

This dissertation comprises a total of seven chapters. Chapter 1 contains a general introduction. The aims and objectives of this study are also presented including the outline of the dissertation. Chapter 2 gives the literature review on the chemistry of titanium dioxide and silicon dioxide as well as reference to previous work on their use as photo-catalysts and the different modifications carried out on the two materials.

Chapter 3 gives a summary of the materials used, general methodology and a description of the techniques used in the characterization of the prepared photo-catalytic materials.

Chapter 4 gives a detailed description of the procedures followed in the preparation of the titanium dioxide nano-particles and their immobilization onto glass support material. Also presented here are the characterization results of the prepared titanium dioxide-silicon dioxide nano-composites.

Chapter 5 outlines the procedures followed in the evaluation of the photo-catalytic properties of the prepared photo-catalysts. The results obtained from the photo-oxidation experiments are presented together with a discussion and a conclusion. The prepared photo-catalysts were evaluated for their photo-catalytic properties using model organic pollutants. The organic pollutants used were methyl orange (MeO) and phenol red (PRed).

Chapter 6 outlines the procedures that were followed in the evaluation of the antimicrobial properties of carbon and nitrogen-doped TiO₂-SiO₂ composites immobilized on glass substrate and the results that were obtained.

Chapter 7 gives a general conclusion of the research and recommendations for future work.

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CHAPTER 2

2. Literature review

2.1 Photo-catalysis

Heterogeneous photo-catalysis involves the use of a semi-conducting material which can be excited by the absorption of light. The applications of photo-catalysis include water treatment and purification, air treatment and purification, and ‘self-cleaning’ surfaces (Kommireddy *et.al*, 2005). Photosynthetic applications are also widely reported including photo-electrolytic water splitting (Fujishima and Honda, 1972), CO₂ reduction and organic synthesis. There is a wide range of materials employed in photo-catalytic research and applications. The important properties of these materials include the magnitude of band gap energy and hence the wavelength of light required for excitation, the chemical and photochemical stability, particle size and surface area. The use of nano-structured materials may lead to improved photo-catalytic efficiencies where the reduction in particle size results in a greater surface area and possibly size quantization effects. Large surface area provides more active sites for reaction and size quantization effects give rise to an increase in the absorption coefficient at specific wavelengths.

The most commonly employed photo-catalyst material for research and industrial applications is titanium dioxide (TiO₂). Titanium dioxide (TiO₂) has been getting attention as a photo-catalyst that can be utilized for the oxidative removal of environmental pollutants, such as nitric oxide (NO_x) and volatile organic compounds (VOC), under ultraviolet (UV) irradiation at a wavelength $\lambda < 380$ nm. (Ibusuki and Takeuchi, 1994; Hoffmann *et.al*, 1995; Sano *et.al*, 2004).

However, the activity of TiO_2 in a closed environment is often low since UV light, which is essential for activating pure TiO_2 , will be insufficient (Dunnill *et.al*, 2009). Therefore, many researchers are making efforts to develop visible-light-responsive photo-catalysts to circumvent this drawback. The major part of indoor light is visible light, and therefore an efficient utilization of visible light should improve the degradation rate of any pollutants using photo-catalysis (Puzenat *et.al*, 2009).

2.2 Attributes of titanium dioxide

Numerous researchers have worked on different semiconductor materials, and examples include metal oxides like WO_3 , ZnO , CeO_2 , Nb_2O_3 , Fe_2O_3 , SnO_2 etc, and also chalcogenides like ZnS , CdTe , ZnSe , CdSe , etc, (Peral *et.al*, 1997). Titanium dioxide was found to be one of the most promising semiconducting metal oxides because of its properties (Eggins *et.al*, 1998; Bryne, 2009). It is the most researched semiconductor material because of the following properties:

- (i) it is photo-stable
- (ii) photo-active
- (iii) relatively non toxic
- (iv) chemically and biologically inert
- (v) possesses adsorption properties
- (vi) its superhydrophilicity
- (vii) antimicrobial action

These properties make titanium dioxide a suitable photo-catalyst for air and water purification and many other uses.

2.3 Mechanism of photo-catalysis and generation of oxidative species

Titania has a band gap energy of around 3.2 eV and is therefore a UV absorber. When TiO_2 is subjected to UV light ($\lambda > 385 \text{ nm}$), an electron/hole pair ($e_{\text{CB}}^-/h_{\text{VB}}^+$) is generated. Electrons are promoted to the conduction band (C.B) and holes are consequently generated in the valence band (V.B) (Equation 2.1). Photo-catalytic reactions take place primarily on the surface of TiO_2 , where the photo-generated electrons and holes are trapped (Devi and Reddy, 2010).



In the absence of an electron or hole trap, recombination of the ($e_{\text{CB}}^-/h_{\text{VB}}^+$) pair will occur. Adsorbed oxygen can act as the electron trap, yielding a superoxide radical ($\text{O}_2^{\cdot -}$), which can act as an oxidant or reductant, hence promoting the extended lifetime of the h_{VB}^+ . In the aqueous media, the hole typically reacts with adsorbed H_2O , hydroxide or surface titanol groups ($-\text{TiOH}$) to produce a hydroxyl radical ($\cdot\text{OH}_{\text{ads}}$), which is a powerful oxidant as illustrated in Equations 2.2 and 2.3 (Blake *et.al*, 1999).



The reactive species (i.e., h_{VB}^+ , e_{CB}^- , $\cdot\text{OH}$, $\text{O}_2^{\cdot -}$, $\cdot\text{O}_2\text{H}$, H_2O_2 , O_2 , etc) generated during TiO_2 photo-catalysis can attack organic (and inorganic) pollutants in the water as illustrated in Figure 2.1. Effectively, each excited particle becomes a nano-electrochemical cell capable of driving

redox reactions at the interface. Dispersed nano-structured (but most likely aggregated) titania can be utilized for water treatment and purification.

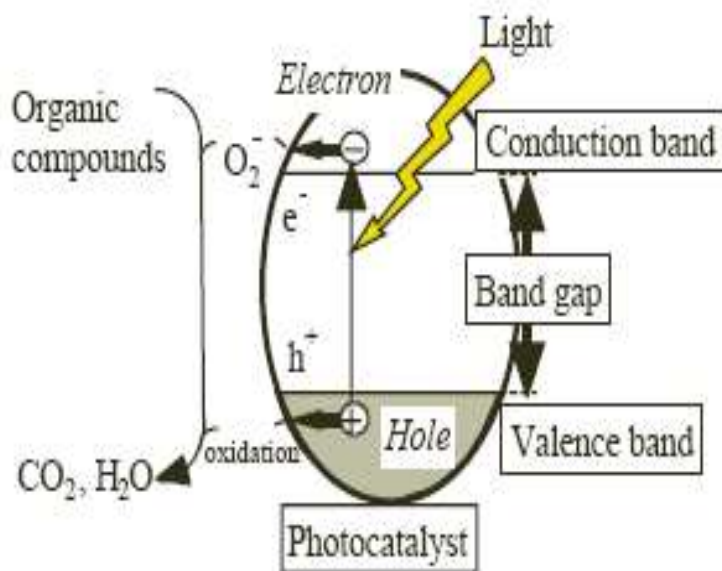


Figure 2.1: Mechanism of photo-degradation of organic pollutants (Lin *et.al*, 2011)

2.4 Antimicrobial properties of TiO_2

There are many circumstances where it is necessary or desirable to remove or kill microorganisms found in water, air, on surfaces or in a biological host. Disinfection of water is required for potable and drinking water as well as in the production of products to be consumed by humans or animals. The most widely used methods are chlorination and ozonation (Blake *et.al*, 1999). Photo-catalytic methods are unique in having several modes of action that can be brought to bear on disinfection. The target of disinfection processes are pathogenic organisms including viruses, bacteria, fungi, protozoa, and algae. Each presents a challenge in terms of the

structure and defence mechanisms that must be overcome. The current disinfection technologies rely on chemically or photo-chemically induced damage or physical removal by filtration.

Purification of environmental toxic substances in water and air using TiO_2 photo-catalysts have been studied extensively (Ollis *et.al*, 1991; Heller, 1995; Hoffmann *et.al*, 1995; Mills and Hunte, 1997; Fujishima *et.al*, 2000). In many studies on water treatment, for example, a fine TiO_2 powder was suspended in the water to be treated and illuminated with a strong light, such as a mercury lamp. This system, however, had two major problems; the recovery of TiO_2 powder and the high cost of providing light from a lamp. In this study the focus is on the photo-catalytic reactions of TiO_2 thin films coated on glass substrate. Some TiO_2 coated tiles with self-cleaning and bactericidal functions have already been commercialized (Watanabe *et.al*, 1993; TOTO LTD., 1995). The self-cleaning function of TiO_2 coated substrates is explained simply by the photo-induced oxidative power of TiO_2 photo-catalysts. The bactericidal function, however, is not well understood, even though numerous reports have described photo-killing of bacteria (Matsunaga and Okochi, 1995; Horie *et.al*, 1996; Jacoby *et.al*, 1998; Maness *et.al*, 1999; Huang *et.al*, 2000), viruses (Watts *et.al*, 1995; Lee *et.al*, 1997) and tumour cells (Cai *et.al*, 1992; Sakai *et.al*, 1994). Because these photo-killing reactions were carried out using TiO_2 powder, the possibility of cell de-activation by the co-aggregation of cells and TiO_2 particles cannot be excluded. In addition, the TiO_2 particles phagocytised by the cells may cause cellular injury (Cai *et.al*, 1991). In fact, Jacob and co-workers reported that TiO_2 particles ingested by phagocytosis caused rapid intracellular damage (Huang *et.al*, 2000).

2.4.1 TiO₂ mode of action on microbes

The OH· radical has been suggested to be the most toxic for microorganisms because of its ability to oxidise many organic substrates like carbohydrates, lipids, proteins and nucleic acids, etc, (Srinivasan *et.al*, 2003). It promotes peroxidation of polyunsaturated phospholipid components of the lipid membrane and induces disorder in the cell membrane (Maness *et.al*, 1999). Since 1985, when Matsunaga *et.al*, reported photo-catalytic inactivation of *Saccharomyces cerevisiae* in the presence of TiO₂ irradiated with UV light, (Matsunaga *et.al*, 1985) the heterogeneous photo-catalysis has become a promising tool allowing detoxification and disinfection. Matsunaga and his co-workers made the first attempt to elucidate the mechanism of titania photo-cytotoxicity. They have demonstrated that oxidation of coenzyme A (CoA) may be a possible mechanism of photo-induced cell death. However, the reactivity of ROS was thought to be non-selective. A possible role of ROS was oxidation of the cell membrane prior to the oxidation of CoA (Matsunaga *et.al*, 1985; Dadjour *et.al*, 2005).

In 1992, Saito *et.al*, reported that decomposition of the cell membrane and loss of its permeability are the main factors responsible for the bacteria cell death. In 1997 Kikuchi and co-workers suggested that the lethal bactericidal agent is H₂O₂ produced from photo-generated superoxide anions. A cooperative effect of various oxidative species was postulated as an explanation of *E. coli* inactivation mechanism (Kikuchi *et.al*, 1997). In 1999, Maness *et.al*, presented results showing that irradiated TiO₂ induces peroxidation of polyunsaturated phospholipid components of the lipid membrane. It causes major disorder in the *E. coli* cell membrane leading to inhibition of fundamental vital processes of the cell and in consequence to

its death. In 2003, Sunada *et.al*, demonstrated that decomposition of the outer membrane caused by peroxidation process resulted in cytoplasmic membrane disorder and subsequently cell death.

The cell damage initiated by photo-catalytic processes may be continued by consecutive post-irradiation reactions due to a relatively high concentration of reactive oxygen species (ROS) (Srinivasan *et.al*, 2003; Maness *et.al*, 1999). A linear correlation between the amount of photo-generated $\text{OH}\cdot$ radical and the extent of *E. coli* inactivation in TiO_2 photo-catalytic disinfection was found by Cho *et.al*, 2004. Their further study clearly showed a dependence of biocidal inactivation on efficiency of surface or bulk hydroxyl radical generation as well as on the type of microorganism (MS-2 phage or *E. coli*) (Cho *et.al*, 2005).

2.5 Contaminants that can be removed by TiO_2

2.5.1 Organics

Titanium dioxide is a semiconductor that is frequently used in organic degradation experiments. Many organic compounds are decomposed in aqueous solution in the presence of titanium dioxide powder illuminated with UV light (Tennakone *et.al*, 1995). Laoufi *et.al*, 2008 examined the decomposition of phenol by photo-degradation in the presence of titanium dioxide under UV illumination and found that the efficiency of the process depended strongly on the experimental conditions employed. Strini *et.al*, 2005 reported a recent evaluation of oxidation rates for benzene and three alkyl benzenes: toluene, ethyl benzene, and o-xylene. The work showed that the reaction rates were proportional to the UV-A photon flux in the range of 0.7 to 1.3 mW cm^{-2} .

2.5.2 Inorganics

Titanium dioxide photo-catalyst can oxidize toxic anions to harmless or less toxic compounds, for example nitrite is oxidized to nitrate; sulphide, sulphite and thiosulphate are converted to sulphates and the cyanide is converted to nitrogen or nitrate (Pollema *et.al*, 1992). Serpone *et.al*, 2003, worked on the photo-reduction and elimination of Hg (II) and CH₃Hg (II) chloride salts from aqueous suspensions of titanium dioxide using AM1 simulated sunlight.

2.5.3 Microbes

Total oxidation of *Escherichia coli* cells has been demonstrated (Jacoby *et.al*, 1998). The reactive oxygen species (ROS) generated by TiO₂ photo-catalytic reactions sometimes causes damage to living organisms. This is not surprising since they consist of significant organic compound content. In 1985, Matsunaga and co-workers reported on the micro-biocidal effect of TiO₂ photo-catalytic reactions (Matsunaga *et.al*, 1996). Since then, research work on TiO₂ photo-catalytic killing has been conducted on a wide spectrum of organisms including viruses, bacteria, fungi, algae, and cancer cells. The first-order reaction kinetics and several modified forms have been proposed for the bactericidal reaction of TiO₂ photo-catalysts (Bekbolet and Araz., 1996; Stevenson *et.al*, 1997). A review of the research was published by Blake *et.al*, 1996. Although the applications of TiO₂ photo-catalyst as a micro-biocide have been receiving increasing attention worldwide, the initial response of living organisms to TiO₂ photo-catalytic reaction has not been reported in detail and the mechanisms leading to cell death have not yet been fully understood.

2.5.3.1 Escherichia coli

Figure 2.2 shows a cross-section of *E. coli* bacterium

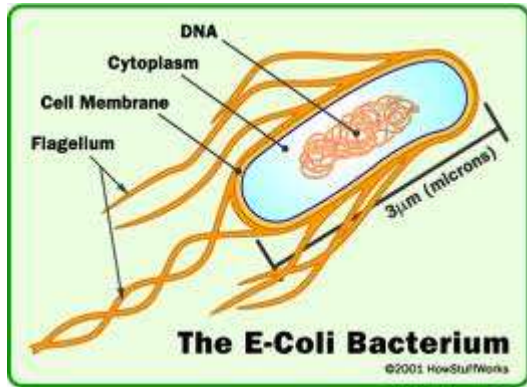


Figure 2.2: Cross-section of *Escherichia coli* bacterium (www.science.howstuffworks.com, accessed 27-11-2011)

Escherichia coli (*E. coli*) are gram-negative bacteria that are anaerobic, with a type of metabolism that is both fermentative and respiratory (Hunter, 2003). Thin hair-like structures (flagella or pili) that allow the bacteria to move and to attach to human cells may or may not be produced, depending on the environment in question (Madappa and Cunha, 2011).

2.5.3.2 Epidemiology

Most of the *E. coli* are non-pathogenic dwellers of the small intestine and colon. However, these non-pathogenic *E. coli* can cause disease if they spread outside of the intestines, for example, into the urinary tract (where they cause bladder or kidney infections), or into the blood stream (sepsis). Other *E. coli* strains cause “poisoning” or diarrhoea even though they usually remain within the intestine and produce toxins or intestinal inflammation (Beutin *et.al*, 2004; Zheng

et.al, 2005; Bielaszewska *et.al*, 2006). Other infections include cholecystitis, bacteraemia, cholangitis, and clinical infections such as neonatal meningitis and pneumonia (Madappa and Cunha, 2011).

The incidence of enterohaemorrhagic *E. coli* (EHEC) infections varies by age group, with the highest incidence of reported cases occurring in children aged under 15 years (0.7 cases per 100 000 in the United States). Sixty-three to 85 % of cases are a result of exposure to the pathogen through food contamination. The percentage of EHEC infections which progress to HUS varies between sporadic cases (3 % - 7 %) and those associated with outbreaks (20 % or more). In epidemiological terms, there is generally a background of sporadic cases, with occasional outbreaks. Some of these outbreaks have involved a high number of cases, such as in Japan in 1996, where an outbreak linked to contaminated radish sprouts in school lunches caused 9 451 cases (WHO, 2011). The first major outbreak of Shiga toxin producing *E. coli* (STEC O157:H7) infection was reported in the United States in 1982 and was linked to eating undercooked ground beef from a fast-food restaurant chain (Riley *et.al*, 1983). Recently however, two reports of human food-borne *E. coli*O157:H7 outbreaks have implicated pork products (Conedera *et.al*, 2007; Jay *et.al*, 2007). Several outbreaks have been reported worldwide, including a large outbreak in Jiangsu and Anhui of Chinese Mainland during 1999 to 2000, which caused more than 200 deaths (Zheng *et.al*, 2005).

A more recent outbreak *E. coli* infection affected 175 Israeli military personnel and at least 54 civilians in the Golan Heights (Huerta *et.al*, 2000). All affected military posts and civilian communities were supplied by a common water pipeline. Samples of water from several points

along the distribution system showed inadequate chlorination and high concentrations of *E. coli*. Daniels and colleagues reported three outbreaks of ETEC infection on cruise ships (Daniels *et.al*, 2000). All three outbreaks were associated with consuming drinks containing ice cubes on board the ship, and two were also associated with drinking unbottled water. The authors suggested that water bunkered in overseas ports was the likely source of the infection and that such water should be treated before use.

2.6 Methods of TiO₂ synthesis

There are many methods that can be employed in the preparation of titanium dioxide nanoparticles. Some of them include; sol-gel, deposition methods, microwave assisted methods, hydro/solvo-thermal methods and oxidation methods. In this study the sol-gel method of synthesis is used.

2.6.1 Sol-gel synthesis

The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (**sol**) and gelation of the sol to form a network in a continuous liquid phase (**gel**). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol consists of particles in a gas phase, while a sol consists of particles in a liquid.

A gel consists of a three dimensional continuous network, which encloses a liquid phase in a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made up of aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved. The idea behind sol-gel synthesis is to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner.

Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds. The sol-gel method prevents problems of co-precipitation, which may cause inhomogeneity and enables mixing at an atomic level and results in small particles, which are easy to sinter. Figure 2.3 shows a schematic of sol gel processing options.

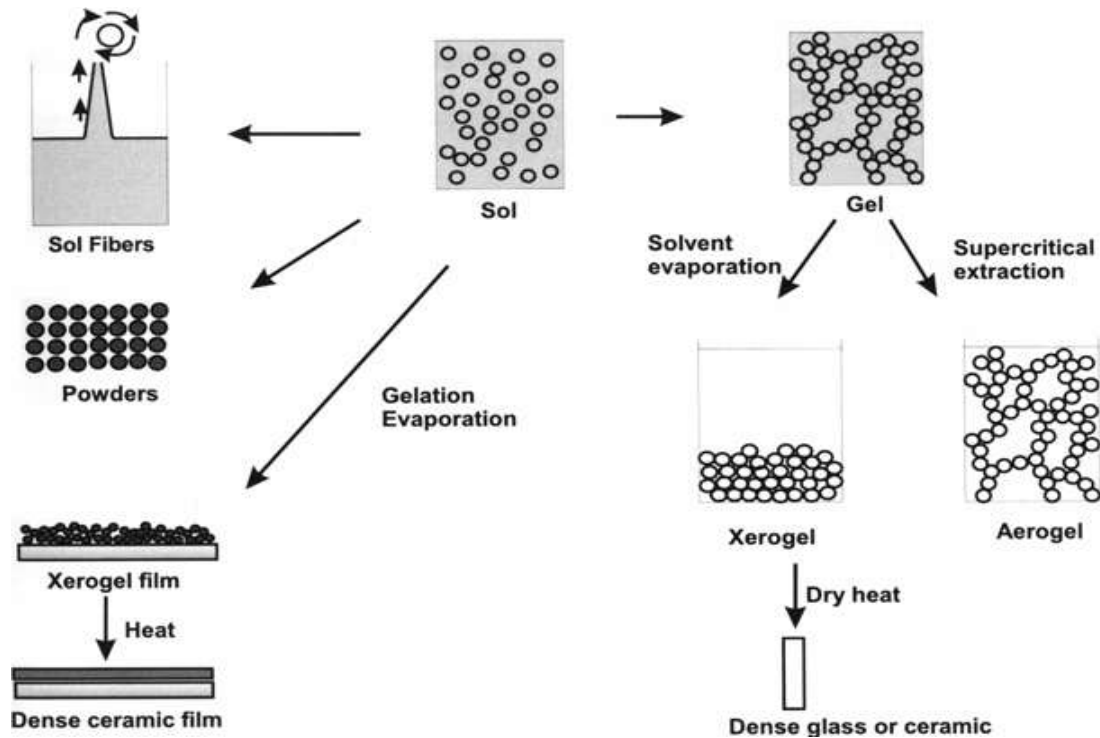


Figure 2.3: Sol-gel processing options (www.gitam.edu, accessed 28-11-2011)

2.7 Modification of TiO_2

There are various ways in which titanium dioxide can be modified to enhance performance or to suit its use. The following sections describe some of the modifications that can be carried out on TiO_2 .

2.7.1 Doping

Doping is the addition of impurities to a semiconductor to control its electrical resistivity. A number of approaches have been used to modify the semiconducting nature of TiO_2 for its use in visible light photo-catalysis. Impurity doping is one of the typical approaches to extend the spectral response of a wide band gap semiconductor to visible light. One approach of doping

TiO₂ with transition metals has been investigated extensively (Eggins *et.al*, 1998; Puzenat *et.al*, 2009; Ren *et.al*, 2007; Nosaka *et.al*, 2005). However, the photo-catalytic activity of metal doping was found to be impaired by thermal instability and an increase in carrier-recombination (Ren *et.al*, 2007 and Choi *et.al*, 1994). Recently, some researchers (Ren *et.al*, 2007) have reported TiO₂ doping with non-metallic atoms like nitrogen, carbon, sulphur, iodine and co-doping with nitrogen and fluorine. All showed high photo-catalytic activity under visible light owing to band gap narrowing (Agostiano *et.al*, 1997). It has been found that doping with fluorine modifies the electronic structure of TiO₂ by creating oxygen vacancies on the surface due to charge compensation between F⁻ and Ti⁺⁴ but without a significant change in spectral response (Wong *et.al*, 2008).

Ren *et.al*, 2007 prepared a visible light sensitive TiO₂ photo-catalyst using a hydrolytic process, with Ti (SO₄)₂ and ammonia solutions (Ihara *et.al*, 2000). They found that 540 ppm of acetone were decomposed within 36 hours and a stoichiometric yield of CO₂ was obtained by using blue-light-emitting diodes as a light source, and concluded that the oxygen-deficient sites were responsible for the visible light activity.

2.7.1.1 Carbon doping

There are many ways of incorporating carbon into titanium dioxide to effect C-doping on TiO₂. Spray pyrolysis of a TiCl₄ and glucose solution has been used to prepare C-modified TiO₂ films displaying high photo-efficiencies. Irie *et.al*, 2003, prepared carbon-doped anatase TiO₂ powders by oxidative annealing of Ti-C under O₂ flow at 600 °C (Li *et.al*, 2005). The catalyst used showed good photo-catalytic activity under visible light irradiation at 400-530 nm. Sakthivel and

Kisch, 2003, synthesized carbon doped TiO₂ through the hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide followed by calcinations at 400 and 500 °C. Most of these methods invoke the use of very high temperatures to bring about carbonization. So it is still a challenge to prepare carbon-doped TiO₂ at a low temperature, especially an energy-efficient production of visible-light driven photo-catalyst on a large scale for pollutants removal (Enrique *et.al*, 2009). In other experiments it was reported that crystallization of titanium dioxide could occur at the same time during carbon doping using glucose under hydrothermal treatment at a temperature as low as 160 °C (Ren *et.al*, 2007).

2.7.1.2 Nitrogen doping

Several researchers (Kobakawa *et.al*, 2005; Wang *et.al*, 2005; Yuan *et.al*, 2006) have reported that N-doped titanium dioxide shows a considerable shift of the absorption edge to the lower energy in the visible light region. The nitrogen doping can be attained by various methods such as the sputtering of TiO₂ in an N₂–Ar atmosphere, the heating of TiO₂ powder in an ammonia atmosphere over several hundred degrees Celsius, the hydrolysis of organic and inorganic titanium compounds such as titanium tetraisopropoxide, titanium (IV) sulphate and titanium (III) chloride with ammonia water, followed by heating of the resultant precipitates. The heating of TiO₂ powder with urea is also another way of N-doping (Aoki *et.al*, 2001). Substitutional doping is the replacement of a lattice element by one of its neighbouring atoms. Research has proven that substitutional doping of N atom is very effective, because its p states contribute to band gap narrowing by combining with the 2p of oxygen (Nosaka *et.al*, 2005; Batzill *et.al*, 2006).

2.7.2 Compositing with silicon dioxide

The efficiency of some commercial TiO_2 , such as Degussa P-25, in the treatment of exhaust gas and wastewater contaminated with organic and inorganic pollutants has been proved (Zhang *et.al*, 1998). However, their effective applications are hindered by two serious disadvantages. Firstly, small particles tend to agglomerate into large particles, reducing catalyst efficiency. Secondly, the separation and recovery of catalyst is difficult (Zhu *et.al*, 2000, Yu *et.al*, 2002). For these reasons many researchers have been focused on finding suitable mesoporous materials for supporting titania catalysts so that spent TiO_2 can easily be removed from the treated water and no agglomeration occurs.

Introducing titanium species into mesoporous silicate materials has attracted much interest because the titanium-containing mesoporous materials have much higher active surface areas ($> 200 \text{ m}^2\text{g}^{-1}$) in comparison to pure titania (Maschmeyer *et.al*, 1997), which makes them more effective as photo-catalysts. Another method of grafting titanium onto mesoporous materials is to modify the inner mesopores with a titanium precursor (Aronson *et.al*, 1997; Luan *et.al*, 1999).

2.7.2.1 Proposed mechanism of TiO_2 activation in the presence of silicon

Kim *et.al*, 2005, proposed two models for titanium dioxide activation in the presence of silicon dioxide. These deductions were based on the results they obtained from the decomposition of benzene. Figure 2.4 shows the two models that were proposed to explain the results obtained. Based on their results, the titanium dioxide band gap energy was changed into a higher form of energy through the introduction of silicon dioxide. Generally the photo-catalytic efficiency towards volatile organic compounds (VOC) removal increases when the band gap decreases, but

in their case it was the reverse. So to explain their results, they proposed two models as shown in figure 2.4.

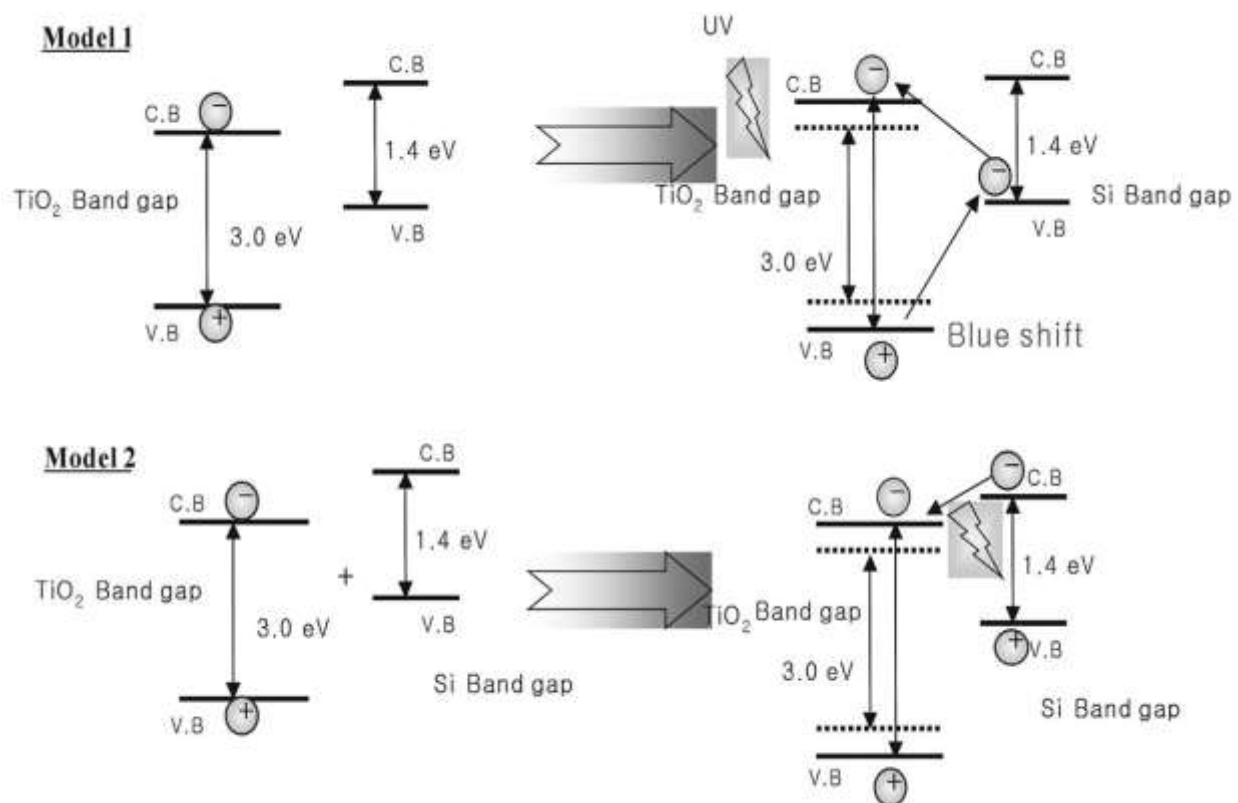


Figure 2.4: Activation mechanism of TiO_2 in the presence of silicon (Kim *et.al*, 2005): C.B = conduction band, V.B = valence band, eV = electron volts, Si = silicon, UV = ultra violet.

Initially, if TiO_2 was exposed to UV radiation, the electrons released from the valence band of TiO_2 could readily be transferred to the valence band of SiO_2 when compared to that occurring in the conduction band of TiO_2 . The electrons could then move to the conduction band of TiO_2 (Model 1). Their results showed that as the number of electrons transferred to the conduction band of TiO_2 increased, so did the rate of benzene decomposition. In Model 2, if the silicon dioxide covering the TiO_2 particles was exposed to UV radiation, the electrons of the valence

band in the SiO₂ could transfer to the conduction band of TiO₂. The number of electrons used to generate OH radicals would therefore increase (Kim *et.al*, 2005).

2.8 Support material for titanium dioxide

Photo-catalytic oxidation has been proposed since the 1980s as a solution to the problem of toxic water pollutants (Alexiadis and Mazzarino, 2005; Kabra *et.al*, 2004). The key to the problem of industrializing the technology seems to be immobilization of TiO₂ nano-particles, as the most successful photo-catalyst used in researches (Hong *et.al*, 2005; Fernandes *et.al*, 2005), on solid media suitable for the treatment process without lowering its photo-catalytic efficiency. Processes of the photo-catalytic degradation of organic impurities in majority operate in systems where the photo-catalyst is suspended in the reaction mixture. However, in this case the photo-catalyst should be separated from the reaction mixture after the process is completed. Removal of the catalyst from the reaction mixture is an additional step in the process that increases its costs. Different researchers have tried to minimize these problems by immobilizing TiO₂ on various solid supports or on reactor walls, which eliminates the arduous step of separation (Fernandez *et.al*, 1995; Goetz *et.al*, 2009).

TiO₂ powder, can by itself, photo-degrade pollutant molecules when radiated with UV radiation. If titania powder is deposited in a pool of polluted water under sunlight, it will degrade the pollutant in the water. However, researchers have discovered that during the photo-degradation process, interaction by certain pollutant molecules or their intermediates could cause the TiO₂ powder to coagulate, thereby reducing the amount of UV radiation from reaching the TiO₂ active centres (due to reduction of its surface area) and thus reducing its catalytic effectiveness (O'Shea

et.al, 1999). It is agreed that the critical step of organic compounds oxidized in a reaction is initiated by hydroxyl radicals produced on the photo-catalyst surface; hence the extent of adsorption of the pollutants onto the photo-catalyst surface is an important factor in evaluating the efficiency of the photo-catalytic reaction. Matthews *et.al*, 1994 suggested that the use of titanium dioxide coated on sand promotes economic scaling up of the process. Many approaches have been used in the immobilization of photo-catalyst on support material, for example, dip coating from suspension, sol spray coating (Chen *et.al*, 1999), reactive direct current magnetron sputtering (Takeda *et.al*, 2001), sol gel-related methods (Tryba *et.al*, 2003), and electro deposition (Karuppuchammy *et.al*, 2002).

Brezova *et.al*, 1994 immobilized a thin film composed of Degussa P25 TiO₂ and polyvinyl acetate. In this approach, a layer is formed by coating a photochemical reactor wall with a mixture of titanium powder and a commercial dispersion of the polymer, followed by drying and calcination. Matthews *et.al*, 1994 developed a nano-colloidal thin film of titania on conducting glass by electrophoretic deposition from Degussa P25 dispersion. The colloid was obtained by grinding a thick paste made of titania and 2-methoxyethanol in a ceramic mortar, and by subsequent dilution with the same solvent. After deposition, the film was aerated and annealed at 500 °C.

A simpler technique for catalyst fixation on polymer membranes was proposed by Tennakone *et.al*, 1995. In this approach they coated a polythene film functioning as the catalyst support, using a dry process. The method involved the even spreading of the powdery titania catalyst over all the film support by rubbing with cotton wool and subsequent ironing (with an iron plate at 74

°C). This was followed by rinsing with sodium hydroxide, and washing out loosely bonded particles. The resulting coated film was tested after drying, in the degradation of phenol with promising results, according to the authors.

An optically transparent electrode was coated with semiconductor thin film by partially painting a plate of a conducting glass with a sonicated suspension of titanium dioxide (Degussa P25) and by further drying in an oven at 400 °C. The electrode was successfully employed by these authors in the photo-degradation of acid orange 7, 4-chlorophenol and textile dyes in a UV illuminated electrochemical cell, in which a biasing potential was applied (Vinodgopal *et.al*, 1995).

A good photo-catalyst material should in general have the following attributes:

- The material should be transparent or at least allow some UV radiation to pass through it
- Be chemically inert or non-reactive to the pollutant molecules, its intermediates and the surrounding aqueous system
- The material should sufficiently bond either physically or chemically to the TiO₂ without reducing the reactivity of titanium dioxide
- The material should have a high surface area and a strong adsorption affinity towards the pollutants to be degraded
- The material should allow for fast and easy photo-catalyst recovery and re-use with or without regeneration.

Many substrates have already been proposed as catalyst supports for the photo-degradation of water contaminants. Most of these supports are based on SiO₂, either as a glass reactor wall or in the form of sand and silica gel. Glass beads, glass tubes, fiberglass, woven mesh, steel mesh, quartz, stainless steel, aluminium, metal fibres, and many types of plastics and ceramics such as alumina have also been tried as support material (Chan *et.al*, 2002). In this study glass is to be used as the photo-catalyst support material.

2.8.1 Attributes of glass as a support material

Use of glass substrate as a support for titanium dioxide photo-catalyst has the following advantages;

- (1) Glass is affordable and recyclable
- (2) The main constituent of glass is SiO₂ which is abundant in nature
- (3) It presents a surface for catalyst support
- (4) It is transparent to the UV radiation required to activate TiO₂
- (5) Silicon dioxide is a good adsorbent.

The above mentioned attributes are the reasons why a glass substrate was chosen as the support material for TiO₂ photo-catalyst.

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CHAPTER 3

3. Experimental: Materials and general procedures

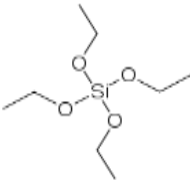
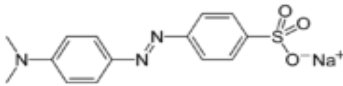
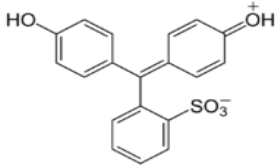
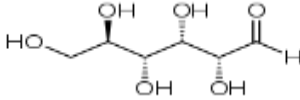
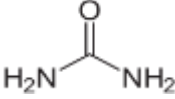
3.1 Introduction

This chapter gives details of the materials and reagents used in the study and the methodology followed.

3.2 Materials and chemical reagents

Titanium tetrachloride (TiCl_4) (99 % Merck) was used as the precursor material. Glucose (MET –U-ED Chemical Co.) was used for carbon doping and urea (99 % Kanto Chemical Co.) was used as the nitrogen dopant source. Methyl orange (99.5 % Sigma-Aldrich) and phenol red (Searle Co.) were used as model organic contaminants in the photo-degradation analysis. Ordinary glass was used as support for titanium dioxide photo-catalyst. Hydrofluoric acid (48 % Merck) was used for etching the glass surface to introduce hydroxyl groups. Tetraethyl orthosilicate was employed as the coupling agent for immobilization of photo-catalyst on glass support. Hydrochloric acid was used for the treatment of the titanium dioxide photo-catalyst to generate hydroxyl groups. Deionized water was also used in this research. For microbial evaluation the following materials were used; sterile cotton swabs, agar gel, nutrient broth, normal saline, plates for incubation and *E. coli* ATCC 25922 bacteria. Table 1 gives the chemical names, formulae, molecular structures and molecular masses of reagents.

Table 1: Chemical names, formulae, molecular structures and molecular masses of reagents

Chemical name	Molecular mass /gmol ⁻¹	Molecular formula	Chemical structure
Titanium tetrachloride	189.71	TiCl ₄	
Tetraethyl orthosilicate	208.33	Si(OCH ₂ CH ₃) ₄	
Methyl orange	327.33	C ₁₄ H ₁₄ N ₃ NaO ₃ S	
Phenol red	354.38	C ₁₉ H ₁₄ O ₅ S	
Glucose	180.16	C ₆ H ₁₂ O ₆	
Urea	60.06	CH ₄ N ₂ O	

3.3 Characterization techniques

This section describes the analytical techniques that were used for the characterization of the photo-catalysts that had been prepared. Samples were characterized using the following techniques: Fourier transform infrared spectroscopy (FT-IR), Brunauer-Emmet-Teller (BET) surface area analysis, X-ray diffraction (XRD) analysis, Transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDX), and Diffuse reflectance spectroscopy (DRS). Ultraviolet-visible spectroscopy (UV-VIS) was used for the quantitative analysis of the organic model pollutants during photo-degradation studies.

3.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy is a measurement technique whereby spectra are collected based on measurements of the coherence of a radiative source, using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation. FT-IR is used to identify functional groups in samples of either inorganic or organic compounds.

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two different molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for the determination of the functional groups present in compounds and other analyses (Abragam, 1968; Atkins, 2006).

3.3.2 Brunauer Emmet Teller (BET) surface area analysis

BET surface area analysis is a technique used to determine the specific surface area of powders, solids and granules. The values are expressed in meter square per gram. Clean solid surfaces adsorb surrounding gas molecules and Brunauer, Emmett and Teller theory (BET) provides a mathematical model for the process of gas sorption. This physical adsorption of a gas over the entire exposed surface of a material and the filling of pores is called physisorption and is used to measure the total surface area and pore size of nano-pores, micro-pores and mesopores. The BET surface area measurement is crucial in understanding the behaviour of a material, as the material reacts with its surroundings via its surface. A higher surface area material is more likely to react faster, dissolve faster and adsorb more gas than a similar material with a lower surface area.

Surface Area is a measure of the exposed surface of a solid sample on the molecular scale. The BET (Brunauer, Emmet, and Teller) theory is the most popular model used to determine the surface area. Samples are commonly prepared by heating while simultaneously evacuating or flowing gas over the sample to remove the liberated impurities. The prepared samples are then cooled with liquid nitrogen and analysed by measuring the volume of gas (typically N₂ or Kr) adsorbed at specific pressures. Usually, Krypton gas is used when the measured surface is expected to be less than 2 m²g⁻¹, which is typical for pharmaceutical samples and natural organic materials (Brunauer *et.al*, 1938).

3.3.3 Diffuse reflectance spectroscopy (DRS)

Diffuse Reflectance Infrared Fourier Transform Spectroscopy is a technique that collects and analyses scattered IR energy. It is used for measurement of fine particles and powders, as well as

rough surfaces (e.g., the interaction of a surfactant with the inner particle, the adsorption of molecules on the particle surface). Sampling is fast and easy because little or no sample preparation is required.

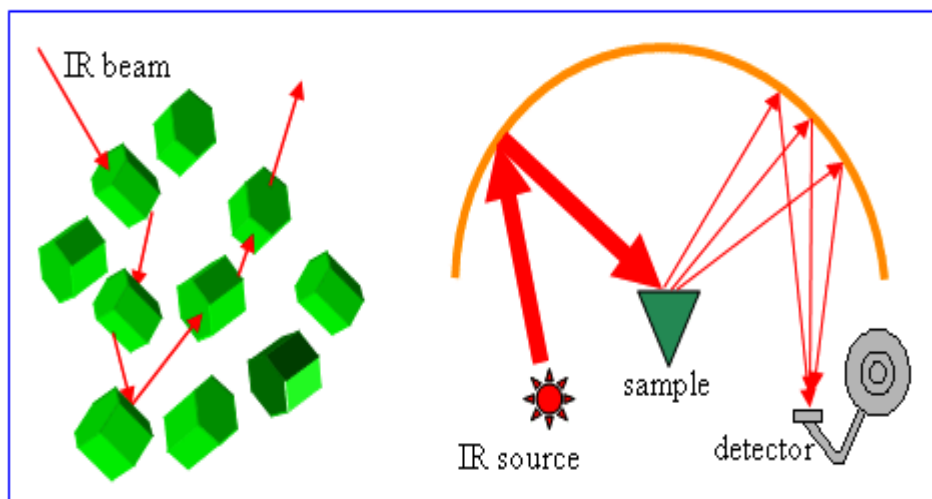


Figure 3.1: Schematic diagram of DRS instrument (Jensen, 2001)

When the IR beam enters the sample, it can either be reflected off the surface of a particle or be transmitted through a particle. The IR energy reflecting off the surface is typically lost. The IR beam that passes through a particle can either reflect off the next particle or be transmitted through the next particle. This transmission-reflectance event can occur many times in the sample increasing the path length. Finally, such scattered IR energy is collected by a spherical mirror that is focused onto a detector. The detected IR light is partially absorbed by particles of the sample, resulting in sample information (Jensen, 2001; Scott, 1988).

3.3.4 X-ray diffraction

This is a method in which X-rays are diffracted from the planes of a crystal (diffraction analysis). It depends on the wave character of the X-rays and the regular spacing of the planes in a crystal. Although diffraction methods are normally used for quantitative analysis, they are most widely used for qualitative identification of crystalline phases.

X-ray powder diffraction analysis is a powerful method by which X-rays of a known wavelength are passed through a sample. X-ray diffraction techniques are based on the elastic scattering of X-rays from structures that have long-range order. The wave nature of the X-rays means that they are diffracted by the lattice of the crystal to give a unique pattern of peaks of 'reflections' at different angles and intensity, just as light can be diffracted by a grating of suitably spaced lines. The diffracted beams from atoms in successive planes cancel out unless they are in phase, and the condition for this is given by the Bragg relationship:

$$n\lambda = 2d\sin\theta \quad (3.1)$$

where, λ is the wavelength of the X-rays, d is the distance between different plane of atoms in the crystal lattice and θ is the angle of diffraction. The X-ray detector moves around the sample and measures the intensity of these peaks and the position of these peaks (diffraction angle 2θ). The highest peak is defined as the 100 % peak and the intensity of all the other peaks are measured as a percentage of the 100 % peak (www.plasma-biotol.com/xraydif1.html, Accessed 28-11-2011).

3.3.5 Transmission electron microscopy (TEM)

Transmission electron microscopy is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, or a layer of photographic film, or to be detected by a sensor such as a charge-coupled device (CCD) camera (Egerton, 2005).

Electron microscopes are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail, even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEM finds application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research.

At smaller magnifications, TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging (Champness, 2001).

3.3.6 Energy dispersive X-ray spectroscopy (EDX)

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a technique used in conjunction with chemical microanalysis by scanning electron microscopy (SEM). EDS techniques detect X-rays emitted from a sample during bombardment by an electron beam to characterize the elemental composition of the volume analysed. Functions or steps as small as 1 micron or less can be analysed.

When the sample is bombarded by an electron beam in SEM, the electrons are ejected from atoms comprising the sample surface. The resulting electron vacancies are filled by electrons from a higher state, and an X-ray is emitted to balance the energy difference between the states the two electrons'. The X-ray energy is characteristic of the element from which it was issued.

EDS X-ray detector measures the relative abundance of X-rays against their energy. The detector is typically a lithium-drifted silicon solid-state device. When an incident x-ray hits the detector, a pulse of charge that is proportional to the energy of X-ray is created. The pulse charge is converted to a pulse voltage (which is proportional to the energy X-ray) by a charge sensitive preamplifier. The signal is then sent to a multichannel analyser where the pulses are sorted by the tension. The energy, as determined by measuring the voltage per incident x-ray is sent to a computer for display and further data evaluation. The spectrum of X-ray energy versus number of counts is evaluated to determine the elemental composition of the sample volume (www.uksaf.org/tech/edx.html, accessed 28-11-2011).

3.3.7 Ultra-violet/ visible spectroscopy

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and by applying the Beer-Lambert Law.

Since the UV-Vis range spans the range of human visual acuity of approximately 400 - 750 nm, UV-Vis spectroscopy is useful in characterizing the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters. This more qualitative application usually requires recording at least a portion of the UV-Vis spectrum for characterization of the optical or electronic properties of materials.

The light source is usually a deuterium discharge lamp for UV measurements and a tungsten-halogen lamp for visible and near infrared measurements. The instruments automatically swap lamps when scanning between the UV and visible regions. The wavelengths of these continuous light sources are typically dispersed by a holographic grating in a single or double monochromator or spectrograph. The spectral bandpass is then determined by the monochromator slit width or by the array-element width in array-detector spectrometers.

Spectrometer designs and optical components are optimized to reject stray light, which is one of the limiting factors in quantitative absorbance measurements (Pavia *et.al*, 2001).

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CHAPTER 4

4. Preparation and characterization of carbon or nitrogen doped titanium dioxide and its immobilization on glass support material

4.1 Introduction

This chapter reports on results obtained by doping of titanium dioxide nano-particles with carbon and nitrogen followed by immobilization of the nano-composites on glass. The major purpose of this study was to synthesize carbon and nitrogen doped titanium dioxide using the sol gel method, and immobilization of the photo-catalyst onto glass support material. Optimum conditions established in previous work (Nyamukamba *et.al*, 2012) were used in these procedures. The sol gel technique is a simple method that allows easy control of particle size, morphology and distribution. It is a hydrolysis and condensation reaction process that is used primarily for the fabrication of materials especially metal oxides starting from a chemical solution which acts as a precursor. Figure 4.1 gives a schematic of the sol-gel process using a titanium tetrachloride precursor.

Doping was carried out in situ during the sol gel process. Silicon dioxide was introduced via tetraethyl orthosilicate (TEOS) which was used as a coupling agent. Characterization of the materials was done using FT-IR, TEM, DRS, BET, and XRD.

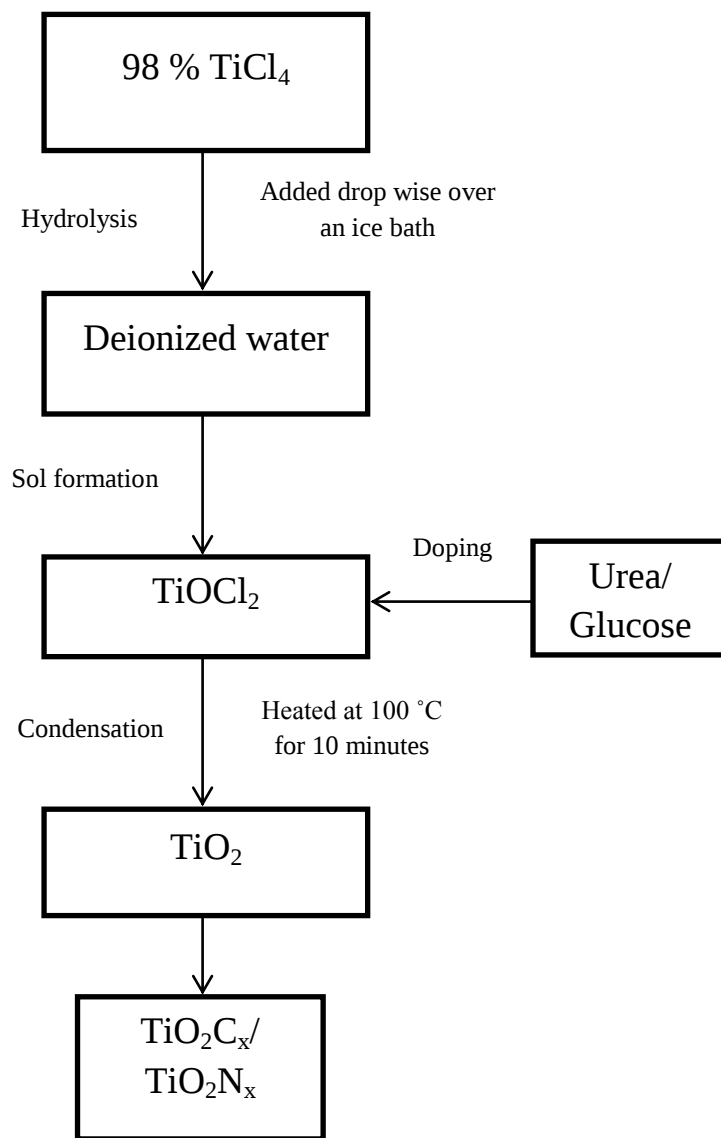


Figure 4.1: A schematic diagram to represent the Sol gel process using TiCl_4 precursor

4.2 Experimental

This section presents the procedures followed in the preparation of the photo-catalysts.

4.2.1 Preparation of undoped titanium dioxide

A volume of 11 mL of 9 M titanium tetrachloride (TiCl_4) was added drop-wise into 200 mL of distilled water in a beaker placed on an ice bath. The reaction is highly exothermic so very low temperatures were maintained throughout. The resulting sol was heated for ten minutes at a temperature of 100°C to allow hydrolysis. A white solution was formed.

The resulting precipitate was collected via filtration and re-suspended in deionized water. The pH was then adjusted to 8.0 using 0.1 M potassium hydroxide (KOH). The precipitate was washed several times with deionized water to remove excess chloride ions. It was collected via centrifugation and then dried at 60°C in an oven.

4.2.2 Calcination of the $\text{Ti}(\text{OH})_4$

The precipitate obtained from the sol gel process is amorphous, so calcination was performed to allow transformation from amorphous to the anatase phase of titanium dioxide. Calcination of titanium dioxide also helps improve the crystallinity of the nano-particles, which enhances photo-catalytic activity (Zhang *et.al*, 2003). Calcination was carried out in a programmable furnace, shown in Figure 4.2. The heating rate was $5^\circ\text{C}/\text{min}$ up to 600°C , and then maintained at 600°C for three hours to allow total conversion to anatase phase of titanium dioxide.



Figure 4.2: Programmable muffle furnace for calcination

4.2.3 Preparation of Carbon or nitrogen doped TiO_2

A carbon doped nano-crystalline TiO_2 photo-catalyst ($\text{TiO}_{2-x}\text{C}_x$) was prepared using a solution-phase carbonization method without adding any surfactants as templates. The procedure followed is similar to the one described in Section 4.2.1 for the preparation of undoped titanium dioxide except that 0.5 g of glucose was added during the heating process. Heating continued for ten minutes after which the resulting gel $\{(\text{Ti}(\text{OH})_4\text{C}_x)\}$ was collected in a similar fashion as described earlier. Nitrogen doped titanium dioxide ($\text{TiO}_{2-x}\text{N}_x$) was also prepared in a similar fashion, but using urea as the source of nitrogen.

4.2.4 Preparation of glass support

The glass substrate was cut into smaller plates that measured 6.5 cm by 6.5 cm. The glass plates were then washed with detergent, thoroughly rinsed with distilled water, and then dried in an oven at 60 °C. One of the surfaces was then treated with 40 % hydrofluoric acid for a period of 15 minutes. After the 15 minute period had lapsed, the acid was thoroughly rinsed off with running distilled water. The pH of the washings was checked to make sure that the surfaces were free of any acid. The glass plates were air dried, and then coated with a paste of the different photo-catalysts prepared. The hydrofluoric acid had an effect of introducing OH groups on the glass surface through etching as illustrated in Figure 4.3.

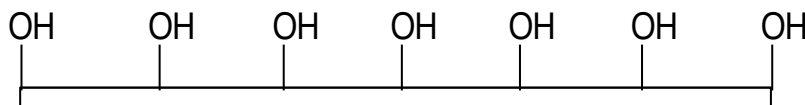


Figure 4.3: Glass surface after the etching process

4.2.5 Preparation of the photo-catalyst coating paste

A gram of titanium dioxide was weighed into a small beaker and 500 μL of ethanol, 200 μL of deionised water and 50 μL of hydrochloric acid were added under stirring. After 5 minutes of stirring, 1 mL of tetraethyl orthosilicate and 700 μL of a surfactant Triton X100 were added. Stirring was continued for another ten minutes. The purpose of the hydrochloric acid was to hydrolyse both titanium dioxide and tetraethyl orthosilicate (TEOS) to introduce OH groups. The TEOS acted as both coupling agent and precursor for silicon dioxide. The beaker contents were sonicated at 25 °C for 5 minutes to remove any air bubbles and to produce a lump-free paste. The

resulting paste was uniformly applied onto the etched surface of the glass plates, and dried in an oven at 60 °C before calcination in a muffle furnace at 600 °C for 2 hours to allow annealing to take place. Figure 4.4 illustrates the polymerization of TiO₂ with silicon dioxide on glass substrate.

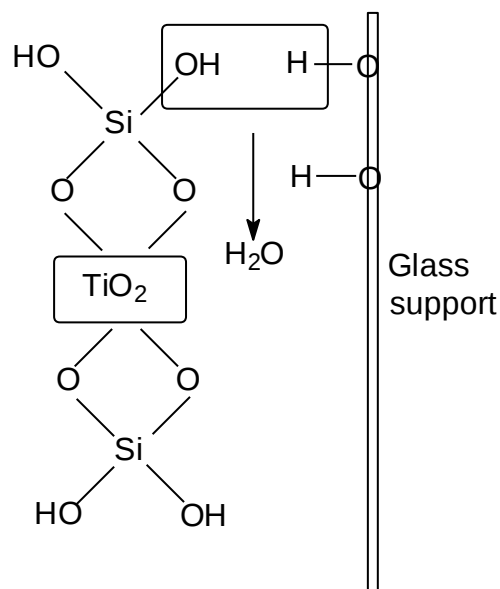


Figure 4.4: Polymerization of TiO₂ with SiO₂ on glass substrate

4.3 Characterization techniques

4.3.1 Fourier-transform infrared spectroscopy (FT-IR)

Infrared spectroscopy was used to identify the functional groups present in the synthesized samples of titanium dioxide. Fourier transform infrared (FT-IR) spectra of original and modified TiO₂ samples were obtained on a Perkin Elmer 2000 system. Scanning was done in the 4000 to 370 cm⁻¹ frequency range. Dried solids were pressed with KBr (FT-IR grade, Aldrich) and the pellets scanned 15 times using transmission mode with a resolution of 4 cm⁻¹.

4.3.2 X-ray diffraction (XRD)

Powder X-ray diffraction was used for crystal phase identification and estimation of the crystallite size using Equation 4.1. The x-ray diffraction analysis was carried out in locked couple mode with a Bruker-AXS D8 Advance diffractometer (Cu K α radiation with $\lambda = 1.5406$ Å) equipped with a PSD Lynx-Eye Si-strip detector (with 196 channels), at room temperature. The accelerating voltage and applied current were 40 kV and 40 mA respectively.

$$L = K\lambda / (\beta \cos \theta) \quad (4.1)$$

where λ is the wavelength of the X-ray radiation (Cu K $\alpha = 0.15406$ nm), K is a constant taken as 0.89, β is the line width at half maximum height, and θ is the diffracting angle.

4.3.3 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectra were obtained to check the shift in absorption edge of titanium dioxide after doping. Diffuse reflectance spectra (DRS) were acquired at room temperature using a diffuse reflectance attachment of a Cary 500 UV-Vis-NIR spectrophotometer. Spectra were acquired in the 200-800 nm range.

4.3.4 Surface area. The Brunauer-Emmett-Teller (BET)

The Brunauer-Emmett-Teller (BET) surface area was determined using a Micromeritics Pulse Chemisorb 2700 nitrogen adsorption apparatus. The samples were dried in a flow of helium gas at 250 °C and the surface area of the samples estimated by N₂ chemisorption.

4.3.5 Transmission electron microscopy (TEM)

Transmission electron microscopy was used to determine the composition and estimate particle thickness of the prepared photo-catalysts. The TEM images were recorded on a JEM 200CX transmission electron microscope (JEOL, Tokyo, Japan) at an accelerating voltage of 120 kV.

4.4 Results and discussion

This section describes the results obtained from the characterization of the materials that were prepared in this study.

4.4.1 FT-IR analysis of carbon doped photo-catalysts

FT-IR analysis was used to identify the functional groups expected in TiO_2 , $\text{TiO}_2\text{-SiO}_2$ composite, and carbon doped $\text{TiO}_2\text{-SiO}_2$ composite. Figure 4.5 shows the FT-IR spectra of the above mentioned photo-catalysts. The $\text{TiO}_2\text{-SiO}_2$ composite was prepared in a 1:1 ratio, the amount of carbon dopant was 5 %, and all the samples were calcined at 600 °C.

The labelled peaks can be ascribed to OH stretching vibration (around 3415 cm^{-1}), Si-O-Si band asymmetric stretching vibrations (1114 cm^{-1}), and Ti-O-Si linkage stretching band (961 cm^{-1}). The existence of Si-O-Ti bond in FT-IR analysis may be attributed to the existence of covalent bonding between amorphous SiO_2 and crystalline TiO_2 . The band for the asymmetric Si-O-Si stretching vibration was observed for all composite samples. The presence of Si-O-Si bond in FT-IR is caused by the formation of SiO_2 in the samples.

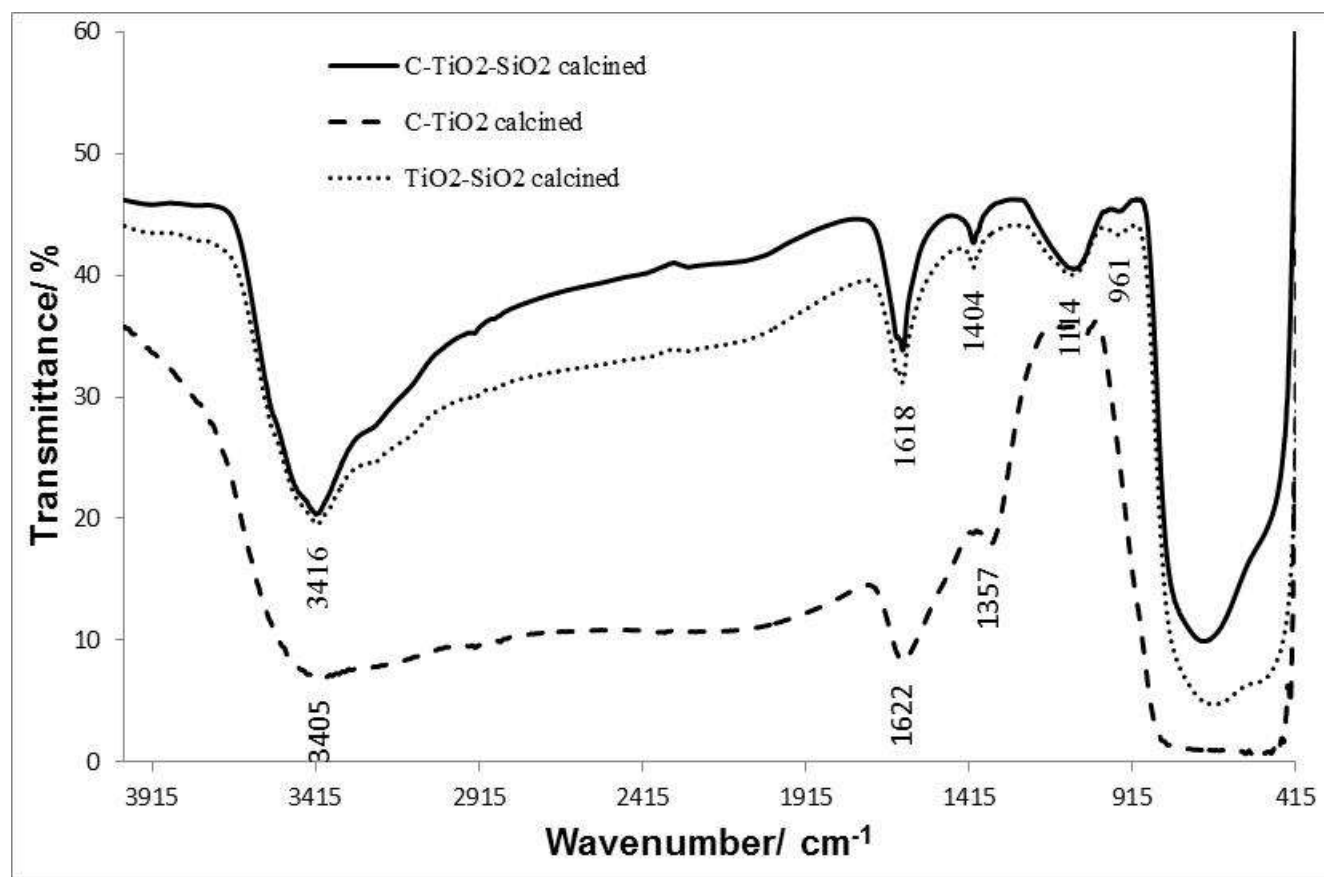


Figure 4.5: FT-IR spectra of C-TiO₂, C-TiO₂-SiO₂, and TiO₂-SiO₂

The results we obtained are in agreement with those reported by Guo *et.al*, 2011; and Lafond *et.al*, 2004. The peak around 1620 cm⁻¹ is due to the bending vibration of OH bond, which is assigned to the chemisorbed water, and the peak around 3415 cm⁻¹ is assigned to the stretching mode of OH bond and related to free water. The FT-IR spectra of anatase and rutile titanium dioxide are similar to each other, with both having a broad peak between 800 and 470 cm⁻¹ but with the anatase form displaying a valley in the peak centered around 600 cm⁻¹ (Jackson, 1998).

4.4.2 XRD analysis of C-TiO₂, C-TiO₂-SiO₂, and TiO₂-SiO₂

XRD analysis was used to identify the phase composition of the prepared photo-catalysts and establish the average particle sizes through the Scherrer equation 4.1. Figure 4.6 shows the XRD diffractograms of C-TiO₂, C-TiO₂-SiO₂, and TiO₂-SiO₂.

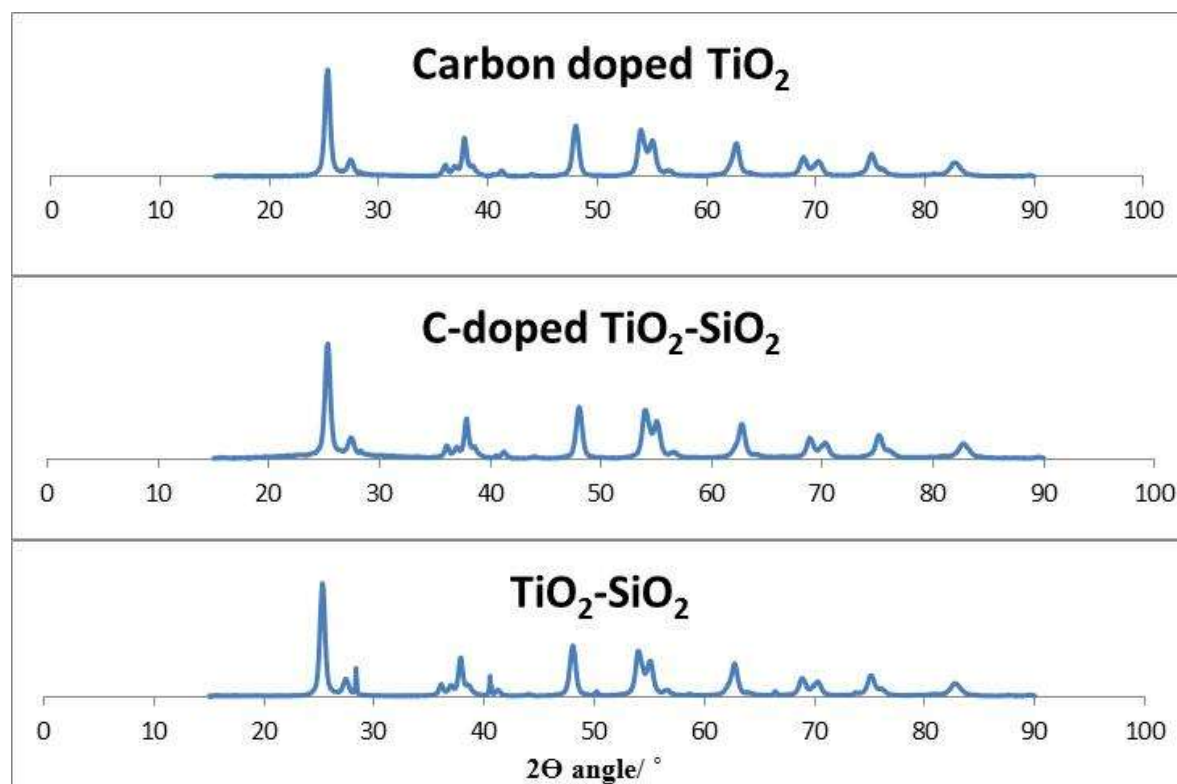


Figure 4.6: XRD diffractograms of C-TiO₂, C-TiO₂-SiO₂& TiO₂-SiO₂

The XRD analysis revealed that the prepared catalysts (C-TiO₂, C-TiO₂-SiO₂, and TiO₂-SiO₂) were predominantly in the anatase phase. The rutile phase was also observed although it was not as much as the anatase. The anatase phase of titanium dioxide has the most photo-catalytic activity (Sclafani and Herrman, 1996), so the prepared catalysts exhibited the desired phase for the purpose of photo-catalytic activity. This means that the anatase structure was still maintained

even after doping, and the doping was probably substitutional whereby the dopant replaces some of the lattice oxygen atoms (Singh *et.al*, 2008). The diffractograms of C-TiO₂ and C-TiO₂-SiO₂ showed similar patterns, but the one for TiO₂-SiO₂ showed peaks at 2 Theta angles of 28 and 41 which were not present in the former suggesting that these could have been removed by carbon doping. Table 2 shows the average particle dimensions that were calculated from the XRD major peaks using the Scherrer equation 4.1.

4.4.2.1 Scherrer particle size

Equation 4.1 (Scherrer) was used to calculate the average crystal size of the photo-catalysts. Table 2 shows the Scherrer particle sizes of prepared photo-catalysts determined from XRD analysis.

Table2: Scherrer particle sizes of prepared photo-catalysts determined from XRD analysis

Photo-catalyst	Scherrer particle size (nm)
C-TiO ₂	11.2
C-TiO ₂ -SiO ₂	14.7
TiO ₂ -SiO ₂	15.0

Carbon doped titanium dioxide had the smallest nanoparticle size (11.2 nm) followed by carbon doped titanium dioxide silicon dioxide composite (14.7 nm) and titanium dioxide silicon dioxide composite (15.0 nm). Compositing titanium dioxide with silicon dioxide had an effect of increasing the overall particle size after calcination at 600 °C as well as improved photo-catalytic activity.

4.4.3 BET surface area analysis of C-TiO₂, C-TiO₂-SiO₂, & TiO₂-SiO₂

The surface area of the prepared photo-catalysts was analyzed using BET surface area analysis.

Table 3 below summarizes the BET surface area measurements for the TiO₂-SiO₂ composites.

Table 3: BET surface area analysis results for photo-catalysts

Photo-catalyst	Surface area (m ² g ⁻¹)	Pore size (nm)
C-TiO ₂	95.4	19.5
C-TiO ₂ -SiO ₂	72.2	22.4
TiO ₂ -SiO ₂	56.8	23.6

Carbon doped titanium dioxide presented the largest surface area (95.4 m²g⁻¹), followed by carbon doped titanium dioxide-silicon dioxide composite (72.2 m²g⁻¹) and lastly undoped titanium dioxide-silicon dioxide which had a surface area of 56.8 m²g⁻¹. An increase in surface area correlates to an increase in the photo-catalytic activity since a large surface will be exposed for the reactions to occur although several other factors contribute to the overall performance of a photo-catalyst besides surface area. Considering the results in Tables 2 and 3, it was observed that an increase in BET surface area corresponded to a decrease in the particle size of the photo-catalyst prepared. Also a decrease in pore size corresponded to a decrease in the particle size.

4.4.4 DRS analysis of C-TiO₂, C-TiO₂-SiO₂, & TiO₂-SiO₂

Diffuse reflectance spectroscopy analysis was used to calculate the band gap energy and to establish the shift in the absorption band edge of the prepared photo-catalysts. Figure 4.7 shows

the diffuse reflectance spectra and derivatives of carbon modified titanium dioxide-silicon dioxide composites.

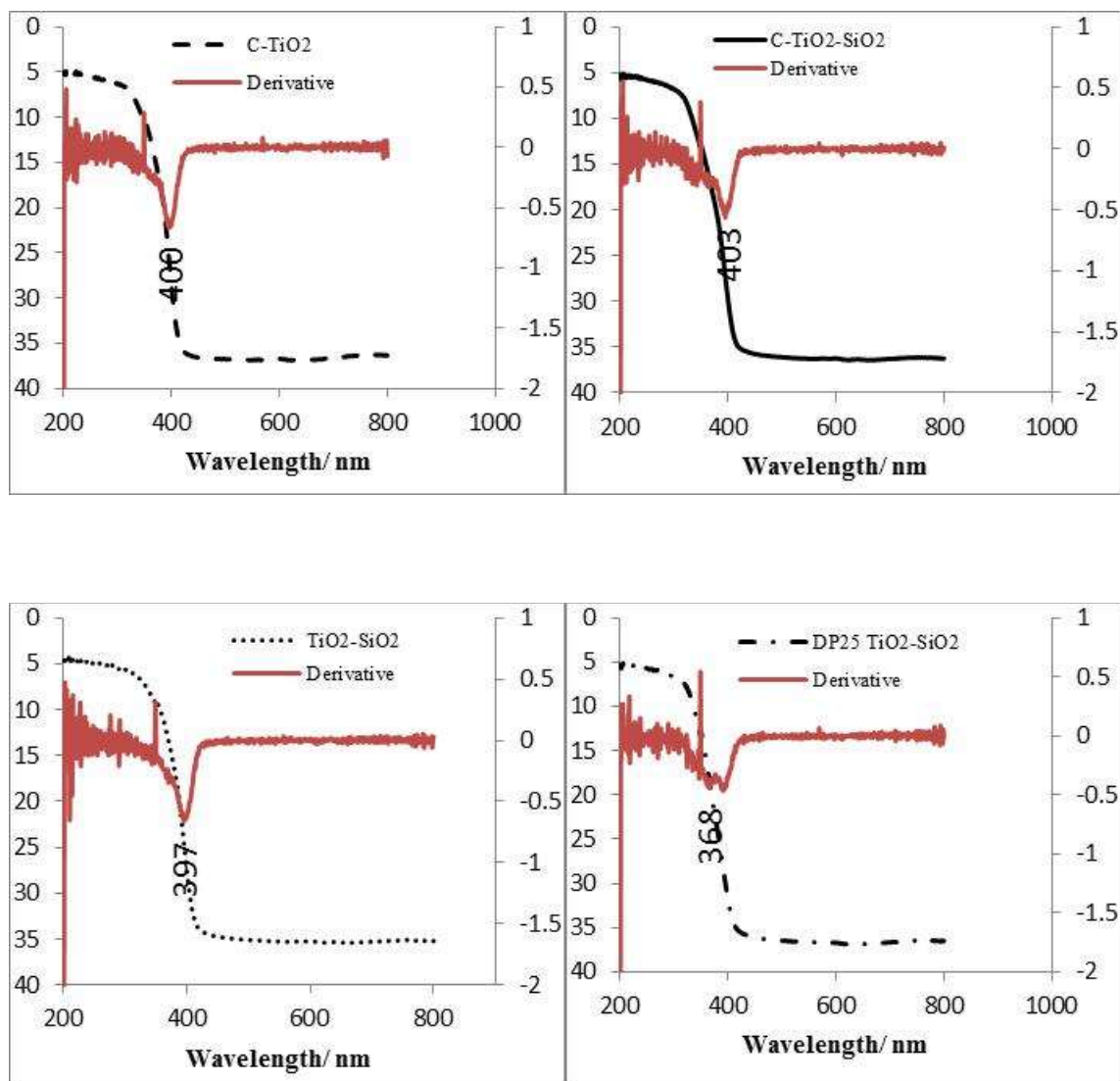


Figure 4.7: DRS spectra & derivatives of C-TiO₂, C-TiO₂-SiO₂, TiO₂-SiO₂, & DP25 TiO₂-SiO₂

Degussa P25 titanium dioxide composite with silicon dioxide had an absorption band edge of 368 nm, sol gel-prepared titanium dioxide-silicon dioxide composite had an absorption band edge of 397 nm while carbon doped titanium dioxide had an absorption band edge of 400 nm and carbon doped titanium dioxide-silicon dioxide composite had an absorption band edge of 403

nm. From the diffuse reflectance data obtained it was noticed that combining titanium dioxide with silicon dioxide did not shift the absorption band edge of titanium dioxide although it had an effect on the performance of the photo-catalyst. Doping titanium dioxide with carbon allowed the reduction of its band gap. After doping the absorption band edge of titanium dioxide shifted from the UV region into the visible region (400 nm for C-TiO₂). Xu *et.al*, 2006 reported a visible light responsive titanium dioxide after doping with carbon.

Band gap energies of the photo-catalysts were calculated using diffuse reflectance data and Equation 4.2.

$$E_g = \frac{1239}{\lambda} \quad (4.2)$$

Table 4 shows the results obtained from the band gap energy calculations.

Table 4: Band gap energies of photo-catalysts

Photo-catalyst	Band gap
C-TiO ₂	3.0
C-TiO ₂ -SiO ₂	3.0
TiO ₂ -SiO ₂	3.1
DP25-TiO ₂ -SiO ₂	3.3

Carbon doped titanium dioxide exhibited a band gap of 3.0 eV, so the doping process had an effect on band gap reduction. Carbon doped titanium dioxide silicon dioxide composite also

exhibited a similar band gap energy of 3.0 eV. Compositing titanium dioxide with silicon dioxide had no effect on band gap energy reduction as can be seen from the result obtained. $\text{TiO}_2\text{-SiO}_2$ gave a band gap energy of 3.1 eV which was typical of unmodified titanium dioxide. Degussa P25 titanium dioxide composite with silicon dioxide gave a band gap energy of 3.3 eV, which suggests that modifying titanium dioxide with silicon dioxide does not alter the band gap of titanium dioxide but increases particle size.

4.4.5 FT-IR analysis of nitrogen doped photo-catalysts

FT-IR analysis was used to identify the functional groups present in nitrogen doped titanium dioxide-silicon dioxide composites. Figure 4.8 shows the FT-IR spectra of N-TiO_2 , $\text{N-TiO}_2\text{-SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$. The $\text{TiO}_2\text{-SiO}_2$ composite was prepared in a 1:1 ratio, the amount of nitrogen dopant was 5 %, and all the samples were calcined at 600 °C. The peaks identified were as follows 3417 cm^{-1} OH stretching vibrations, 1619 cm^{-1} OH bending mode of chemisorbed water, 1107 cm^{-1} Si-O-Si asymmetric stretching vibrations and 959 cm^{-1} Ti-O-Si linkage stretching band. The broad peak between 800 and 470 cm^{-1} identifies titanium dioxide and the valley at around 600 cm^{-1} was due to the anatase phase of titanium dioxide. FT-IR analysis confirmed the presence of the expected functional groups.

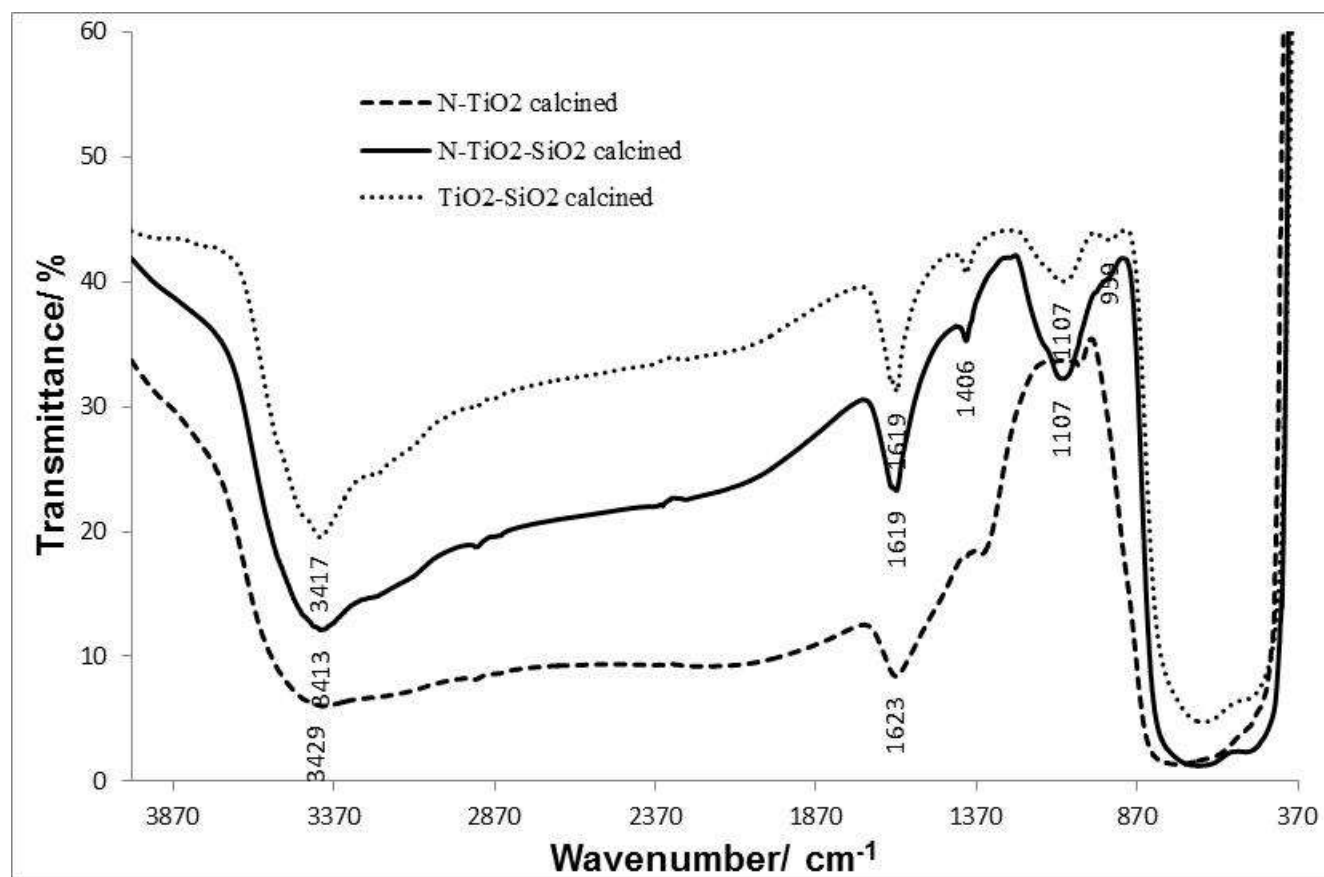


Figure 4.8: FT-IR spectra of N-TiO₂, N-TiO₂-SiO₂, & TiO₂-SiO₂

4.4.6 XRD analysis of N-TiO₂, N-TiO₂-SiO₂, and TiO₂

X-ray diffraction analysis was used to identify the TiO₂ phases of the nitrogen doped photo-catalysts. The diffractograms are shown in Figure 4.9. The three photo-catalysts were found to be predominantly anatase. However, a few rutile peaks at 2 Theta angles of 27.5, 36, 39, 44 and 54.2 were observed. The temperature used for calcination was 600 °C, which is the temperature at which transformation to the rutile phase of titanium dioxide begins. The diffractograms for both nitrogen and carbon doped titanium dioxide-silicon dioxide composites were similar and could thus not be used to establish the different effects resulting from each of the two dopants.

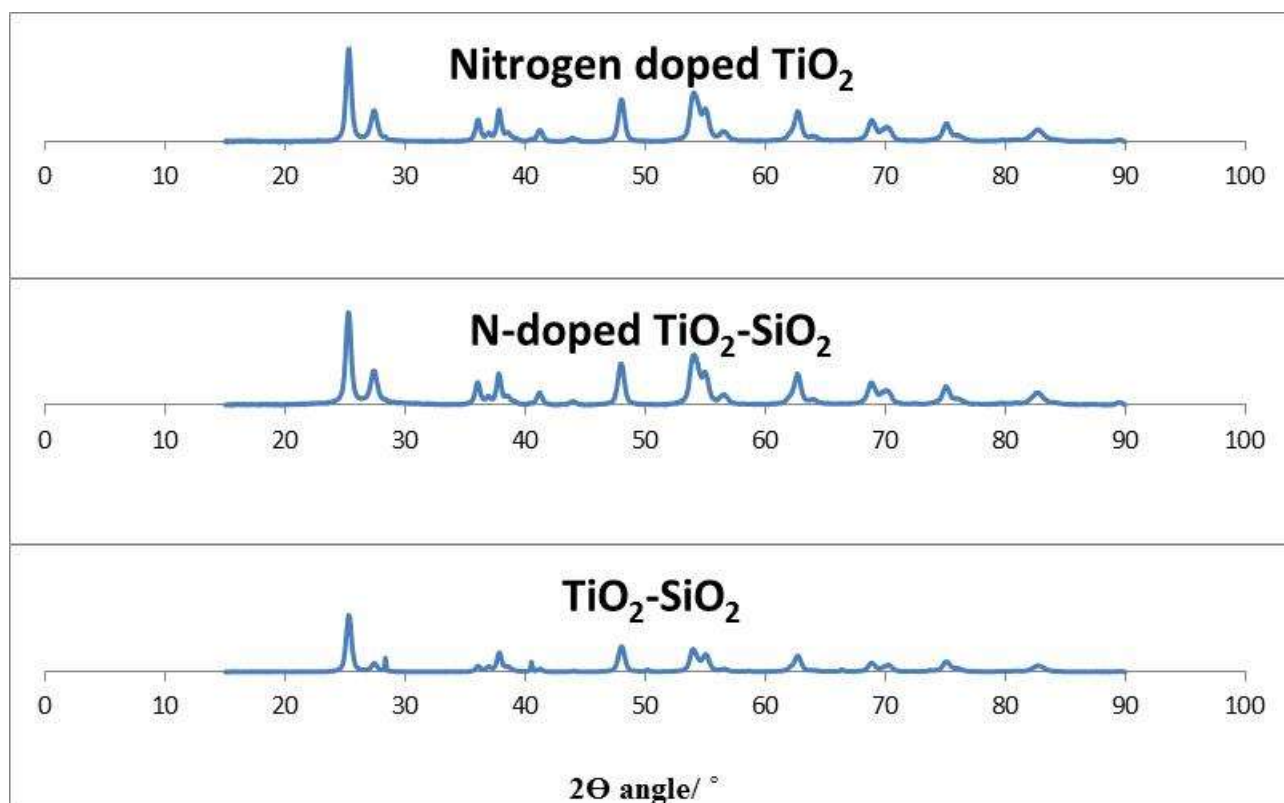


Figure 4.9: XRD diffractograms of N-TiO₂, N-TiO₂-SiO₂ & TiO₂-SiO₂

Table 5 shows the average particle dimensions that were calculated from the XRD major peaks using the Scherrer equation.

4.4.6.1 Scherrer particle size

Table 5 shows the average crystal thickness obtained through the Scherrer equation. The particle sizes obtained were as follows 15.5 nm, 15.9 nm, and 15.0 nm for N-TiO₂, N-TiO₂-SiO₂ and TiO₂-SiO₂ respectively. From the results, it can be concluded that nitrogen doping resulted in larger particle size compared to carbon doping. It seemed that carbon doping reduced particle size while nitrogen doping increased particle size.

Table 5: Scherrer particle size of N-TiO₂, N-TiO₂-SiO₂, & TiO₂-SiO₂

Photo-catalyst	Scherrer particle size (nm)
N-TiO ₂	15.5
N-TiO ₂ -SiO ₂	15.9
TiO ₂ -SiO ₂	15.0

4.4.7 BET surface area analysis of N-TiO₂, N-TiO₂-SiO₂, & TiO₂-SiO₂

BET surface area analysis was used to establish the pore sizes and surface areas of the following compounds: N-TiO₂, N-TiO₂-SiO₂ and TiO₂-SiO₂. Table 6 shows the BET surface area analysis data obtained.

Table 6: BET surface area analysis results for nitrogen doped photo-catalyst

Photo-catalyst	Surface area (m ² g ⁻¹)	Pore size (nm)
N-TiO ₂	52.2	24.1
N-TiO ₂ -SiO ₂	44.4	25.0
TiO ₂ -SiO ₂	56.8	23.6

In general, as particle size decreases the BET surface area increases. The BET surface areas obtained tallied with the particle sizes. TiO₂-SiO₂ had the smallest particle size (15.0 nm) with the largest surface area of 56.8 m²g⁻¹ followed by N-TiO₂ which had a particle size of 15.5 nm and surface area 52.2 m²g⁻¹, and lastly N-TiO₂-SiO₂ which had a particle size of 15.9 and surface area 44.4 m²g⁻¹. Commercial titanium dioxide is reported in literature to have on average a BET

surface of $50 \text{ m}^2\text{g}^{-1}$ (Guo *et.al*, 2011). Nitrogen doping seemed to increase pore size as well as particle size but reduced BET surface areas as shown by a comparison between N doped and undoped $\text{TiO}_2\text{-SiO}_2$ composites.

4.4.8 DRS analysis of N-TiO₂, N-TiO₂-SiO₂& TiO₂-SiO₂

The nitrogen doped photo-catalysts were analyzed by diffuse reflectance spectroscopy to establish the amount of shift in their absorption band edges. Figure 4.10 shows the diffuse reflectance spectra obtained and their derivatives. Doping titanium dioxide with nitrogen allowed the reduction of its band gap resulting in a shift in its absorption band edge from UV into the visible region. The obtained absorption band edges were 402 nm, 400 nm, 397 nm, and 368 nm for N-TiO₂, N-TiO₂-SiO₂, TiO₂-SiO₂, and DP25 TiO₂ respectively.

A shift into the visible region allows the utilization of visible light in the activation of the titanium dioxide photo-catalyst. The visible region has an advantage in that it is a much wider spectrum compared with the ultraviolet region; hence it improves the performance of the titanium dioxide photo-catalyst. Other researchers have reported similar results after carrying out nitrogen doping on titanium dioxide (Asahi *et.al*, 2001; Morikawa *et.al*, 2001).

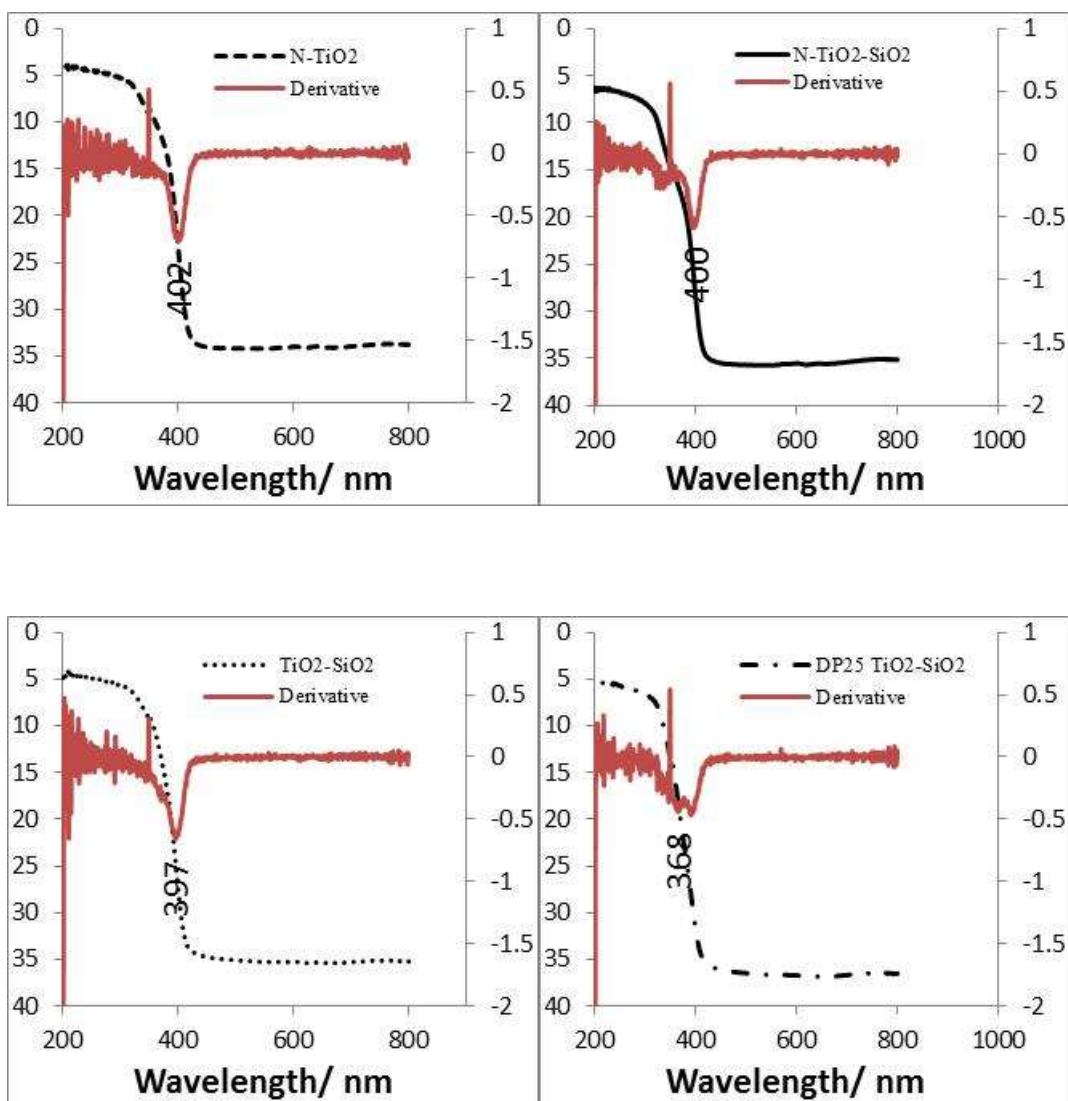


Figure 4.10: DRS spectra of N-TiO₂, N-TiO₂-SiO₂, TiO₂-SiO₂, & DP25 TiO₂

The diffuse reflectance data obtained was also used to calculate the band gap energies of the prepared photo-catalysts using Equation 4.1. The results obtained are shown in Table 7 showing that N-TiO₂ and N-TiO₂-SiO₂ gave band gap energy of 3.0 eV, while TiO₂-SiO₂ and DP25 TiO₂ gave 3.1 and 3.3 eV respectively. After doping with nitrogen, a reduction in the band gap of

titanium dioxide was achieved. Unmodified titanium dioxide has a band gap energy of 3.2 eV, so nitrogen doping resulted in a 0.2 eV reduction in the band gap energy of titanium dioxide.

Table 7: Band gap energies of N-TiO₂, N-TiO₂-SiO₂, TiO₂-SiO₂ & DP25 TiO₂

Photo-catalyst	Band gap energy (eV)
N-TiO ₂	3.0
N-TiO ₂ -SiO ₂	3.0
TiO ₂ -SiO ₂	3.1
DP25 TiO ₂	3.3

4.4.9 TEM analysis

Transmission electron microscopy was used to analyse the final three photo-catalysts that were to be used in the photo-decomposition studies of the two model organic contaminants (methyl orange and phenol), and also in the evaluation of antimicrobial properties. TEM images were obtained for the nano-composites TiO₂-SiO₂, C-TiO₂-SiO₂, and N-TiO₂-SiO₂ as shown in Figure 4.11. The images were taken at a scale of 500 nm. The particles obtained were ovoid in shape. The particle sizes were estimated using the scale bar on the bottom right hand side of the images, and the estimated particle sizes are recorded in Table 8.

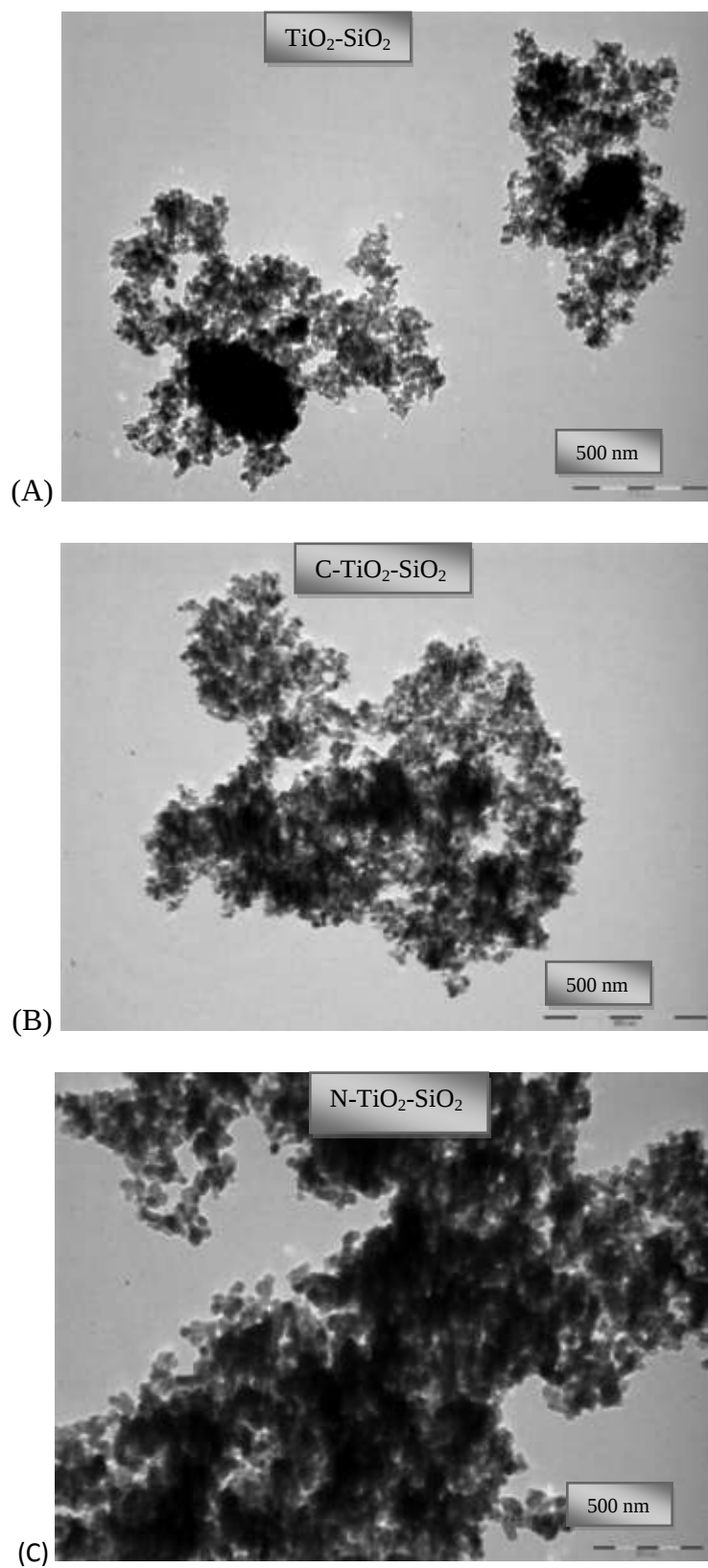


Figure 4.11: TEM images of $\text{TiO}_2\text{-SiO}_2$ (A), $\text{C-TiO}_2\text{-SiO}_2$ (B), & $\text{N-TiO}_2\text{-SiO}_2$ (C)

Table 8: TEM particle sizes of $\text{TiO}_2\text{-SiO}_2$, $\text{C-TiO}_2\text{-SiO}_2$, & $\text{N-TiO}_2\text{-SiO}_2$

Photo-catalyst	TEM particle size (nm)
$\text{TiO}_2\text{-SiO}_2$	14.7
$\text{C-TiO}_2\text{-SiO}_2$	14.4
$\text{N-TiO}_2\text{-SiO}_2$	16.6

The carbon doped composite ($\text{C-TiO}_2\text{-SiO}_2$) gave the smallest particle size (14.4 nm), followed by the $\text{TiO}_2\text{-SiO}_2$ composite (14.7 nm), and the $\text{N-TiO}_2\text{-SiO}_2$ composite had a particle size of 16.6 nm. The trend in particle sizes for the three composites agreed with the one obtained from XRD data through the use of the Scherrer equation. Carbon proved to be a more effective dopant than nitrogen in terms of particle size reduction.

4.4.10 EDX analysis

Energy dispersive X-ray analysis was used for elemental analysis to determine if carbon or nitrogen dopant had been incorporated into the titanium dioxide lattice. Figure 4.12 shows the EDX spectra obtained for C-TiO_2 and N-TiO_2 . EDX analysis revealed that carbon and nitrogen dopants were successfully incorporated into the titanium dioxide lattice. The EDX spectrum for nitrogen doped titanium dioxide also showed the presence of carbon. This can be explained from the fact that urea was used as the nitrogen source, and urea also contains carbon which resulted in the co-doping of titanium dioxide. The amount of carbon incorporated into the titanium dioxide lattice was 4.5 % and that of nitrogen 5.2 %. Doping of titanium dioxide was successfully carried out.

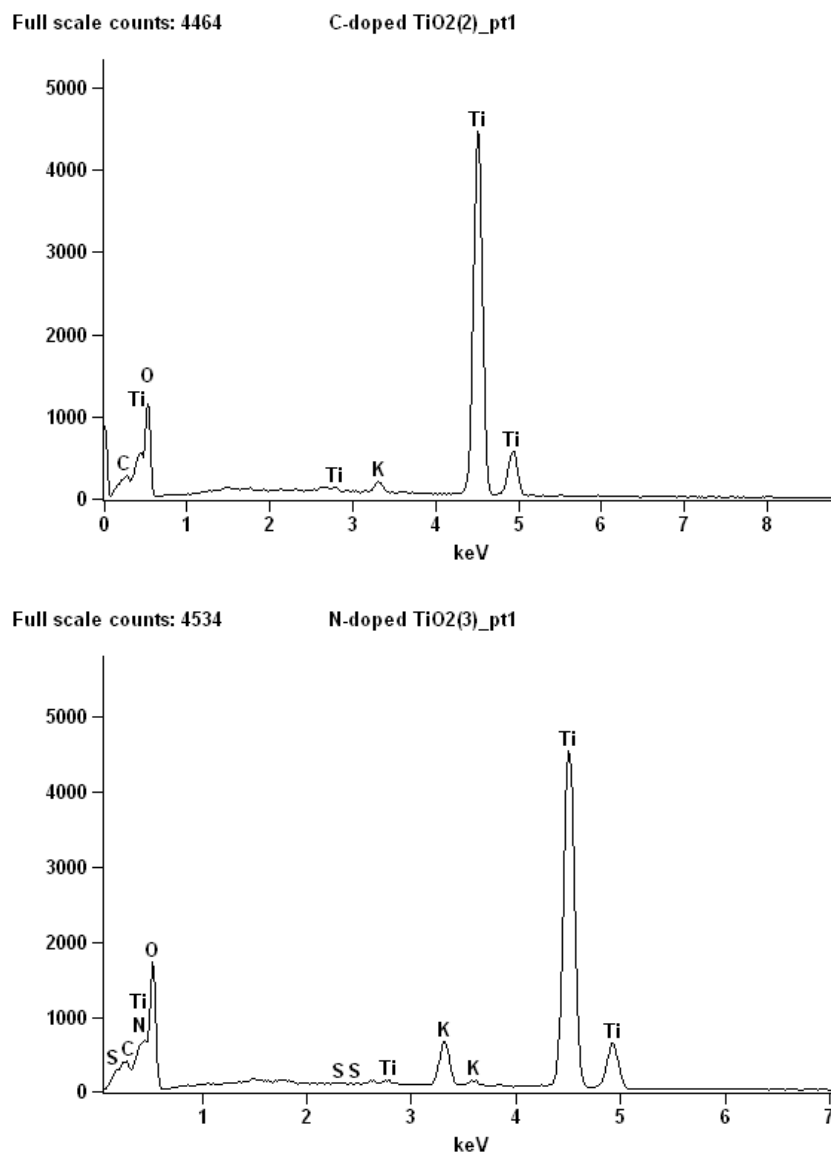


Figure 4.12: EDX spectra of C-TiO₂ and N-TiO₂

4.4.11 Conclusion

Photo-catalytic nano-composites (TiO₂-SiO₂, C-TiO₂-SiO₂, and N-TiO₂-SiO₂) of titanium dioxide and silicon dioxide were successfully prepared using the sol-gel method and acid hydrolysis of tetraethyl orthosilicate the precursor to incorporate silicon dioxide. FT-IR, XRD, and EDX analyses confirmed the successful preparation of these carbon and nitrogen doped

nano-composites. Particle size, surface area, and band gap values were established through XRD, TEM and DRS analyses. The particle sizes obtained were well in the nano-range. The doping process allowed the utilization of the visible light spectrum by the photo-catalysts, through the reduction of the band gap energy which shifted the absorption band edge from the UV region of 368 nm into the visible light region of 403 nm. The immobilization of the nano-composites onto glass substrate was successfully carried out using tetraethyl orthosilicate which acted as both a binder and precursor for silicon dioxide.

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CHAPTER 5

5. Evaluation of the photo-catalytic activity of carbon/nitrogen doped $\text{TiO}_2\text{-SiO}_2$ immobilized on glass substrate

5.1 Introduction

This chapter describes the procedures followed in the evaluation of the photo-catalytic properties of the prepared photo-catalysts. The results obtained from the photo-oxidation experiments are presented together with a discussion and a conclusion. The prepared photo-catalysts were evaluated for their photo-catalytic properties using model organic pollutants. The organic pollutants used were methyl orange (MeO) and phenol red (PRed).

The photo-catalysts used in the photo-oxidation studies were titanium dioxide silicon dioxide composite ($\text{TiO}_2\text{-SiO}_2$), carbon-doped titanium dioxide-silicon dioxide composite ($\text{C-TiO}_2\text{-SiO}_2$), and nitrogen doped titanium dioxide silicon dioxide composite ($\text{N-TiO}_2\text{-SiO}_2$). Photo-oxidation experiments were carried out to establish the rate of photo-catalytic breakdown of organics by each photo-catalyst.

5.2 Photo-catalytic activity measurements

All photo-catalytic activity measurement experiments were carried out in an 800 mL beaker, which had its sidewalls covered with aluminium foil to prevent light from other sources from entering the beaker. This ensured that all the light came from one direct source. The top of the beaker was kept open to allow free air circulation. The reactor setup used for the photo-oxidation

experiments is shown in Figure 5.1. All the experiments were carried out in a dark room to eliminate other light sources.



Figure 5.1: Photo-oxidation reactor setup

For each run, 250 mL of synthetic organic pollutant dissolved in water was exposed to a photocatalytic surface measuring 42 cm^2 . The system was kept stirring to homogenize, and temperature maintained at 30°C . Aliquots were drawn hourly after exposure to the light source, and changes in concentration of the organics monitored using a Perkin Elmer Lambda 25

UV/VIS spectrophotometer. The initial concentration for both methyl orange and phenol red was 10 mg/L.

5.2.1 Determination of lambda max for methyl orange & phenol red

The lambda max for both methyl orange and phenol red were determined using the scan mode of the UV/VIS spectrophotometer. The lambda max gave the peak wavelength at which the two dyes absorb. Methyl orange gave a λ_{max} of 462.0 nm and phenol red was at 557.9 nm. The instrument was then set at these two wavelengths in the concentration mode to allow the determination of concentration as the photo-degradation process proceeded.

5.2.2 Preparation of calibration standards

Calibration standards were prepared for both methyl orange and phenol red. Five standards were prepared for each dye, with concentrations 2, 4, 6, 8, and 10 mg/L. A 10 mg/L stock solution for both methyl orange and phenol red was prepared from which serial dilutions were made to get to the desired concentrations. Figure 5.2 shows the calibration curve for methyl orange.

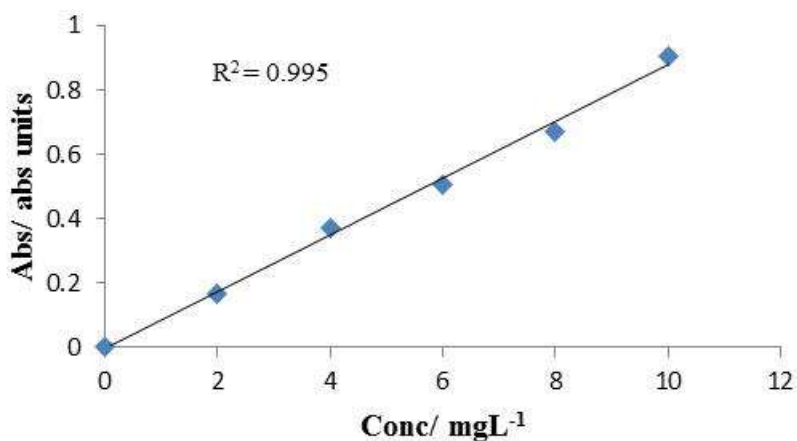


Figure 5.2: Calibration curve for methyl orange

The calibration curve obtained for phenol red is shown in Figure 5.3.

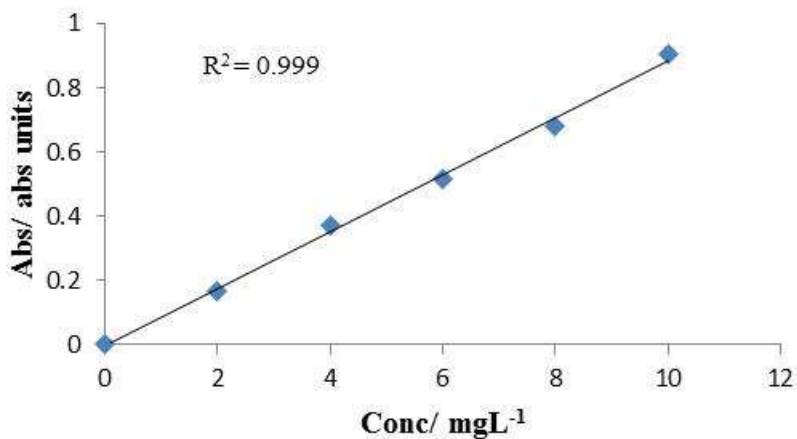


Figure 5.3: Calibration curve for phenol red

5.3 Results and discussion

This section presents the results obtained from the photo-degradation measurements. Photo-oxidation was carried out both under ultraviolet and visible light irradiation. The UV light source used was a Camag 40 watt lamp operating at two wavelengths, 254 nm and 366 nm and the visible light source was sunlight.

5.3.1 Photo-degradation of methyl orange using TiO₂-SiO₂

Photo-oxidation of methyl orange was carried out under both strict UV and visible light irradiation. Figure 5.4 shows the photo-degradation profiles obtained over a period of ten hours. Before irradiation of the photo-catalyst with UV or visible light, an hour was allowed in order to

account for any changes in concentration due to adsorption of organics on the photo-catalyst surface.

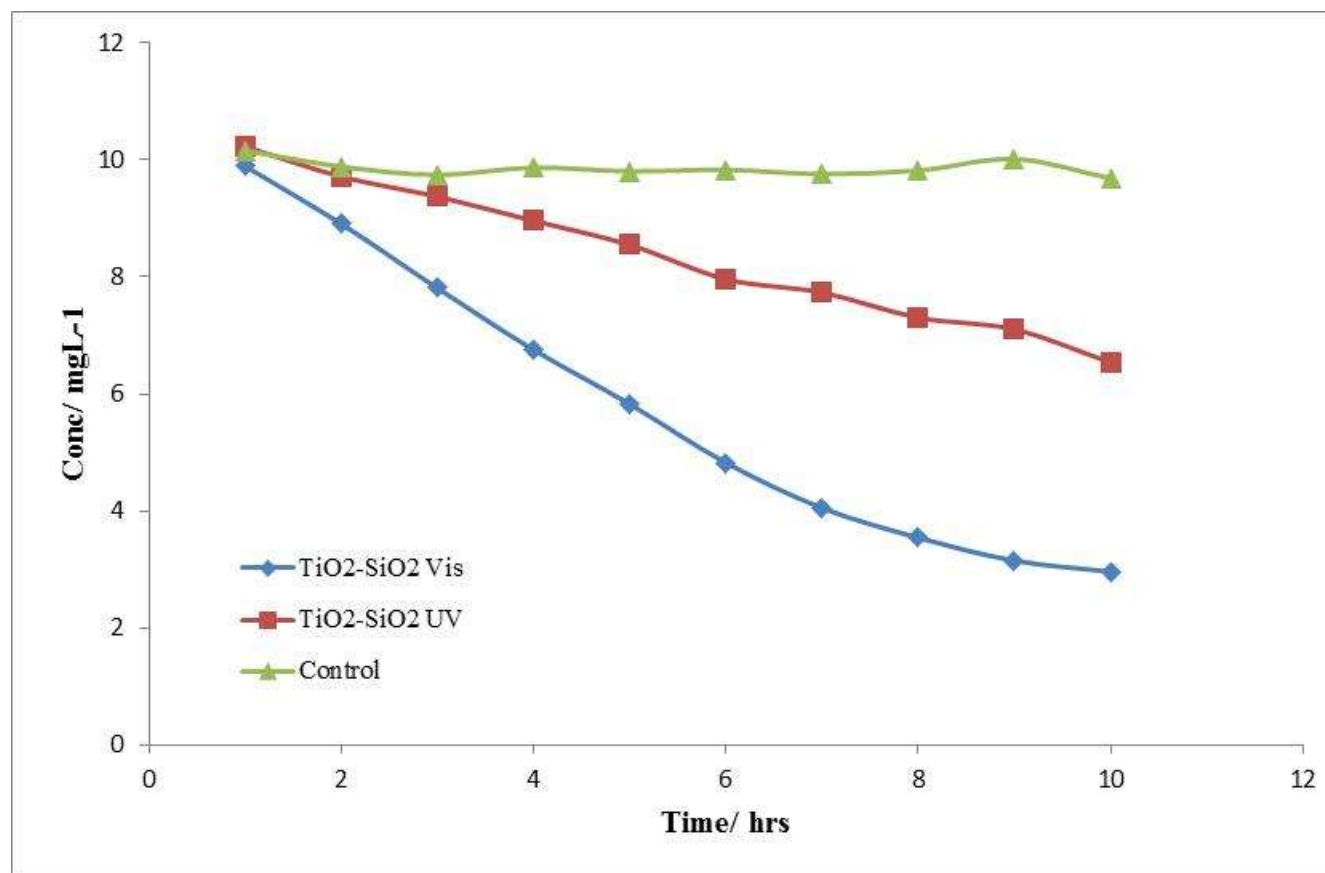


Figure 5.4: Photo-degradation profiles of MeO using TiO₂-SiO₂ photo-catalyst under UV lamp (366 nm) and visible light

The control of the experiment was kept in a darkroom in the presence of both catalyst and methyl orange. Only slight changes in concentration were observed, and these can be attributed to adsorption of methyl orange onto the TiO₂-SiO₂ surface. In the photo-degradation of methyl orange by TiO₂-SiO₂ under UV light irradiation the rate of breakdown was significant. To investigate the visible light activity of the immobilized TiO₂-SiO₂ photo-catalyst, the experiment

was carried out under sunlight irradiation, and there was marked improvement in the rate of photo-catalytic breakdown of methyl orange. The introduction of silicon into the system which has a much smaller band gap allowed the utilization of the visible light which led to an increased rate of photo-decomposition of MeO. Kim *et.al*, 2005 did similar work, and they proposed two models to explain their results. The first one involved movement of electrons from the valence band of TiO_2 to that of silicon then back to the conduction band of TiO_2 which allows the utilization of longer wavelength light and the second one involved movement of electrons from the valence band of silicon to its conduction band, then to the conduction band of TiO_2 .

5.3.2 Photo-degradation of MeO by C- TiO_2 - SiO_2 , N- TiO_2 - SiO_2 & TiO_2 - SiO_2

The performance of the three different nano-composite photo-catalyst materials was investigated in the photo-decomposition of MeO under the irradiation of UV or visible light. Figure 5.5 shows the trend observed in the photo-degradation of MeO in water.

Under UV light irradiation, photo-degradation of methyl orange proceeded at a much slower rate. There was not much of a difference in the performance of the photo-catalysts TiO_2 - SiO_2 , N- TiO_2 - SiO_2 , and C- TiO_2 - SiO_2 (indicated in Figure 5.5 by the middle three profiles respectively). The photo-catalyst C- TiO_2 - SiO_2 had a slightly faster rate of MeO breakdown, followed by N- TiO_2 - SiO_2 , and lastly TiO_2 - SiO_2 . All the runs were done in triplicate and the average taken. The experiment was also carried out under visible light irradiation and the performance of the three photo-catalysts was significant as compared to those run under strict UV light irradiation. There was marked improvement in the rate of photo-catalytic breakdown of methyl orange. Under

visible light irradiation N-doped $\text{TiO}_2\text{-SiO}_2$ gave the fastest rate of photo-catalytic breakdown of MeO, then $\text{TiO}_2\text{-SiO}_2$, and lastly C-doped $\text{TiO}_2\text{-SiO}_2$.

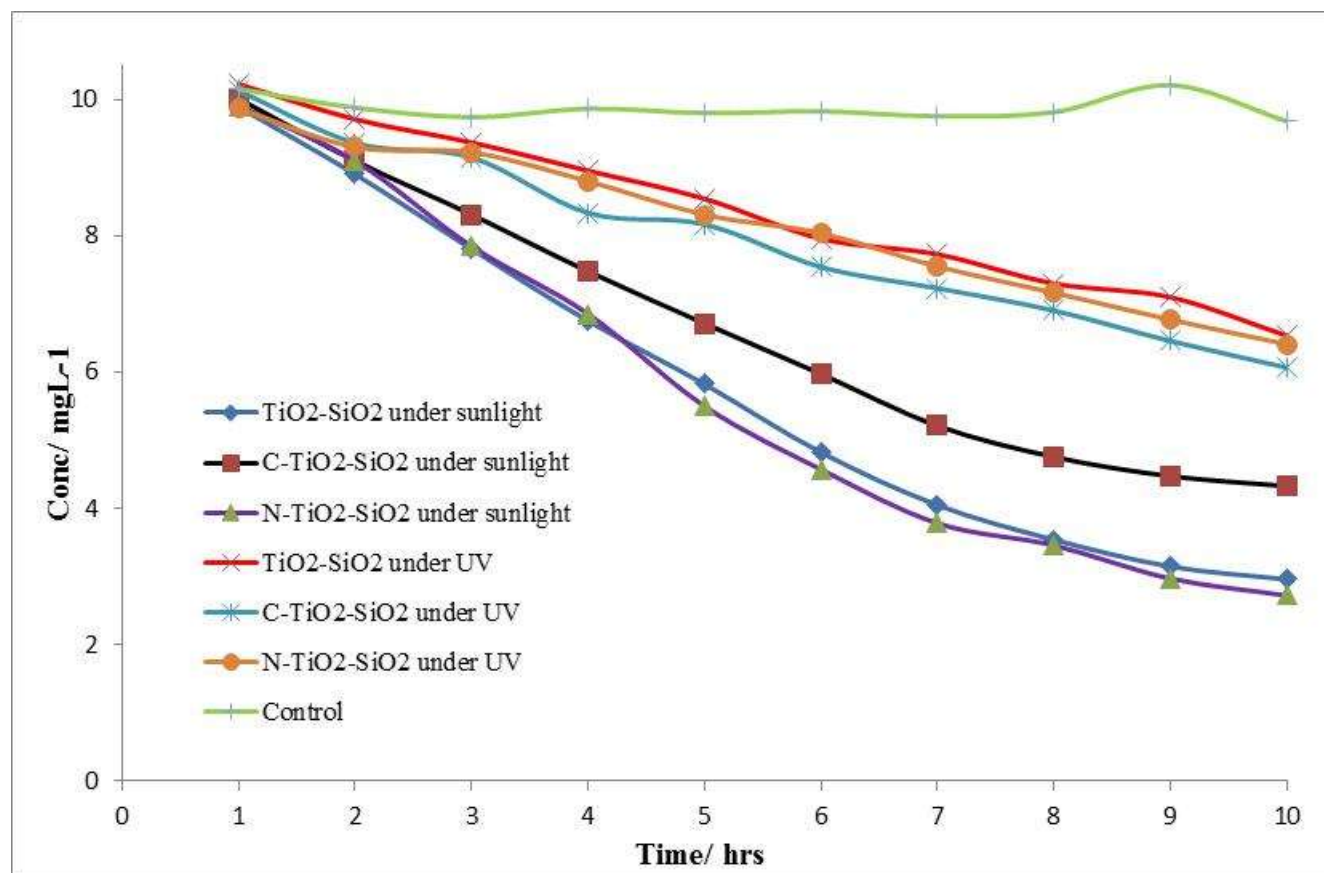


Figure 5.5: Photo-degradation profiles of MeO using C-TiO₂-SiO₂, N-TiO₂-SiO₂, & TiO₂-SiO₂ as photo-catalysts

The visible region is a much wider spectrum, so this increases the chances of light of the correct wavelength hitting the surface of the photo-catalyst to activate it (Xu *et.al*, 2006). Modification with carbon, nitrogen, and compositing with silicon dioxide allowed the photo-catalysts to be visible light responsive, although they maintained some UV light activity. After seven hours of exposure to visible light, about 70 % of the methyl orange had been broken down.

5.3.3 Comparison of the performances of immobilized and powder TiO_2

The performance of immobilized titanium dioxide was compared to that of free powder TiO_2 in breaking down methyl orange. Figure 5.6 shows the degradation profiles obtained.

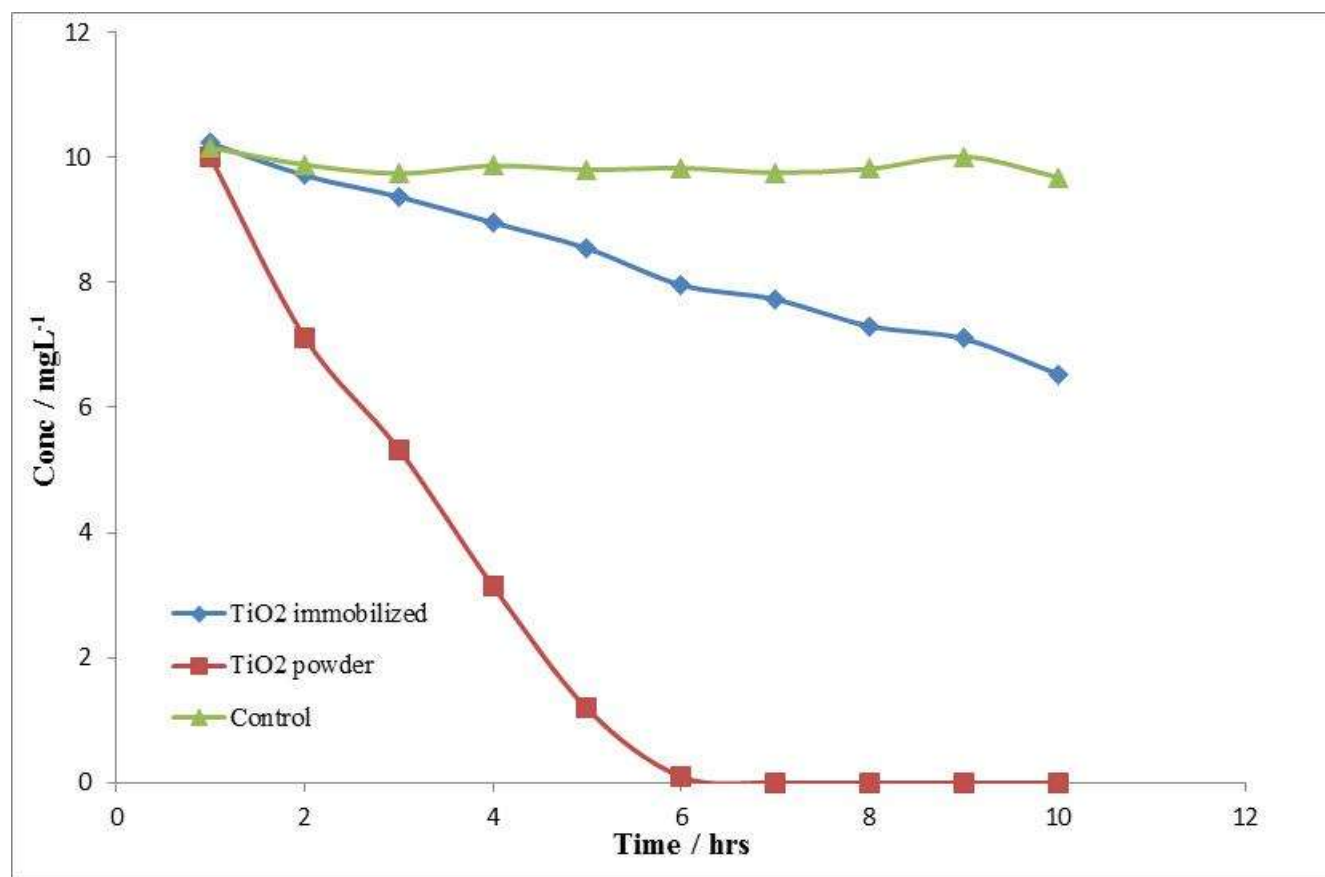


Figure 5.6: Photo-degradation profiles of MeO using powder and immobilized TiO_2 as photocatalysts under strict UV light

The experiment was carried out under strict UV light irradiation and it was observed that immobilization of titanium dioxide greatly reduced the rate of photo-degradation of MeO. Reduction of the available surface area for the reactions to occur is one of the major reasons

leading to the drop in the rate of photo-oxidation. When using powdered TiO_2 , a larger surface area is presented, so more of the MeO can be adsorbed onto the surface of the catalyst which helps speed up the rate of breakdown. In four and half hours about 95 % of the methyl orange had been broken down using free TiO_2 powder. The rate of photo-oxidation of methyl orange was three times faster using powder TiO_2 compared to immobilized TiO_2 . The amount of catalyst (0.5 g) used was the same as that immobilized onto the glass substrate for consistency. Nevertheless, use of the powder form of TiO_2 has got its own drawbacks, especially its separation from the aqueous environment (Calza *et.al*, 1997; Mills and Wang, 1998), and that is what led many researchers to work on the immobilization of TiO_2 onto support material (Kim *et.al*, 2005; Hosseini *et.al*, 2008; Amlouk *et.al*, 2006). The advantages of using immobilized TiO_2 photo-catalyst outweigh those of using powder TiO_2 , which has encouraged on-going research on the immobilization techniques and use of different support materials.

5.3.4 Photo-degradation of phenol red using $\text{TiO}_2\text{-SiO}_2$

A second organic contaminant (phenol red) was photo-degraded using the prepared photo-catalysts to establish their trend in the photo-oxidation of organic pollutants in water. The experiments were carried out under the same conditions used in the photo-oxidation of methyl orange. Figure 5.7 shows the photo-oxidation profiles obtained in the breakdown of phenol red.

The trend observed in the photo-oxidation of phenol red using $\text{TiO}_2\text{-SiO}_2$ was similar to that obtained in the photo-oxidation of methyl orange, except for the slight differences in the rate of photo-oxidation both under UV and visible light irradiation.

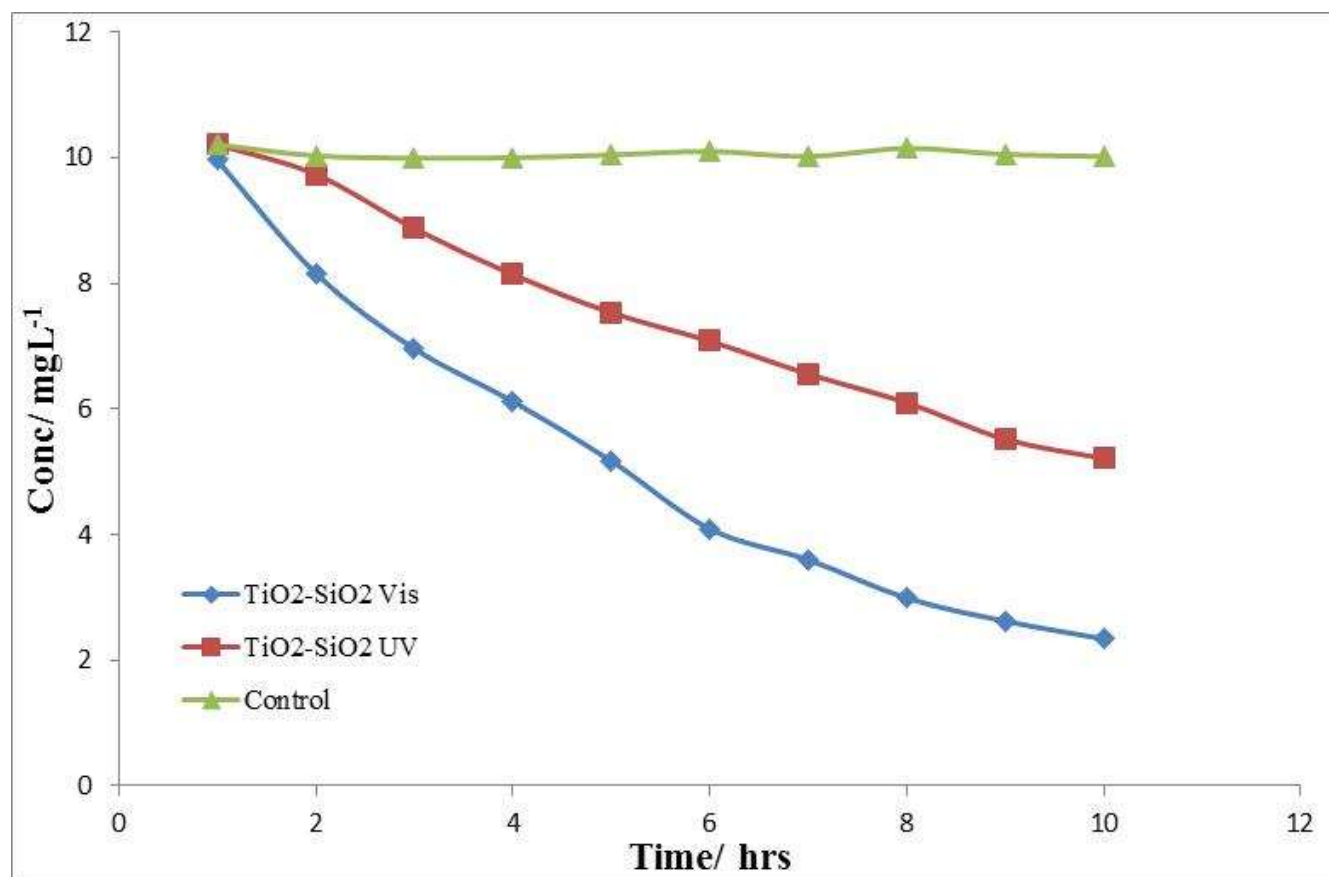


Figure 5.7: Photo-degradation profiles of PRed using TiO₂-SiO₂ under UV and visible light

The rate of breakdown of PRed was much faster under visible light irradiation as compared to just UV light, which confirms that modification of TiO₂ with silicon allows the utilization of visible light. Silica has a large specific area and no absorption in the UV region (Guo *et.al*, 2011).

5.3.5 Photo-degradation of PRed using $\text{TiO}_2\text{-SiO}_2$, $\text{C-TiO}_2\text{-SiO}_2$, $\text{N-TiO}_2\text{-SiO}_2$

The performance of the prepared catalysts was investigated in the photo-oxidation of phenol red under both UV and VIS irradiation. The photo-mineralization profiles obtained are shown in Figure 5.8. Carbon doped $\text{TiO}_2\text{-SiO}_2$ proved to be more effective in the photo-oxidation of phenol red both under UV and visible light irradiation unlike in the photo-oxidation of methyl orange where nitrogen doped $\text{TiO}_2\text{-SiO}_2$ was more effective. There was a considerable increase in the rate of photo-decomposition of phenol red for all the photo-catalysts under visible light irradiation. The photo-catalyst $\text{C-TiO}_2\text{-SiO}_2$ had the highest rate of photo-oxidation of phenol red, followed by $\text{TiO}_2\text{-SiO}_2$ and lastly $\text{N-TiO}_2\text{-SiO}_2$. Modification of TiO_2 with carbon, nitrogen and silicon proved to be effective in shifting the absorption band edge of TiO_2 into the visible region. The increased adsorption of organics brought about by the incorporation of silicon dioxide into the TiO_2 matrix enhanced the rate of photo-oxidation of phenol red (Guo *et.al*, 2011).

Carbon and nitrogen doping has been found to allow band gap narrowing (Nyamukamba *et.al*, 2012; Yuan *et.al*, 2006; Huang *et.al*, 2008) which enhances photo-degradation. The visible region is a much wider spectrum (about 40 % of the solar spectrum) as compared to the UV region (about 5 % of the solar spectrum), so the chances of TiO_2 activation are much higher when using visible light. After six hours of exposure to visible light about 80 % of PRed had been photo-oxidized using $\text{C-TiO}_2\text{-SiO}_2$, 65 % using $\text{TiO}_2\text{-SiO}_2$, and about 55 % using $\text{N-TiO}_2\text{-SiO}_2$ nano-composites. The control of the experiment remained nearly constant; there were only

minute changes in concentration which were probably due to adsorption of phenol red onto the surface of the nano-composites.

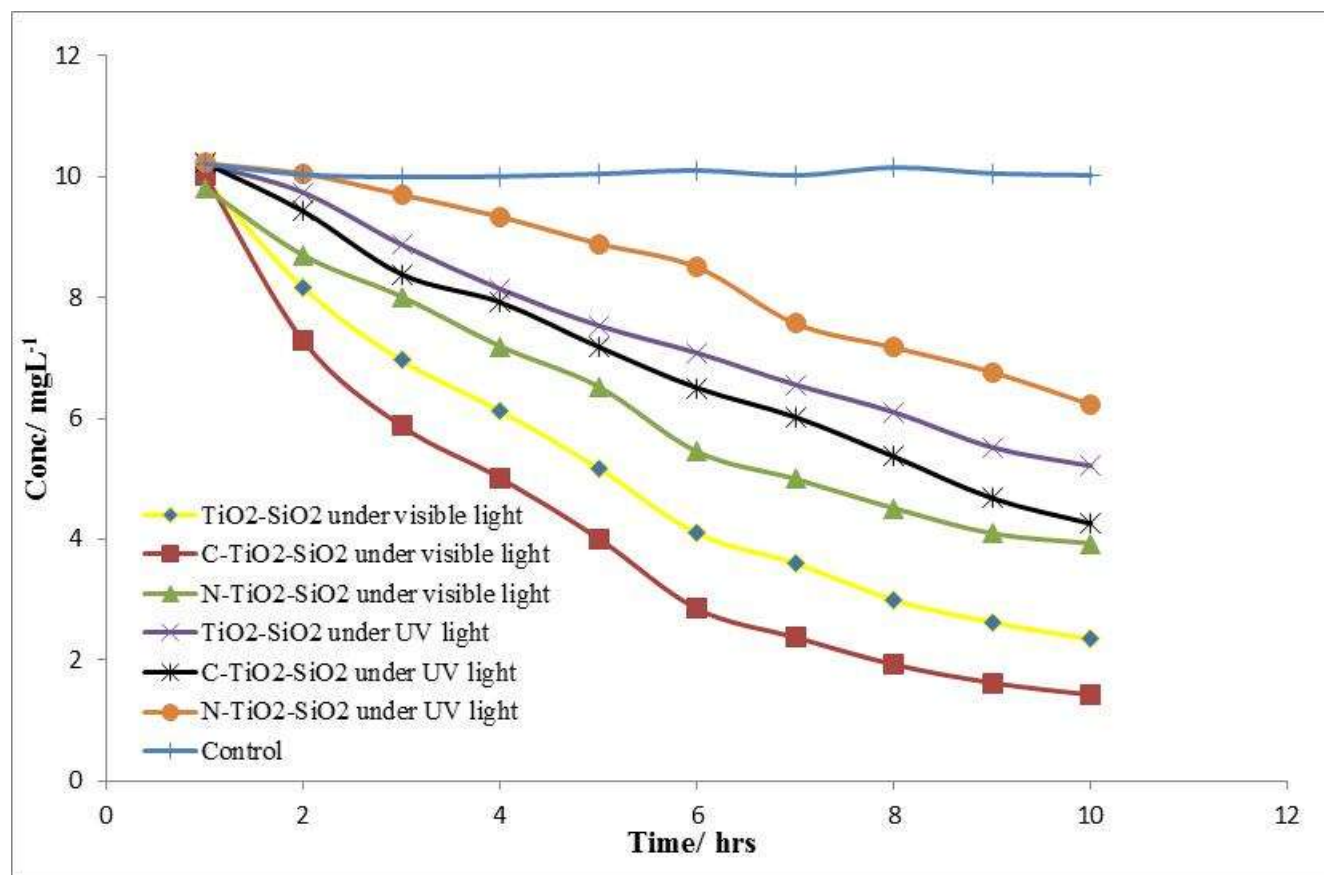


Figure 5.8: Photo-degradation profiles of PRed using TiO₂-SiO₂, C-TiO₂-SiO₂, & N-TiO₂-SiO₂

5.4 Conclusion

The modified photo-catalysts were capable of utilizing visible light for activation in the photo-degradation of methyl orange and phenol red. Immobilization of photo-catalysts onto glass support reduced surface area, which translated into a reduced rate of photo-oxidation of the organic pollutants by the photo-catalysts in water. However a considerable rate of photo-

mineralization is maintained and the benefits of using immobilized photo-catalyst outweigh those of using free powder. Some of the advantages include easy separation of photo-catalyst from aqueous environment and reusability, unlike powder TiO_2 which is difficult to isolate and invokes use of separation techniques like filtration and centrifugation which result in loss of some of the photo-catalyst, and raising the cost of water treatment. Carbon doped $\text{TiO}_2\text{-SiO}_2$ performed best in the photo-oxidation of phenol red, while nitrogen doped $\text{TiO}_2\text{-SiO}_2$ showed the best performance in the breakdown of methyl orange. Undoped $\text{TiO}_2\text{-SiO}_2$ had an average performance for both methyl orange and phenol red.

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CHAPTER 6

6. Evaluation of antimicrobial activity of carbon or nitrogen doped TiO₂-SiO₂ immobilized on glass support

6.1 Introduction

This chapter describes the procedures that were followed in the evaluation of the antimicrobial properties of C/ N-doped TiO₂-SiO₂ composites immobilized on glass substrate and reports on the results that were obtained as well. The mechanisms of bacterial photo-killing are not very well researched and understood, so the main aim of this procedure was to evaluate the performance of immobilized photo-catalyst. A non-pathogenic strain of *Escherichia coli*, ATCC 25922 was used in all the antimicrobial experiments carried out.

6.2 Methodology

6.2.1 Materials

The following materials were used in the antimicrobial experiments: sterile cotton swabs, nutrient agar, normal saline (NaCl), plates for incubation and *E. coli* ATCC 25922 bacteria.

6.2.2 Preparation of a McFarland turbidity standard

A McFarland 0.5 turbidity standard was used for all the antimicrobial experiments carried out. The standard was prepared by mixing 0.05 mL of a 1 % solution (w/v) of BaCl₂ with 9.95 mL of a 1 % solution (v/v) of H₂SO₄ (McFarland, 1907; Murray *et.al*, 2007). The standard gave an

absorbance of 0.08 abs units at a wavelength of 625 nm. The prepared standard was then used to estimate bacterial densities of *E. Coli* ATCC 25922 in saline solution by comparing absorbance. Table 9 shows the approximate densities of organisms for each McFarland standard.

Table 9: McFarland standards for visual/ spectrophotometric comparisons of bacterial densities in saline or liquid growth medium

Standard		0.5	1	2	3	4
Approximate bacterial density $\times 10^8$ / mL		1.5	3	6	9	12

6.2.3 Preparation of nutrient agar

The nutrient agar that was used in all the antimicrobial experiments carried out was prepared by dissolving 31g of agar in one litre of distilled water. After dissolution, the solution was sterilized by autoclaving at 121 °C. The nutrient agar was then poured into agar plates and allowed to set. All the plates were then stored in a refrigerator at 4 °C ready for use.

6.2.4 Culturing of *Escherichia coli* ATCC 25922

Escherichia coli ATCC 25922 were transferred onto freshly prepared nutrient agar using a cotton swab. The bacterial cells were spread by gently rubbing the cotton swab onto the surface of the nutrient agar material. The plate was then incubated at 37 °C for 24 hours. After the incubation period the *Escherichia coli* were transferred into a saline solution (0.85 % NaCl) using a sterilized loop to make up the 0.5 McFarland standard containing approximately 1.5×10^8

organisms. The standardized saline solution containing the *Escherichia coli* ATCC 25922 was then used in all the antimicrobial experiments carried out.

6.2.5 Antimicrobial experiments

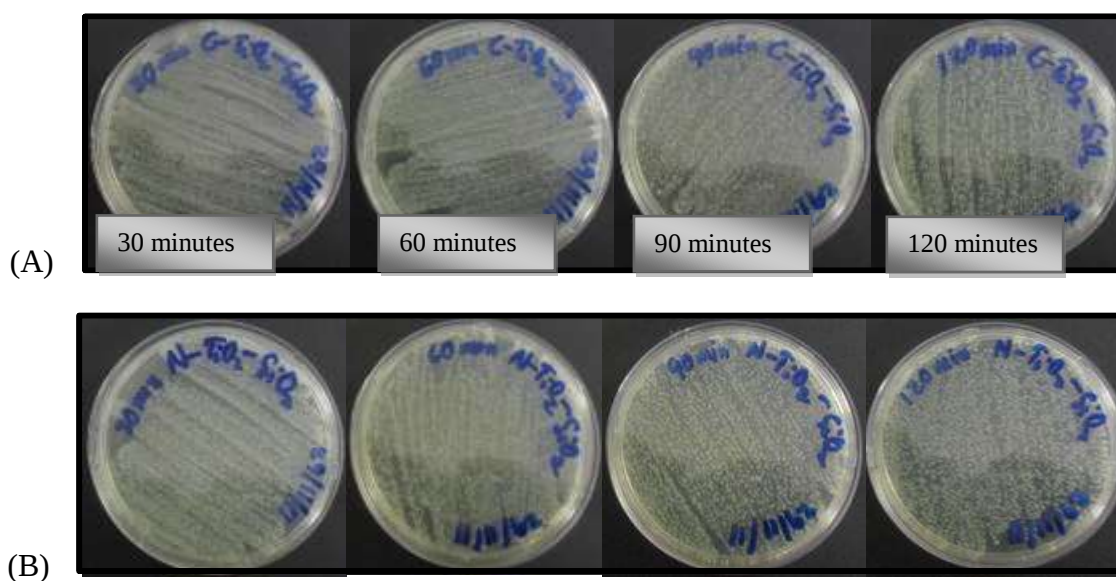
The antimicrobial experiments were carried out under visible light irradiation. The reactor setup used was similar to that used in the photo-oxidation experiments of methyl orange and phenol red described in Section 5.2. Five experiments were carried out in triplicate, using the four catalysts $\text{TiO}_2\text{-SiO}_2$, $\text{C-TiO}_2\text{-SiO}_2$, $\text{N-TiO}_2\text{-SiO}_2$, and TiO_2 . The fifth setup was the control of the experiment, which only had the microbes in the saline medium and no catalyst added. The other four had the four different catalysts and 150 mL of the saline medium containing the *E. coli* ATCC 25922. In this experiment a comparison of the performance of powder catalyst and immobilized catalyst was carried out. Every 30 minutes swabs were taken from each reactor vessel and plated on the freshly prepared nutrient agar plates. The process was done for 3 hours. All the plates were labelled and then placed in a Cocono incubator operating at 37 °C for 24 hours.

6.3 Results and discussion

This section presents the results obtained from the antimicrobial evaluation experiments using immobilized titanium dioxide silicon dioxide composites and also powder titanium dioxide.

6.3.1 Inactivation of *E. coli* under TiO₂ photo-catalytic reaction

The number of active *E. coli* cells after treatment with TiO₂ was determined by colony counting after 24 hours of incubation. Within the first 30 minutes of exposure, no effect was observed; all the *E. coli* cells remained viable. There was overgrowth on the plates such that colony count could not be executed. From 60 minutes onwards, a very small gradual decrease in the number of *E. coli* was observed for those vials that were exposed to immobilized photo-catalysts; TiO₂-SiO₂, C-TiO₂-SiO₂ and N-TiO₂-SiO₂. This showed that immobilized TiO₂ composites with silicon dioxide had little effect on the *E. coli* cells. Figure 6.1 shows the results obtained from the antimicrobial tests carried out using A: C-TiO₂-SiO₂, B: N-TiO₂-SiO₂ and C: TiO₂-SiO₂ and D: Control.



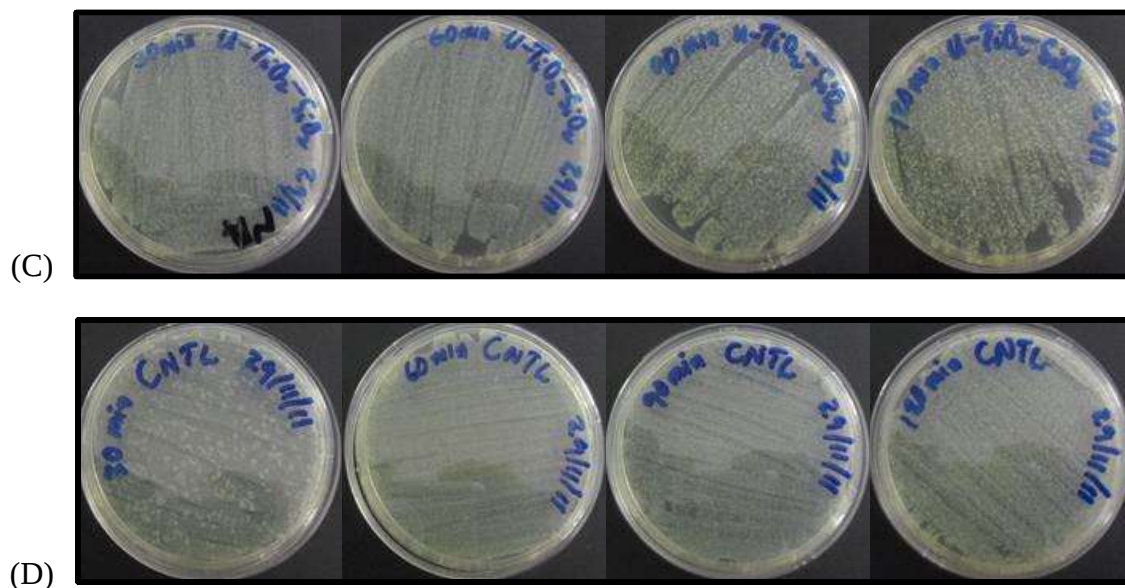


Figure 6.1: Images of *E. coli* ATCC 25922 treated with immobilized photo-catalyst C- $\text{TiO}_2\text{-SiO}_2$ (A), N- $\text{TiO}_2\text{-SiO}_2$ (B), $\text{TiO}_2\text{-SiO}_2$ (C), & control (D)

The control of the experiment showed uninhibited growth of *E. coli* cells. The result obtained in these tests is clear evidence that TiO_2 photo-catalyst is less effective towards bacterial cell inactivation. Another test was carried out using powder titanium dioxide to check the difference in the mode of action in powdered and immobilized titanium dioxide. The results obtained are shown in Figure 6.2.

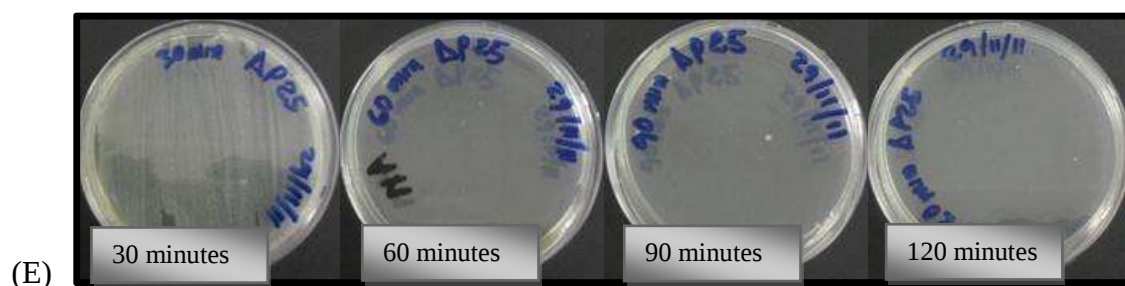


Figure 6.2: Images of *E. coli* ATCC 25922 treated with non-immobilized DP25 TiO_2 (E)

When *E. coli* ATCC 25922 was treated with powder TiO_2 , there was no effect within the first 30 minutes, but after exposure for 60 minutes about 98 % of the bacterial colonies had been destroyed. This proved that TiO_2 photo-catalyst is more effective in its powder form. The bactericidal function, however, is not well understood, even though numerous reports have described photo-killing of bacteria (Matsunaga and Okochi, 1995; Horie *et.al*, 1996; Jacoby *et.al*, 1998; Maness *et.al*, 1999; Huang *et.al*, 2000). Here the possibility of cell inactivation by the co-aggregation of cells and TiO_2 particles cannot be excluded since TiO_2 powder was used in the photo-killing reaction. Titanium dioxide particles ingested by phagocytosis are known to cause rapid intracellular damage (Huang *et.al*, 2000; Cai *et.al*, 1991). The fact that immobilized titanium dioxide was less effective in the inactivation of *E. coli* than the powdered one is a clear indication that some modes of action of TiO_2 do not come into play when the photo-catalyst is immobilized. It is possible that one side of the bacteria was shielded by glass thus reducing the complete ingestion through phagocytosis.

6.4 Conclusion

Immobilized titanium dioxide photo-catalyst was shown to be less effective in the deactivation of *E. coli* bacteria. The three nano-composite photo-catalysts; $\text{TiO}_2\text{-SiO}_2$, C- $\text{TiO}_2\text{-SiO}_2$, and N- $\text{TiO}_2\text{-SiO}_2$ showed little cytotoxicity (the degree to which an agent possesses a specific destructive action on certain cells) towards the growth of *E. coli* ATCC 25922 while powder titanium dioxide proved to be very effective towards the inactivation of *E. coli* ATCC 25922 bacteria. Within 60 minutes of exposure to the powder TiO_2 photo-catalyst, close to 98 % of the *E. coli* ATCC 25922 bacteria had been inactivated. Bacterial cells have got to come into contact with TiO_2 for it to show cytotoxicity towards them. The control of the experiments carried out

showed uninhibited growth of the E. coli ATCC 25922 bacteria since no photo-catalyst was added to the vial.

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CHAPTER 7

7. Conclusions and recommendations

7.1 Conclusions

Carbon and nitrogen doped titanium dioxide nano-particles were prepared via the sol gel method. The prepared photo-catalysts were immobilized onto glass support material through the use of tetraethyl orthosilicate, which served as both a coupling agent and precursor for silicon dioxide which was required to generate the desired titanium dioxide-silicon dioxide nano-composites. The prepared materials ($\text{TiO}_2\text{-SiO}_2$, $\text{C-TiO}_2\text{-SiO}_2$ and $\text{N-TiO}_2\text{-SiO}_2$) were evaluated for their photo-catalytic and antimicrobial properties using methyl orange and phenol red as model organic contaminants and *Escherichia coli* ATCC 25922 as the microbial contaminant.

Nano-composites of titanium dioxide with silicon dioxide were successfully prepared (14.7 nm, 15.0 nm, and 15.9 nm for $\text{C-TiO}_2\text{-SiO}_2$, $\text{TiO}_2\text{-SiO}_2$, and N-TiO_2 respectively). The best ratio for TiO_2 to TEOS binder was found to be 1:1 and it resulted in a smooth coating paste for the nano-composite thin films. Using BET measurements, carbon doped TiO_2 was found to have a larger surface area compared to nitrogen doped TiO_2 . However, immobilization of the photo-catalysts onto glass support material using TEOS binder resulted in a slight decrease in the exposed surface area even though they were easy to remove from water and could be reused upon cleaning. The surface areas ($\text{C-TiO}_2\text{-SiO}_2$ $72.2 \text{ m}^2\text{g}^{-1}$, $\text{TiO}_2\text{-SiO}_2$ $56.8 \text{ m}^2\text{g}^{-1}$) were still greater than that measured for the commercial titanium dioxide, Degussa P25 ($50 \text{ m}^2\text{g}^{-1}$). However, $\text{N-TiO}_2\text{-SiO}_2$ presented an unusually low surface area; $44.4 \text{ m}^2\text{g}^{-1}$.

The modified photo-catalysts were found capable of utilizing visible light in the photo-oxidation tests that were carried out using methyl orange and phenol red. The undoped and doped TiO_2 - SiO_2 nano-particles showed an improvement in optical absorption, that is, a shift of 0.20 eV for C- TiO_2 - SiO_2 and N- TiO_2 - SiO_2 , and 0.1 eV for TiO_2 - SiO_2 . It was shown that the incorporation of silicon into the titanium dioxide matrix also allowed utilization of visible light for activation since silicon has a much smaller band gap and has no absorption in the UV region.

Carbon doped TiO_2 - SiO_2 gave the highest rate of photo-oxidation of phenol red, and N- TiO_2 - SiO_2 gave the highest rate for methyl orange photo-oxidation. The reason for differences in the performances of the photo-catalysts could be dependent on the structure of the organic contaminant and the mechanisms involved in the decomposition process. However, it was established that the powder form of titanium dioxide gave a rate of photo-oxidation that was three times that of immobilized titanium dioxide. Nevertheless the main drawback with using the powder form was the difficulty in removing spent powder from water, while immobilization of photo-catalyst material allowed easy separation from the water after the treatment process.

The use of immobilized titanium dioxide in the inactivation of *Escherichia coli* bacteria proved to be less effective. After 3 hours of treatment of *E. coli* with immobilized titanium dioxide very little change in the number of active cells was observed, but when the *E. coli* was treated with powder titanium dioxide about 98 % of the bacterial cells were inactivated within an hour. This suggests that titanium dioxide powders have got to come into direct contact with the *E. coli* cells for them to show any cytotoxicity.

7.2 Recommendations

Immobilized titanium dioxide photo-catalyst can be used several times without any significant drop in the rate of photo-oxidation of organic contaminants in water because the catalyst is photo-stable and regenerates at the end of photo-catalytic cycles. In this study, the immobilized photo-catalysts ($\text{TiO}_2\text{-SiO}_2$, $\text{C-TiO}_2\text{-SiO}_2$ and $\text{N-TiO}_2\text{-SiO}_2$) were used in four successive photo-degradation cycles with no drop in the rate of photo-degradation as shown by results in Section 5.3. Further studies can be carried out to investigate the performance of the immobilized photo-catalysts under continuous flow conditions. Also conditions for continuous flow treatment of polluted water ought to be established and tests done to ensure that there is no leaching of TiO_2 from the immobilized thin films. A continuous flow flatbed reactor which is pump-driven could be designed. It could also be beneficial if the whole system can be solar powered, so that it is also suitable for use by rural communities which have no access to electricity. Further work can also be done to improve the antimicrobial properties of immobilized titanium dioxide such as grafting biocides onto the titanium dioxide matrix. This could help in the simultaneous removal of organic and microbial pollutants from potable water.