UNIVERSITY OF NAIROBI

DEPARTMENT OF CHEMISTRY

WATER PURIFICATION USING ORIANG' WOMEN CLAY POTS WITH N-DOPED TITANIUM DIOXIDE

By

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DECLARATION

This thesis is my original work and has never been submitted for the award of degree to this or any other institution of learning.

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DEDICATION

To my parents, the late Mr. and Mrs. John Otieno Wangoye, You would be proud to see this far I have come. I would also like to dedicate this work to Mr. Dismas Opiyo Wangoye, you have always supported me in every stage of my life and have been a continuous source of encouragement and without you I would have never achieved this goal.

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Sincere gratitude to Oriang' Pottery Women Group especially the Secretary, Mama Grace, your kindness and willingness to work with a stranger cannot go unnoticed.

ABSTRACT

Our water bodies are constantly impacted by ecological and environmental changes emanating from natural and anthropogenic activities. A research conducted by UN indicated that about 2.2 million deaths occur yearly in the world linked to water-related diseases with majority being children. UN research also recorded that this situation will not get better, projecting that by the year 2025, potable water shortage will be experienced by 2.7 billion people.

The aim of this research was to provide a low cost, low energy and low environmental impact water treatment solution, suitable for use in rural areas. This research focused on the application of modified TiO_2 based photocatalyst for water purification process. N-doped TiO_2 was prepared using Sol-gel process at room temperature using a precursor termed as titania- Titanium (IV) Isopropoxide and 25% Ammonia Solution as Nitrogen source. The synthesized compound was calcined at 673 K.

The structure and morphology of N-doped TiO_2 powder were examined using scanning electron microscopy (SEM). X-Ray Diffraction (XRD) was used to determine the particle size using the Debye-Scherrer's formula. The XRD gave a particle size of 18.372 nm.

The synthesised N-doped TiO_2 was dissolved into a paste using Polyethylene glycol and coated onto the inner surface of the pots, impregnated into the pore structure and tested against inactivation of *E. coli* and total coliforms. From the results, it indicated that N-doped TiO_2 completely inactivated *E. coli* at 98.5% compared to un-doped TiO_2 and SODIS at 81.1 and 76.7%, respectively. The N-doped TiO_2 paste in pots that had >0.2 g of the photocatalyst deactivated *E. coli* to near 100% compared to 95.5% for the pot only. Further studies on the activity of the photocatalyst on photodecomposition of chemical using methylene blue and methyl red dyes showed that the photocatalyst achieved up to 99.6% and 97.8% degradation efficiency, respectively.

The results suggest that photo catalytic decomposition of methylene blue followed first order with a deceptive reaction rate constant, *k* app. 1.9×10^{-2} min^{-1}. Reaction kinetics was fitted into the Langmuir-Hinshelwood model for pseudo first order rates.

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LIST OF ABBREVIATIONS

AMPATH	Academic Model Providing Access To Healthcare
AOP	Advanced Oxidation Process
CB	Conduction Band
CFU	Colony Forming Units
DBPs	Disinfection by-products
EPA	Environmental Protection Agency
GC/MS	Gas Chromatograph/ Mass Specrometer
MCL	Maximum Contamination Limit
MDG	Millennium Development Goal
NTU	Nephelometric Turbidity Unit
OCPs	Organochlorine Pesticides
PET	Polyethylene Terephthalate
PFP	Potters For Peace
POPs	Persistent Organic Pollutants
POU	Point of Use
ROS	Reactive oxygen Species
SEM	Scanning Electron Microscopy
SODIS	Solar Disinfection
SPE	Solid Phase Extraction
TSS	Total Suspended Solids
TDS	Total Dissolved Solids

UNEP	United Nations Environmental Programme
UNICEF	United NationsInternational Children's Emergency Fund
USEPA	United States Environmental Protection Agency
UV/ Vis	Ultra Violet/ Visible Light
VB	Valence Band
VLA	Visible Light Active
WHO	World Health Organisation
XRD	X-ray diffraction

UNITS OF MEASUREMENT

CFU	Colony Forming Units
g	Gram
L	Litre
mg	Milligram
ml	Milliliter
nm	Nanometer
NTU	Nephelometric Turbidity Unit
ppm	parts per million

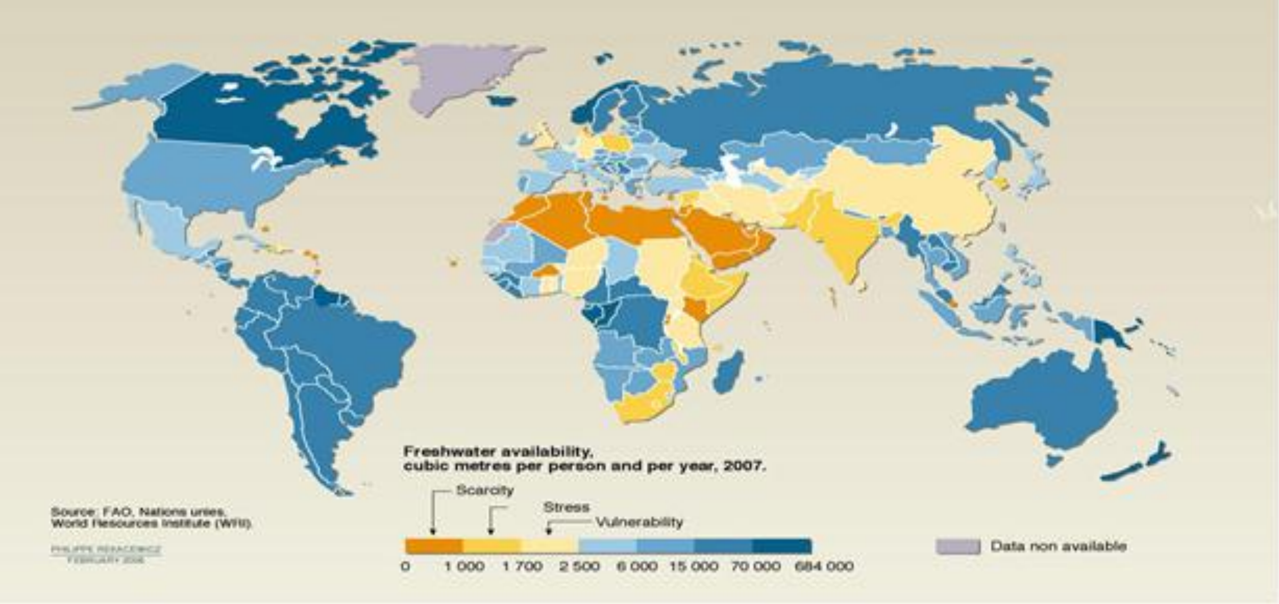
CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the study

Currently most countries are facing drinking water problems with the situation becoming worse particularly with the developing countries (Dhermendra *et al.*, 2008). Depletion of the existing freshwater supplies through prolonged drought, population growth and high demands from different users and more stringent health based regulations (Dhermendra *et al.*, 2008) has led to difficulties in dealing with increasing clean drinking water demand by the world. Uncontaminated water (i.e., water without pathogens and toxic chemicals) is important for both human health and sustainability.

Even though the Earth is known as a water planet (USGS, 2016), only 3% of total water available is fresh water (Ahuja, 2013) with only 0.06% of this said to be easily accessed (Ahuja, 2013). Similarly the distribution of the fresh water is highly variable leaving some countries with a lot of water, while others with water scarce.



Source: FAO, Nations unies, World Resources Institute (WRI).

Figure 1.1: Map illustrating global fresh water distributions

This describes the reason why above 80 countries currently experience water shortage (Ahuja, 2013). In most water scarce countries, millions of the vulnerable people that is, children and women use quite a lot of time each day looking for water from distant sources that are often contaminated (UN, 2013). This has led to 2.2 million deaths occurring yearly linked to water-related diseases, children being the most affected all over the world. A research conducted by UNICEF in 2015 indicated that, approximately 663 million people all over the world still consume drinking water from contaminated water sources, together with unprotected wells, springs and surface water (UNICEF, 2015). Despite water being a very valuable commodity, it is clear that it is scarce and its quality needs to be sustained to assure water sustainability (Ahuja, 2013).

Researcher’s initiatives together with non-governmental organizations have come up with a number of water filtration technologies to reduce potable water shortage (Sobsey *et al.*, 2008, Varkey and Dlamini, 2012). Among the most studied and surveyed techniques applied for water purification all over the world include: aluminium sulphate coagulation (EPA, 2014; chlorination; combined coagulant applied in chlorine disinfection systems; Ultra Violet radiation; techniques involving sunlight exposure such as SODIS (Mahvi, 2007); filtration systems like reverse osmosis (Sorlini *et al.*, 2015); bio-sand filtration (Plappally *et al.*, 2011; Naddafi *et al.*, 2005) and ceramic filtration (Varkey and Dlamini, 2012).

Concerns have however arisen regarding the use of such water treatment techniques generally because of the development of harmful disinfection by-products (DBPs) due to the halide ions and naturally occurring organic matter reacting with the by-products which include trihalomethanes and haloacetic acids (Grieken *et al.,* 2009).

Table 1.1: Harmful Disinfection By-Products (DBPs)

DISINFECTION BYPRODUCTS				
Contaminant	**MCLG (mg/L)**	**MCL or TT (mg/L)**	**Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)**	**Sources of Contaminant in Drinking Water**
Bromate	zero	0.010	Increased risk of cancer	Byproduct of drinking water disinfection
Chlorite	0.8	1.0	Anemia; infants and young children: nervous system effects	Byproduct of drinking water disinfection
Haloacetic acids (HAA5)	n/a	0.060	Increased risk of cancer	Byproduct of drinking water disinfection
Total Trihalomethanes (TTHMs)	--> n/a	--> 0.080	Liver, kidney or central nervous system problems; increased risk of cancer	Byproduct of drinking water disinfection

Also, nitrification and suspended solid particles affects the efficiency of chlorination process, which too requires a lot of funds for cleaning safety equipment such as filter systems and the basic of dechlorination to adhere to the firm regulatory limits of EPA (Carp *et al.*, 2004). On the other hand, Alzheimer's disease has been linked with aluminum sulphate (Zhang *et al*., 2006). Further, there is increased cost for water treatment leading to increased pricing for water treatment in Africa when there is high cost of purchasing synthetic coagulants and disinfectants (Kebreab *et al*., 2005).

Since the majority of people especially from most countries that are developing find it hard to access safe drinking water (UNICEF, 2015), Point of Use (POU) water treatment is emerging (Harris, 2005) as an approach that can help these people to access improved water quality, by treating water at their homes or at the point of use (Sosbey *et al.*, 2008) at a low cost (Harris, 2005). This treatment method prevents recontamination during transport and enables the users to take charge of the safety and quality of their water.

Ceramic filters are an example of POU water purification technology used normally at the household level (Clasen *et al.*, 2004) with millions of them being in use in many regions in Asia, Africa and South America (Plappally *et al.*, 2009, Plappally *et al.*, 2011). A research conducted by non-governmental organization, Food for the Hungry International, on clay ceramic filters performance in Bolivia indicated that there was a 45% decrease in diarrhea cases (Clasen *et al.*, 2006; Clasen *et al*., 2004). In addition, Sobsey *et al*. (2008) and Plappally *et al.*, (2011) reported that, ceramic filters and bio-sand filters suit the sustainability criteria in the field with consumers (Plappally *et al.*, 2011).

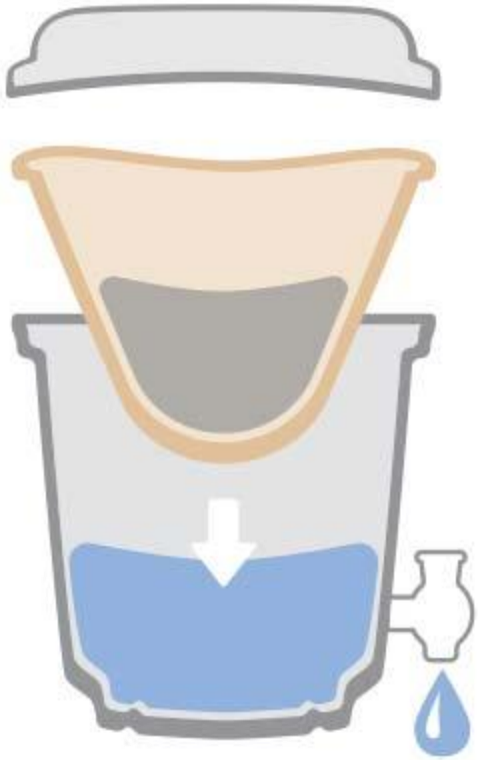


Figure 1.2: Point of use (POU) filtration in cooperating the ceramic filter and a tap to draw out the water.

In Kenya, Academic Model Providing Access to Healthcare's (AMPATH) newest programme, Maji Safi, has many elements designed to help tackle the important issues of safe water and sanitation. Since many of AMPATH's clients find it hard to access municipal water, they are required to get their water from nearby dug wells, unprotected springs or polluted streams. Because this is the norm and not the exception, it is important for a safe water program to target in-home treatment (AMPATH, 2011). The filter is essentially a clay "flower pot" (without a bottom hole!) that hangs by its lip inside a larger plastic bucket. The poured contaminated water in the clay pot seeps through the clay into a big plastic container. The pot is made from local clay, mixed with sawdust and fired in a kiln. If made properly, it becomes a 1 micron filter which is smaller than any bacteria or protozoa (AMPATH, 2011).

Titanium dioxide ($TiO_{2)}$ is a pure raw mineral that exists in plenty naturally. It is common in regions such as Africa, Sweden, Australia and Canada (Third World Academy of Sciences, 2002). It has been used as a chemical photocatalyst and in the electronic industry. Reactions of the photo catalyst at the surface of (TiO_2) have appealed to many researchers due to their practical applications in the cleaning of the environment which includes: cleaning of glasses, tiles and windows (Zaleska, 2008, Nosaka *et al.,* 2005). Titanium dioxide is among the effective photocatalysts applicable in self-cleaning surfaces and in water and air purification (Zaleska, 2008).

Additionally, due to its strong oxidation activity and hydrophilicity, TiO_2 can be used as antibacterial agent (Fujishima and Zhang, 2006; Zaleska, 2008). The mineral also has high chemical stability and reactivity when exposed to UV light (λ<387 nm) (Zaleska, 2008) with energy surpassing 3.3eV band gap (Zaleska, 2008; Gota and Suresh, 2014), in the crystalline phase of anatase (Zaleska, 2008). The development of photocatalysts exhibiting high reactivity under visible light (λ> 400 nm) (Zaleska, 2008) should allow the main part of the solar spectrum (Zaleska, 2008), even under poor illumination of interior lighting, to be used (Zaleska, 2008; Gota and Suresh, 2014).

There has been a number of proposed approaches for TiO_2 modification (Gota and Suresh, 2014): metal-ion implanted TiO_2 (Gota and Suresh, 2014) (with transition metals which include Cu, Ni, Co, Cr, Mn, Mo, Nb, Vn, Fe, Ru, Ag, Hg and Pt) Gota and Suresh, 2014, reduced TiOx photocatalysts (Ihara *et al.,* 2001; Gota and Suresh, 2014; Takeuchi *et al.,* 2000), non-metal doped-TiO_2 (Nitrogen, Sulphur, Carbon, Boron, Phosphorus, Iodine and Fluorine) (Ohno *et al.,* 2003; Yu *et al.,* 2003), composites of TiO_2 with semiconductor having lower band gap energy such as Cd-S particles (Hirai *et al.,* 2001), and sensitizing of TiO_2 with dyes such as thionine (Chatterjee and Mahata, 2001; Gota and Suresh, 2014).

The current study sought to develop a modified TiO_2 based photocatalyst that can be used for purification by point of use water technology for the rural communities along the Kenyan part of Lake Victoria Basin (Figure 1.1). Communities in rural Kenya mostly rely on surface water that has been reported to be contaminated with microbial, pesticides, heavy metals, nutrients among other contaminants. There is therefore need to treat the water before consumption. However, Chlorination which is a major POU method of water treatment system employed in this area may produce by-products which are carcinogenic. Chlorination also does not address the turbidity issue which is a major problem in most parts of the country. A cost effective system that addresses both the microbial and turbidity challenges among other threats to quality drinking water should be sought. It is in this light that this study was conducted to investigate how effective ceramic clay filters impregnated with N-doped TiO_2 can be used as a cost effective method of accessing safe water in the rural communities. Figure 1.1 indicates the map of Lake Victoria (MARINE, 2014).

Figure 1.3 Lake Victoria Basin

1.2 Problem Statement

Lake Victoria has been under great environmental pressure (Odada *et al*., 2004) from a variety of interlinked human activities (Odada *et al*., 2004), including over-fishing and destructive fishing practices (Bakibinga-Ibembe *et al*., 2011), pollution from human and industrial activities (Bakibinga-Ibembe *et al*.,2011), siltation from the erosion of deforested watersheds (Bakibinga-Ibembe *et al*., 2011), and greater urban runoff with a lot of sediment loads and huge volumes of waste products (Bakibinga-Ibembe *et al*., 2011). The sources of pollution are many (Bakibinga-Ibembe *et al*., 2011), and include, untreated sewage, human activities contaminating lake water directly at the shore line, animal and human wastes discharge into channels and streams and transport wastes from maritime (Bakibinga-Ibembe *et al*., 2011). These negative impacts have accumulated in lake Victoria, and this is evident by the lake showing different signs of environmental suffering (Bakibinga-Ibembe *et al.*, 2011) including: eutrophication, depleted oxygen level, minimum transparency and increasing chemical and microbiological pollution points (Bakibinga-Ibembe *et al.*, 2010; Wandiga *et al*, 2009).

Also some inflow of residues from the use of agro-chemicals (Okungu *et al.,* 2005) in some areas of the lake-catchment, and activities such as gold mining, are viewed as potential sources of heavy metal and pesticides pollution (Okungu *et al.,* 2005). The small-scale gold mining activities in Mwanza and Mara regions increased (Okungu *et al.*, 2005) and the use of mercury in recovery of gold posed potential contamination of waterways leading to the lake (Okungu *et al.*, 2005).

The increased faecal contamination of the near shore lake waters (Okungu *et al.,* 2005) is associated with increased cases of water-borne diseases (Okungu *et al.*, 2005) including diarrhoea, intestinal worms, cholera, typhoid and dysentery. Proliferation of water hyacinth has also increased the habitat for the snails (Okungu *et al.,* 2005) which are the host for the parasite *Schistosoma*, responsible for bilharziasis in humans (Okungu *et al.,* 2005).

Homa Bay County borders Lake Victoria to the West and North. Major water sources for the people in Homa Bay are Lake Victoria, pans and dams (Wambu *et al.,* 2016). Other sources are piped water, rivers and a few boreholes (Wambu *et al.,* 2016). The main sources of water pollution include agro-chemicals, open defecation due to lack of pit latrines and surface run off from contaminated areas such as markets and municipal waste disposal sites into water points. The water obtained from the pans is also contaminated by livestock wastes since the pans are not protected.

Current estimates of water supply in Kenya also indicate that 75 per cent (Onjala, 2002) (this could be a serious overestimate) of the country's urban population has access to safe drinking water (Onjala, 2002), while only 50 per cent of the rural population has access to potable water (Onjala, 2002) from various schemes, including piped water schemes, bore-holes, protected springs, pans and dams (Onjala, 2002).

1.3 OBJECTIVES

1.3.1 Overall Objective

To develop a point of use water treatment system that can be used to improve the quality of drinking water for the people around the Kenya’s shore of Lake Victoria.

1.3.2 Specific objectives

i) To synthesize and characterize the N-doped TiO_2 capable of absorbing visible light.

ii) To evaluate N-doped TiO_2 photocatalytic reactivity in degradation of pesticides and organic contaminants.

iii) To evaluate N-doped TiO_2 in the inactivation of *E. coli* and other coliforms from contaminated water.

iv) To develop clay moulds with different compositions of N-doped Titanium dioxide and test their water purification capacities.

1.4 Justification

Providing safe and reliable water to every household (Classen, 2008) is an essential goal, yielding optimal health gains (Classen, 2008) while contributing to the MDG targets (Classen, 2008) for poverty reduction, nutrition, childhood survival, school attendance, gender equity and environmental sustainability (UNEP, 2006; Classen, 2008). The MDGs have recently been revised to Sustainable Development Goals (UN, 2015). The sixth agenda of the SDGs is to ensure availability and sustainable management of water and sanitation for all (UN, 2015). By 2030, achieve universal and equitable access (UN, 2015) to safe and affordable drinking water for all (UN, 2015). While committed strongly to this goal (Classen, 2008) and to incremental improvements in water supplies wherever possible (Classen, 2008), the WHO has called for interim approaches that will accelerate the health gains (Classen, 2008) associated with safe drinking water for those whose water supplies are unsafe (WHO, 2007; Classen, 2008).

Appropriate technologies are needed to address the drinking water problem in the developing world. An estimated 780 million people do not have access to an improved drinking water source (UNICEF, 2012). This is a global problem (WHO, 2007). The purpose of this research is to develop a self-sustaining and an inexpensive point of use system that will rid the naturally available water from a wide variety of contaminants and pathogens, making it suitable for human consumption.

The new compounds synthesized will open up new applications of the ore, TiO_2 which do not exist in Kenya today.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Water Quality Issues

Humans require water for life, however one-sixth of the global human population (WHO, 2006) lacks access to safe water (Bordalo and Savva-Bordalo, 2007). In Africa, this condition is mostly acute due to the following factors; effects of global warming, presence of Sahara desert, civil unrest and poor governance, a gradual growing population (2.2% a year), migration and poverty (Bordalo and Savva-Bordalo, 2007). Lack of adequate safe water and sanitary infrastructure in rural areas leaves millions with poor water quality hence increasing the harshness of daily life (Bordalo and Savva-Bordalo, 2007).

Diseases related to water and sanitation in developing countries jointly account for 80% of sickness that occur (UN, 2003; Ahuja, 2013). Approximately 2.2 million deaths are accounted for yearly by World Health Organization (WHO) in children (Ahuja, 2013). This is as a result of disease related to insufficient water supply, reduced sanitation (Ahuja, 2013) and hygiene-which is more than annual deaths from malaria, TB and AIDS (Ahuja, 2013). For instance, for the period 2002-2003, 16% mortality of children below the age of five in Kenya was accounted for from diarrheal diseases (Wandiga *et al.,* 2009). Figure 2.1 illustrates the cases of children death from various causes in 2008 in Africa (Black *et al*., 2010).

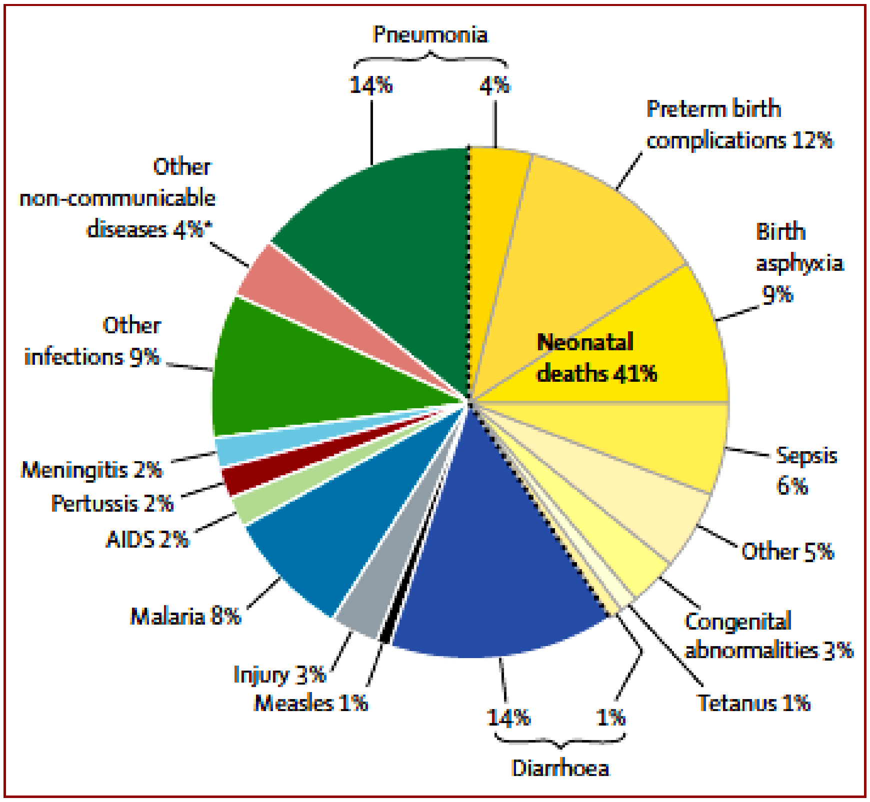


Figure 2.1: Causes of 8.795 Million Child Deaths in 2008.

A research conducted by World Bank in 2006 indicated that in the year 2002, Sub-Saharan Africa had a leading percentage of people living in poverty globally (44%) following water resources' increased pressure (World Bank, 2006).

The continent's surface water is polluted with large deposits of sediments, disease-causing biological microorganisms, and agricultural and industrial chemicals (Wandiga, 2014). About one-seventh of the global human population still practice open defecation, of which 949 million reside in rural areas, and Africa is the major (Wandiga, 2014).

Africa's involvement in high incidences of water-related diseases (UNDESA, 2014) like malaria, cholera, Guinea worm and river blindness (UNEP, 2006) is due to poor sanitation and limited access to safe drinking water. In the year 2005, cholera cases of 14,303 were diagnosed (Bordalo and Savva-Bordalo, 2007) of which 252 deaths finally occurred in Guinea-Bissau alone, during the wet season, (Bordalo and Savva-Bordalo, 2007). However, World Health Organization approximates cases of diarrhea as 0.75 per person (Addo *et al*., 2014), per year worldwide, the rate varying between regions (Addo *et al*., 2014). Africa's Sub-Saharan for example has the highest rate (Addo *et al*., 2014), with 1.29 cases per person annually (Addo *et al*., 2014), whereas the rates in Europe and United States are 0.18 and 0.07 cases per person per year, respectively (Addo *et al*., 2014). Figure 2.2 illustrates the typical situations experienced around Lake Victoria where women and children are the most susceptible to water related challenges (WHO, 2000).

Figure 2.2: Lake Victoria serves as source of water for domestic use

Below are some of the main water pollutants and their sources in a summary form (TERI, 2009).

a) **Microbial contamination:** This generally arises from sewages which are untreated or inadequately treated. Lack of sanitation and sewage treatment facilities is the main cause for microbial contamination (Bakibinga-Ibembe *et al.,* 2010). Water contaminated by faecal coliforms is also a main source of hepatitis, cholera and typhoid (Cabral, 2010) together with opportunistic infections that attack individuals with low immunity such as children and the elderly (TERI, 2009).

b) **Heavy metals:** Contaminated waste water from industrial activities(Palanisamy *et al*., 2013) which include; electroplating, textile dyeing; tanneries (Palanisamy *et al*., 2013) and many others which if ineffectively treated can end up into the surface or ground water source (Hu *et al.*, 2007; Palanisamy *et al*., 2013). In addition leaching from solid waste dumpsites (Palanisamy *et al*., 2013) (e.g., wastewater treatment plants' sludge, fly ash ponds) also contributes to heavy metal pileup (Hu *et al.*, 2007; Palanisamy *et al*., 2013).

c) **High salinity:** This arises from high evaporation rate due to climate change, decreasing groundwater levels and seawater intrusion (Praveen *et al.*, 2013; Kumar, 2012). Agricultural run offs rich in salts also worsens this condition (Praveen *et al.*, 2013).

d) **Nitrate, Arsenic and fluoride:** These contaminants exist in sedimentary rocks hence making them available in groundwater aquifers (Praveen *et al.*, 2013). However, contamination by these chemicals has been further worsened by excessive groundwater withdrawals (Praveen *et al*., 2013).

e) **Micro-pollutants:** This group of pollutants include pesticides, endocrine disrupting substances, and surfactants which occur in very low concentrations but highly toxic. The major sources include agricultural run offs, industrial activities and effluent from sewage treatment plants (Olujimi *et al.*, 2010).

Sustainable Development Goals target nutrition, childhood survival, poverty reduction, school attendance and environmental sustainability, gender equity, provision of uncontaminated, consistent, piped water to every household as important ,as this will yield optimal health gains to contribute to the goals (UNEP, 2015). During the United Nations Sustainable Development Summit 2015, ensuring water and sanitation accessibility for all was shown as goal number six. Interim approaches were called for by WHO and other organizations to hasten the health gains associated with uncontaminated drinking water for areas with water supplies which are unsafe (WHO, 2010; UNEP, 2015).

Effective interventions of water treatment by point of use if correctly and consistently used can reduce chemical and microbiological contamination of drinking water at the point of ingestion significantly (WHO, 2013), by addressing water recontamination during collection, storage and use in households (WHO, 2013). Point-of-use water treatment refers to water treatments by the end user they are operated and maintained by the individual households. The device must operate optimally and efficiently, with little need for additional costs for maintenance to be successful (Wandiga, 2014).

Frequently, water at the source contains lower levels of bacteria than supplies from stored water as reported by researchers (Wright *et al*., 2003; Clasen, 2008). For instance, harvested rainwater is often safe once is at point of collection (Clasen, 2008) but gets subsequent contamination in the home (Clasen, 2008). Generally this is as a result poor handling at the period of either collection (Clasen, 2008), transport or use in the household (Clasen, 2008). For the case of boiled water, addition of cold water to the boiled water so as to cool it can also lead to recontamination (Clasen, 2008). Change in behavior that can help proper handling as well as sanitation can minimize recontamination (Clasen, 2008). However, a solution which can be more effective in preventing hand contact is by use of storage vessel equipped with a narrow mouth for filling together with a tight fitting cap (Clasen, 2008) and spout or tap for pouring or drawing water from the vessel rather than dipping into it (Clasen, 2008).

2.2 Use of Clay Ceramics

Since 1998, there has been assistance by Potters for Peace (Robbins, 2011) in the production of a ceramic water purifier which is of low-cost, low-tech and colloidal silver-enhanced (CWP) (Robbins, 2011) all over the world (Varkey and Dlamini, 2012). Over 30 countries are now applying technology by Potters and Peace package to produce ceramic water purifiers at over 50 independent factories (Potters for Peace, 2006).

Ceramic filters are made of clay mixed with water and a combustible material (Varkey and Dlamini, 2012), like sawdust and then fired (UNICEF, 2007). Firing burns out the sawdust (Lemons, 2009) leaving out tiny pores that allow water molecules to pass through while particles are retained (Lemons, 2009). The pore size and flow rate of these filters varies depending on the size of combustible material (Lemons, 2009) used in the mixture (Sobsey and Stauber, 2008). The pores can be reduced by size exclusion in microfiltration range down to 0.2 µm for effective removal of all bacteria and protozoa (Isikwue and Emmanuel, 2011). Having been used in several forms long time ago, small-scale ceramic filtration has a long history (Sobsey, 2002; UNICEF, 2007). Various countries in continents such as South America, Asia and Africa use millions of these filters- porous clay ceramic filters (Plappally *et al*., 2009).

In the year 1981, a researcher from Guatemala known as Dr. Fernando Mazariegos of the Central American Industrial Research Institute (ICAITI) developed the filter design used by Potters for Peace (PFP) (Lemons, 2009). The aim was to develop a low-cost filter for the poor people that could be fabricated at the community level so as to make water contaminated with bacteria safe for them. The Potters for Peace clay pot, has been used in countries such as Nicaragua and

Cambodia for some time, but the silver used as the anti-bacterial material is simply painted onto the surface.

The advantages of the ceramic pot-style filters that have been produced locally include; portable, lightweight (UNICEF, 2007), chemical free and relatively inexpensive, (UNICEF, 2007), effective, low-maintenance and easy to use (UNICEF, 2007). With 1 to 3 liters per hour typical flow rates, microorganisms can be removed from water by filters by gravity filtration through porous ceramics (UNICEF, 2007). Filters with internal cracks or larger pores may lead to a flow beyond the maximum flow rate (Rayner, 2009) hence permitting pathogens to pass through (Rayner, 2009).

Through evapotranspiration, clay ceramics cool the treated water and by proper storage receptable and use, store water safely for use (UNICEF, 2007).

2.2.1 Variables in Clay Pot Manufacturing

The flow rate of each filtering element (Rayner, 2009) is used as a primary form of quality (Rayner, 2009) control once a filter mixture formulation has been established and effectiveness confirmed with microbiological testing (Rayner, 2009). There are many variables in the manufacturing process (Rayner, 2009) which are considered to influence the flow rate (Rayner, 2009) and/or effectiveness of the filtering element (Rayner, 2009) including the type of clay (particle size, distribution, sand content and plasticity), the burn-out material (type and size, humidity of burn-out material), (Rayner, 2009) the clay to burn-out material ratio, the amount of water added to the mixture, the manufacturing method (Rayner, 2009) (moulded by hand, pressed, wheel thrown), drying time and conditions, (Rayner, 2009) firing temperature, time and location in kiln, size of the filtering element (Rayner, 2009), capacity and the thickness of the filter (Rayner, 2009).

The pots used in this research were moulded by hand at Oriang' Pottery. The ratio of clay to sand was 3:1. The pots were fired openly using dried grass and cow dung. Clay should have an acceptable level of plasticity (Rayner, 2009), rate dry of shrinkage, and after firing, (Rayner, 2009) acceptable rates of total shrinkage and absorption (Rayner, 2009).

2.2.2 Oriang' Women Pottery Group

Pottery is an ancient art that is a source of livelihood for many local communities and its products remain beautiful, functional works of art and craft. At Oriang' Women Pottery Group in Kendu Bay, Homa Bay County, 52 women make a living through the messy but viable enterprise. According to Mrs Dorina Nyasi, the secretary of group, they can make at least 30 pots in a day which takes only two to three days to dry before firing them in the kiln.

The soil is excavated about a 10km away from their pottery site where the women knead the clay using their hands. This is done to eliminate air bubbles and to make it more pliable and easier to work with. Little sand is also sieved and mixed with wet clay to make the mixture finer.

The clay pots are decorated using a brush that is dipped in aloe known as *okaka* in the local Dholuo language.When the pots are ready, they are allowed to completely dry before undergoing firing which takes about two hours.

This is done to make the pots durable. The vessels are then cooled and a boiled juice that is extracted from the bark of a thorn plant is sprinkled on them to give a shiny dark colour.

The modified clay pot exhibits a flat base for stability and a narrow neck to prevent access which reduces the chances of contamination. The only challenge they face is the breakage and spillage of pots which occur during the firing and when they are being transported to the markets. Since it is a group project, 10 per cent of the money goes to the savings account while 90 per cent is divided equally among the members.

In response to the growing demands for safe water facilities in the rural area, the secretary says that ceramic pots have been on high demand in the markets and the retail price has grown much higher.

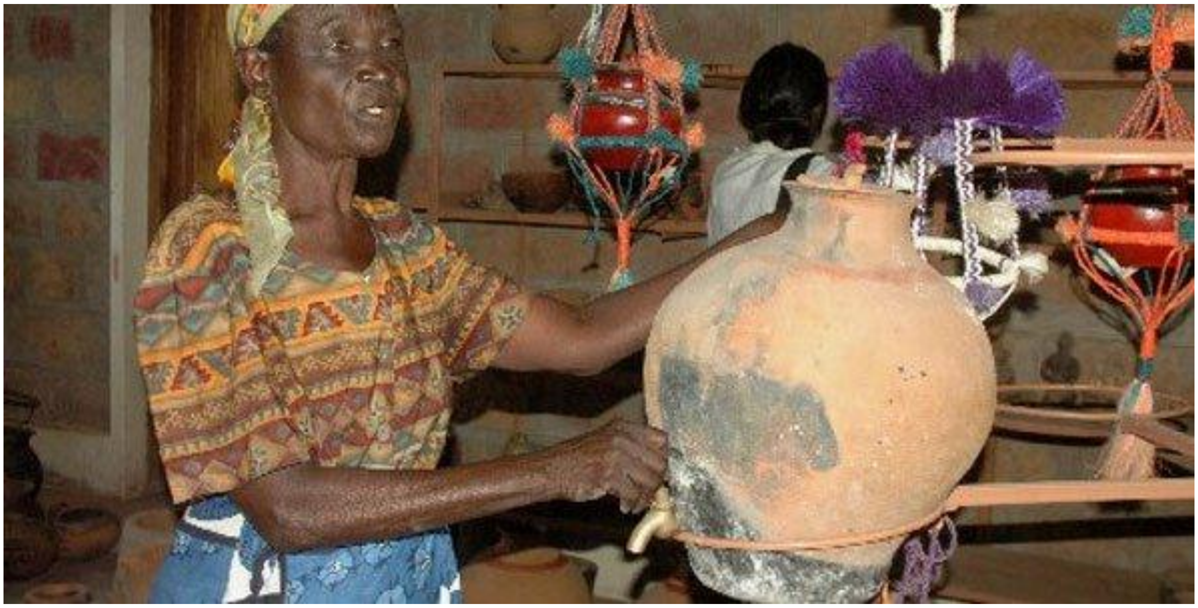


Figure 2.3: Ms Dorine Nyasi, a member of the Oriang Women's Pottery Group displays a water pot fitted with a tap.

2.2.2.1 Microbiological Effectiveness of the Clay Pots

The Academic Model Providing Access to Healthcare's (AMPATH) Maji Safi (Swahili for "safe water") project began in 2009 in an effort to reduce waterborne diseases and provide clean drinking water to the people of Western Kenya. AMPATH's Maji Safi department has sold over 2,000 ceramic water filters in Western Kenya (AMPATH, 2011).

Field studies carried out in different parts of the world indicate that quality of drinking water has improved due to the effectiveness of the ceramic pot filters and also reducing diarrhea (Plapally *et al.*, 2011). Tests carried on water quality in Cambodia showed that about 99% of the filters resulted in water with low-risk range of less than 10 E.coli per 100 Ml that is after distribution of 1000 ceramic filter pots (UNICEF, 2007; Rayner, 2009).

However, there was a decrease in diarrhea cases by 45% as reported by the nongovernmental organization Food for the Hungry International in Bolivia in their studies on clay ceramic filters performance (Plapally *et al.*, 2011; Clasen *et al.*, 2006). Consultation and training has been provided by PFP in many other countries globally (Potters for Peace, 2006). These water filters have been developed by the Family Foundation of the Americas (AFA) (Varkey and Dlamini, 2012) since 1994 for the poor in El Salvador, Guatemala and Honduras (Varkey and Dlamini, 2012).

A case study conducted in Swaziland on clay pot filter with 600 μm pore size showed that there was a yield of water completely free of *E. coli* (Varkey and Dlamini, 2012) by the clay pot filter and a reduction by 99.3% of the concentration of the total coliform (Varkey and Dlamini, 2012). Table 1 shows water quality risk levels associated with microbiological contamination from the scale of zero to 1,000 (Varkey and Dlamini, 2012).

Table 2.1: Water Quality Risk Levels

No. of Thermotolerant (faecal) coliforms or E.coli per 100ml water sample	
0	follows WHO guidelines
1 – 10	Less Risk
10 – 100	Intermediate Risk
100 – 1000	Great Risk
1000+	Very great Risk

2.3 Solar Disinfection (SODIS)

Effective elimination of microbial and reduction of morbidity of diarrheal together with epidemic cholera (Conroy, 2001 has been illustrated frequently through a combination of ultra violet and thermal radiation by Solar Disinfection (McGuigan *et al.*, 2012). This involves aeration of water with lower turbidity (<30 NTU) to increase oxygentation followed by placing it in clear plastic bottles which is usually 1.5-2.0 L PET beverage bottles) and placing the bottles on the roof so as to expose them on the sun (UNICEF, 2008). Sunlight exposure has shown diarrhea-causing organisms being deactivated in contaminated drinking water (Naggi, 2009).

Mechanism of solar radiation effectiveness in inactivation of pathogenic organisms can be explained by the following; (Naggi, 2009):

- Destruction of bacteria’s cell structure and direct metabolism interference by UV-A (Naggi, 2009).
- Reaction between dissolved oxygen in water and UV-A (wavelength 320–400 nm) produces forms of oxygen which are highly reactive (hydrogen peroxides and oxygen free radicals) also believed to causing damage to pathogens (Naggi, 2009).

- Increase in water temperatures above 50 °C (122 °F) leads to increase in disinfection process (three times faster) due to heating water with cumulative solar energy (including the infrared radiation component) (Naggi, 2009).

Depending on light intensity, time of exposure varies from 6 to 48 hours (UNICEF, 2008) (UNICEF, 2008). Similarly, solar and thermal disinfection together with filters do not provide protection against recontamination to the residual water (UNICEF, 2008; Classen, 2008).

2.4 Water Quality Parameters

Real water systems (natural as well as wastewater) are considered to be very complex and comprise of both inorganic and organic species. The rate and efficiency of photocatalytic process may be influenced by dissolved inorganic species inform of cations and anions or even lead to spontaneous photochemical phenomena (Carp *et al.,* 2004).

2.4.1 Physical Parameters

2.4.1.1 Turbidity

This is a measure of the cloudness of water (Seneviratne, 2007) produced by suspended solids (Jadhav and Pingle, 2016) majorly soil particles and plankton that are suspended in water column (Jadhav and Pingle, 2016). To have an ecosystem which is healthy and functioning well i.e ecosystem with plankton at moderate amount to supply to the food chain, moderately low levels of turbidity is required (Jadhav and Pingle, 2016). Turbidity prevents light from reaching the submerged aquatic vegetation and also may raise the surface water temperature due to heat absorption from light facilitated by suspended particles near the surface (Jadhav and Pingle, 2016; Divya and Mahadeva, 2013). Dissolved oxygen may also be reduced by turbidity in water (Divya and Mahadeva, 2013).

Causes of Turbidity:

- Soil erosion – silt and clay deposition
- Urban runoff – road grime; rooftops; parking areas
- Industrial waste – sewage treatment effluent; particulates
- Abundant bottom-dwelling organisms e.g. catfish stirring up the sediment built up on the bottom of the lake.
- Organic matter – microorganisms; decaying plants and animals; petrol, diesel or oil from roads

Effects of Turbidity:

- Reduces water clarity
- Aesthetically unpleasant
- Decreases rate of photosynthesis
- Increases water temperature

2.4.1.2 Conductivity

A measure of the ability of water to allow electric current to pass through is known as conductivity (Gupta and Paul, 2013). Inorganic dissolved solids' presence like nitrates, chlorides, sulfates, sodium, magnesium, calcium, aluminium and iron (Gupta and Paul, 2013) can also be determined indirectly from a measure of conductivity (Gupta and Paul, 2013). These substances once in water bodies elevate water's conductivity (Gupta and Paul, 2013).

2.4.1.3 Total Suspended Solids

These are particles in water that remain suspended but never get settled (Branigan, 2013). Determination of TSS in water can be done by allowing water sample with a known amount to pass through a piece of filter paper which is weighed accurately and the difference between the two weighed filter papers is normally the weight of total suspended solids in ppm(mg solids per litre of water).

2.4.1.4 Total Dissolved Solids

TDS reveals the quality of water purification system and its purity. It measures total amount of charged ions which are mobile including; salts, minerals or metals dissolved in water of a given volume (Ogori and Ogori, 2014). TDS is expressed in mg per unit volume of water (mg/L) (Ogori and Ogori, 2014) and it causes harm to everything that lives, uses or consumes water whether inorganic or organic (Ogori and Ogori, 2014). The recommended maximum contamination level for TDS by secondary regulations of EPA is 500 mg/liter (Brebia and Popov, 2011) and a value exceeding 1000 mg/l as per most of water supplies is taken to be not safe for human consumption (Ebrahim *et al.,* 2011).

2.4.1.5 Dissolved Oxygen

Dissolved oxygen can be defined as the amount of oxygen in gaseous form (O_2) dissolved in the aqueous solution (Al-Ajlouni *et al.,* 2010). Oxygen can get into water from the air surrounding it through diffusion, by aeration (Al-Ajlouni *et al.,* 2010) (rapid movement), and as a byproduct of photosynthesis (Al-Ajlouni *et al.,* 2010). The overall health of water is measured by the amount of oxygen in it whereby if the concentration of dissolved oxygen is high, pollution levels in water are low and if it's vice versa, then that water body is considered not of optimal health.

The following factors affect dissolved oxygen concentration in a stream.

i) Temperature: at low temperatures, oxygen easily dissolves in water.
ii) Flow: amount of oxygen in a stream varies with the volume and velocity of flowing water whereby the faster the flow of white water areas the more it is rich in oxygen because of the atmosphere's addition of oxygen into the water than stagnant areas (EPA, 2007).
iii) Aquatic Plants: aquatic plants in any stream can affect the concentration of dissolved oxygen in it. This is because during photosynthesis oxygen is released into the water by these plants. The process of photosynthesis depends on light therefore it happens during the day when there is sunshine and stops at night. Streams with high accumulated aquatic plants and algae tend to experience fluctuations of dissolved oxygen daily with its peak especially in the late afternoon. Also concentrations of dissolved oxygen may reduce significantly in early morning due to oxygen consumption by plants, just like animals (EPA, 2007).
iv) Altitude: compared to both altitudes, water dissolves more oxygen at the low altitudes than at high altitudes.
v) Dissolved or suspended solids: water with less dissolved or suspended solids easily dissolve oxygen.
vi) Dissolved oxygen can be affected with human Activities which may include:

   a) Elimination of vegetation covering water bodies may lead to reduced oxygen concentrations as a result of increased water temperature due to high levels of suspended solids as a consequence of erosion from bare soils and absence of canopy shade (EPA, 2007).

b) Runoff from impervious surfaces with salts, sediments and other pollutants may result from typical human activities leading to increase in levels of suspended and dissolved solids in stream water hence reducing oxygen concentrations (EPA, 2007)

c) Some wastes like organic wastes and others like discharges from industries and sewers containing nutrients, septic tanks and runoffs from agricultural and urban activities leads to reduced oxygen levels. Large nutrient inputs into the water bodies results in excessive algal bloom which is decomposed by bacteria, and once it dies, it consumes large amount of oxygen (EPA, 2007).

d) Oxygen supply may also be of concern when water is supplied into rivers and streams from the dams' lower part of their reservoirs. This is because despite the reservoirs' water being cooler at the bottom, there will be a reduction in the concentration of dissolved oxygen due to bacteria's decomposition as a result of high levels of organic matter at the bottom (EPA, 2007).

Table 2.1 KEBS, WHO and USEPA maximum permissible level on some drinking water parameters**.**

Substance	**KEBS**	**WHO**	**USEPA**
Ph	**6.5-8.5**	**6.5-8.5**	**6.5-8.5**
Turbidity (NTU)	**5**	**5**	**1**
TDS (mg/l)	**1500**	**500**	**500**
TSS(mg/l)	**Nil**	**Nil**	**30**
Conductivity(□S/cm)	**50-500**	**50-500**	**50-500**
Copper (mg/l)	**0.1**	**1.3**	**1.3**
E *coli*	**Nil**	**Nil**	**nil**

2.4.2 Chemical Properties

2.4.2.1 Water Hardness

Concentration of multivalent cations in water measures water's hardness. They are positively charged cations carrying a charge greater than 1+ (Singh and Kumar, 2014). Commonly, the cations have the charge of 2+ (Singh and Kumar, 2014) and those common in hard water may include Ca^{2+} and Mg^{2+} (Singh and Kumar, 2014) whose presence in water supply may be by leaching from minerals within aquifers (Singh and Kumar, 2014).

2.4.2.2 Nitrates

Nitrate ions (NO_3^-) found in freshwater samples result from a variety of natural and manmade sources. Nitrates are an important source of nitrogen necessary for plants (Sarda and Sadgir, 2015) and animals to synthesize amino acids and proteins.

Through the process called the Nitrogen Cycle, nitrogen (N2) from air is converted to useable forms for plants and animals. These conversions include industrial production of fertilisers, as well as natural processes such as nitrogen fixation by legumes plants, plant and animal decomposition, and animal waste.

Sources of Nitrate ions:

- Agricultural runoff
- Urban runoff
- Animal feedlots and stock yards
- Municipal and industrial wastewater

- Automobile and industrial emissions
- Decomposition of plants and animals

Nitrate levels in freshwater are usually less than 1mg/L but manmade sources of nitrate may elevate levels above 3mg/L. Levels above 10mg/L in drinking water can cause a potentially fatal disease in infants called *methemoglobinemia* (nitrate converts haemoglobin into a form that can no longer transport oxygen).

High nitrate concentrations (and phosphates from grey water/sewage) also contribute to *eutrophication*, ie excessive growth of aquatic plants and algae. Unpleasant odour and taste of water, as well as reduced clarity often accompany this.

2.4.2.3 Phoshates

A small amount of phosphorus is an essential nutrient for all aquatic plants and algae but in high levels, phosphorous can be considered a pollutant. Phosphorous concentration determines the level of eutrophication (increased plant and algal growth due to an excess of nutrients such as phosphorous and nitrates).

Most phosphorous in surface water is in the form of phosphates. The most common sources of phosphorous in water include:

- Human and animal waste – from sewage and excrement from animals living near on in the water body (mainly organically bound phosphates)
- Industrial wastes – condensed phosphates (also called polyphosphates) that are sometimes added to water to prevent formation of scaling and to inhibit corrosion.

- Agricultural wastes – fertilizers contain high levels of phosphates (particularly orthophosphates eg PO_4^{3-} and HPO_4^{2-}) that enter the water through runoff and erosion, due to disturbances to land and vegetation.
- Human disturbance of land – clearing or disturbance of land vegetation increases erosion resulting in more phosphates being washed out of the soil

High levels of phosphates result in:

- Eutrophication
- Increased algal blooms increased Biochemical Oxygen Demand (BOD)
- Decreased Dissolved Oxygen (DO)

2.4.3 Microbial Contamination

Human and animal waste carried into stream systems are sources of pathogenic or disease-causing, bacteria and viruses. Natural aquatic resources can get microbial contamination mainly from the following sources; decontamination stations, discharges from water treatment plants (Jung *et al.*, 2014), point sources industries, hospitals, etc (Jung *et al.*, 2014).

Polluted waters have microorganisms which are several members of viruses, bacteria and protozoa linked with waterborne diseases (cholera, typhoid fever, hepatitis, shegellosis, diarrhea, amoebiasis, jaundice, etc). These include enterococci, fecal coliform, and *E. coli* bacteria (Tyagi *et al.*, 2006).

Significance and abundance of pathogens in water can be determined by the following factors; pathogens' persistence in water bodies, level of contamination, pathogens' capability of moving from one point to another and biological reservoirs (including aquatic plants and sediments) Jung *et al.*, 2014). Other microbial contaminants are annexed in appendix 3.

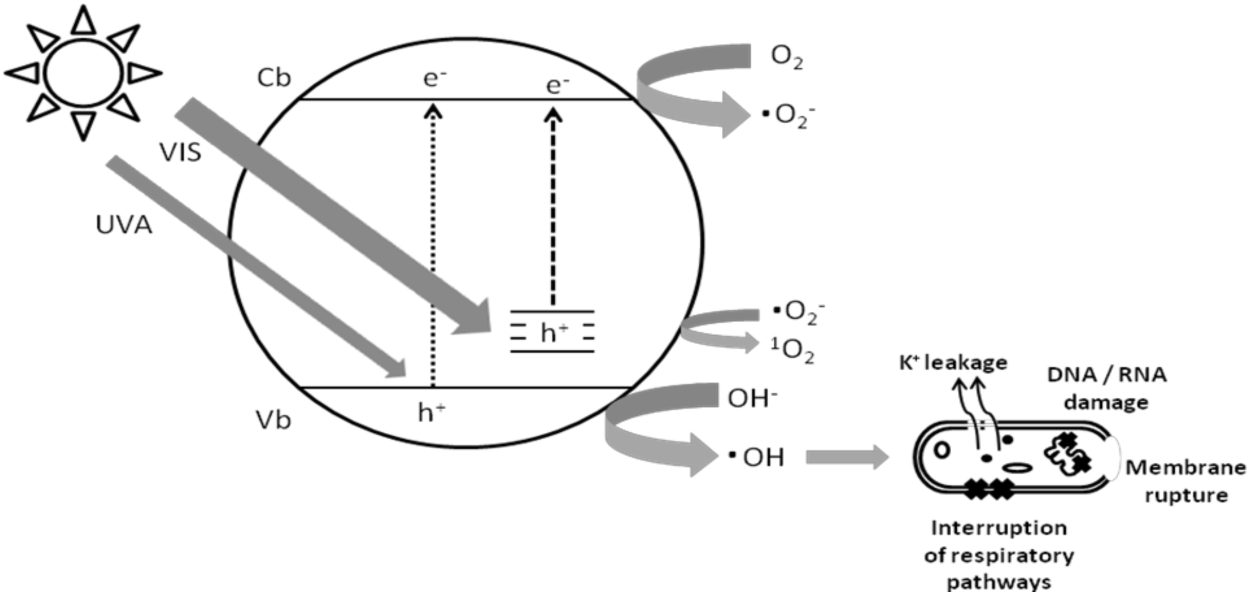


Figure 2.4: Proposed bacterial disinfection mechanism during solar excitation of N, S co-doped TiO_2 (Rengifo-Herrera and Pulgarin,2010).

2.5 Advanced Oxidation Processes (AOP)

AOPs increase the rate of an oxidation process by the use of highly reactive species, the most widely used being the hydroxyl radical, •OH, which can increase a reaction rate by a million to a billion times. Basic oxidation processes involve the conversion of a chemical state of a contaminant to a higher level of oxidized products (some standard oxidizing agents used are O_3, O_2, air or H_2O_2). These radicals subsequently react with the contaminants and through a series of multi-step reactions form the end products such as low molecular weight carboxylic acids that are biodegradable, non-toxic, and unregulated for surface discharge. Complete mineralization to CO_2 and H_2O.

AOPs can be applied to many processes involving contaminated industrial wastewater, groundwater, drinking water, ultrapure water and process water. Many applications have been for groundwater remediation and the removal of volatile and semi-volatile organic compounds such as chlorinated alkenes, ethers, chlorinated alkanes and pesticides. AOPs are also applied for the treatment of industrial wastewater and removal of phenolic compounds, COD, cyanides and ketones. These compounds are commonly encountered in wastewater generated from various industries such as the explosives, resins, wood preservation, aerospace, and electronic industries.

2.6 Titanium Dioxide

This is a semiconductor that is widely investigated as a photocatalyst because of its high stability, low cost, and safety upon both the environment and humans (Gaya and Abdullah, 2008) which makes it be considered as very close to an ideal semiconductor (Gupta and Tripathi, 2011). Due to its bio-compatibility (Majeed *et al.*, 2015) to the human body, titanium dioxide has been applied as a biomaterial in orthopedic implants and dental or prosthesis (Majeed *et al.,* 2015), due to their better lower modulus, corrosion resistance, durability and superior biocompatibility (Majeed *et al.*, 2015).

There has been much advancement with respect to titanium dioxide in the past few years (Pelaez *et al*., 2012). The main initial advance was recorded in the year 1972 when there was a report on splitting of water by photo-electrochemical using Pt counter electrode and TiO_2 anode in Honda and Fujishima (Pelaez *et al*., 2012).

Naturally, the mineral TiO_2 is found in its purest raw form in abundance in Sweden, Australia, Africa and Canada (TWAS, 2002).

2.6.1: Comparison of TiO_2 with other Semiconductors

For the photodegradation of inorganic and organic contaminants, a lot of materials like ZnO, TiO_2, ZrO_2, MoS_2, CdS, WO_3, Fe_2O_3, (Kabra *et al*., 2004) and their many combinations (Kabra *et al*., 2004) have undergone testing and applied as photocatalyst (Kabra *et al*., 2004). The minimum band gap energy needed to make a photon to cause photogeneration of charge carriers over TiO_2 semiconductor (anatase form) is 3.2 eV corresponding to wavelength of 388 nm (Perkowski *et al*., 2006). Figure 2.3 below illustrates valence and conduction bands for several metal oxides (Gupta and Tripathi, 2011).

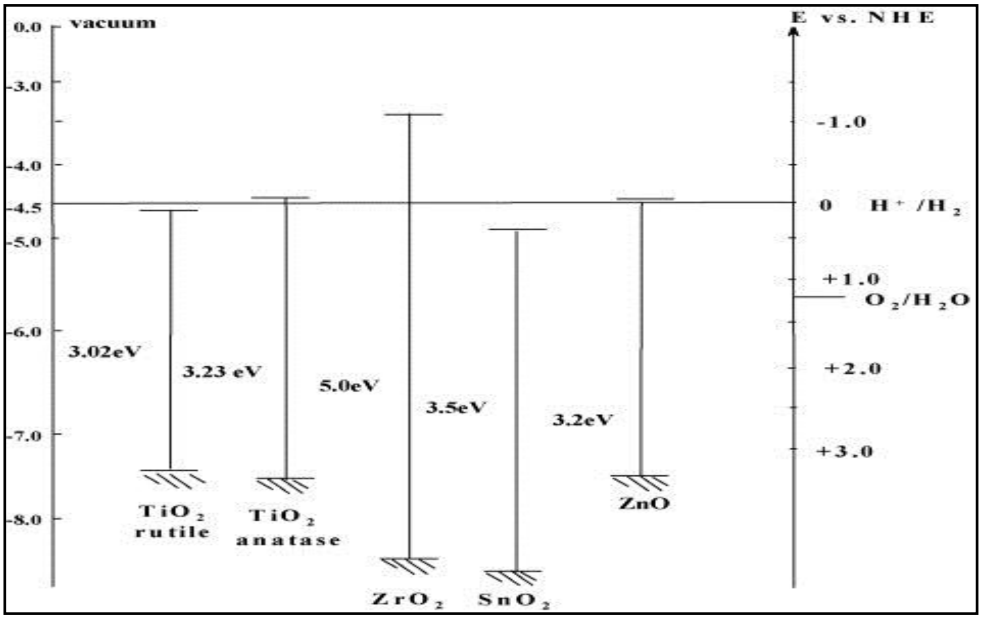


Figure 2.5: The conduction and valence band of select metal oxide semiconductors at pH 0.

The left hand scale represents the internal energies to the vacuum level while the right hand scale is the normal hydrogen electrode scale which allows predictions based on reduction and oxidation.

Characterization of a photocatalyst can be determined by its ability to adsorb two reactants simultaneously, which through an efficient absorption can be oxidized or reduced by a photonic activation (Cardenas *et al*., 2013). The ability of a semiconductor to undergo photoinduced electron transfer to an adsorbed particle is ruled by semiconductor's position, the band energy and the adsorbates' redox potential (Banerjee, 2011).

2.6.2 TiO_2 Structures and Properties

Titanium dioxide (TiO_2) exists majorly in three polymorphs in nature (Moorthy, 2015), anatase (octahedral), rutile (octahedral) and brookite (distorted octahedral) (Moorthy, 2015). The most common polymorphs are anatase and rutile (Moorthy, 2015).

Anatase phase is mostly considered to be having higher photo activity than rutile (Liu *et al.*, 2009b). According to Carp *et al. (*2004) photocatalysis based on TiO_2 (anatase) possess the advantages below:

i) Within few hours, under normal temperature and pressure, Non-selective destruction of both organic and inorganic waste materials can be achieved with absence of polycyclic products (Carp *et al.*, 2004),

ii) Pollutant oxidation in ppb range; (Carp et al., 2004)

iii) Uses oxygen as an oxidant; (Carp *et al.*, 2004)

iv) Ability to simultaneously undergo oxidative and reductive reactions; (Carp *et al.*, 2004)

v) Photocatalysis' effectiveness is specifically applicable for inactive substrates (Carp *et al.*, 2004) such as simple derivatives of alkanes or the alkanes themselves. The inactive substrates have led to perceptions in surfactants elimination, cleaning of oil spill, and dyes from industrial water (Carp *et al.*, 2004)

vi) There is adaptation of significantly active catalysts to particularly systems which are reactor designed (Carp *et al.*, 2004).

The following are reasons as to why anatase has a high photoreactivity: reduced ability for oxygen adsorption, slightly greater level of Fermi (Hussain *et al.*, 2015) and hydroxylation's higher degree in the anatase phase (Hussain et al., 2015). TiO_6 octahedra is formed from coordination of titanium (Ti^{4+}) atoms (Nolan, 2010) to the six atoms of oxygen (O^{2-}) in all titanium (Ti^{4+}) atoms' three forms (Nolan, 2010). Figure 2.4 below illustrates the various unit cells of TiO_2 modifications for brookite, rutile and anatase (Moellhmann *et al.,* 2012).

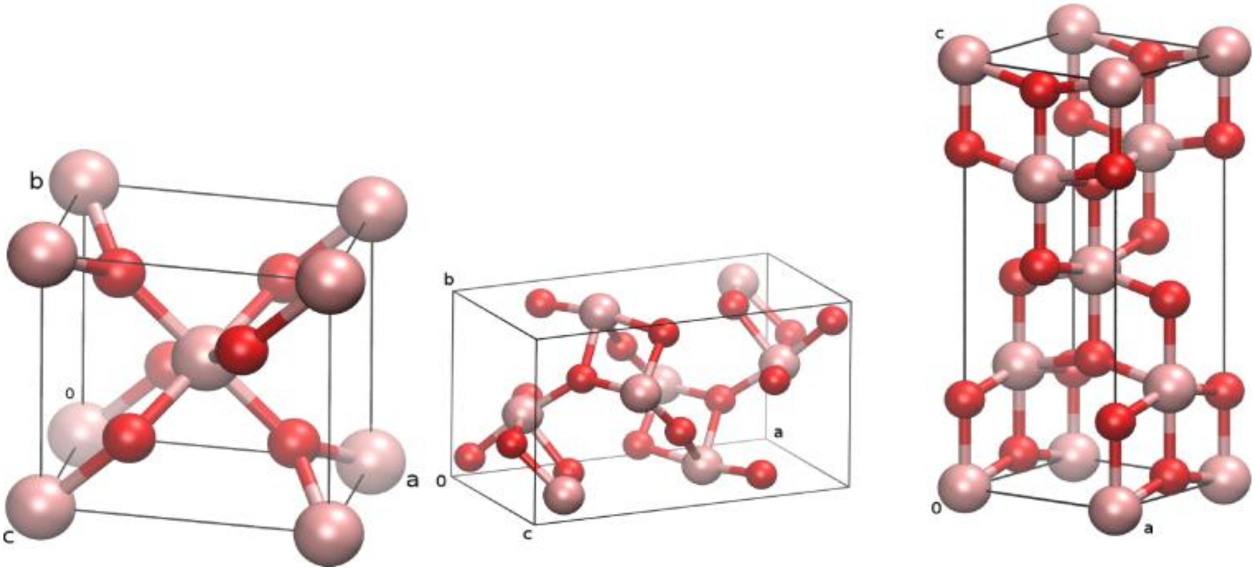


Figure 2.6: Unit cells of the TiO_2 modifications rutile, brookite and anatase

Due to titanium dioxide's oxygen deficiency, it is naturally considered as an n-type semiconductor (Pelaez *et al*., 2012). It has a band gap of 3.0 eV for rutile, 3.2 eV for anatase, , and ~3.2 eV for brookite (Pelaez *et al*., 2012). Anatase TiO_2 photocatalyst is considered to be efficient with an activation wavelength of (λ) < 387 nm and a bandgap energy ($h\nu$) of 3.2 eV (Pelaez *et al*., 2012).

2.6.3 Electronic Processes in TiO_2 Photocatalysis

In photocatalysis, heterogeneous reactions are considered to be complex sequential reactions. According to Herrmann, (1999) and Pirkanniemi and Sillanpaa (2002), the mechanism composes of five main steps which are:

(i) Removal of huge amount of organic contaminant from the liquid phase to the TiO_2 surface (Herrmann, 1999),

(ii) Organic contaminant's adsorption onto the surface of the photon activated TiO_2 (Herrmann, 1999),

(iii) Adsorbed phase on the surface of TiO_2 undergoing photocatalysis reaction Herrmann, 1999),

(iv) Intermediate from the TiO_2 surface undergoes desorption (Herrmann, 1999), and

(v) Mass removal of the intermediate from the interface area to the bulk fluid (Herrmann, 1999).

Once energy radiated absorbed is equal to or greater than semiconductors' bandwidth, a photon makes the electron to be excited from the valence band to the conduction band hence leaving an electronic vacancy (a hole) in the valence band (h^+) (Hupka *et al.*, 2006). The photo-generated holes at the top of the irradiated semiconductor can oxidize (Hupka *et al*., 2006) a variety of hazardous species directly to water or produce ·OH radicals (Hupka *et al.*, 2006).

For anatase TiO_2, the band gap is 3.2 eV, thus UV light (387 nm) is necessary. The valence band of TiO_2 consists of 2p orbitals of oxygen hybridized with the 3d orbitals of titanium, whereas the conduction band is only the 3d orbitals of titanium (Haque and Muneer, 2007). For photocatalysis to happen, electrons will have to move the valence band to the conduction band to form electron-hole pairs which are responsible for reduction and oxidation of pollutants (Haque and Muneer, 2007). Once a photon moves an electron from the valence band to the conduction band, a hole with a positive charge is created in the valence band:

$$TiO_2 + hv \longrightarrow TiO_2^-(e^-_{cb} + h^+_{vb}) \quad \text{……………} \quad \textit{Equation 1}$$

These kinds of holes, which are trapped, makes the bond between the associated Titanium (IV) Oxide and lattice oxygen hence letting oxygen atoms to be liberated, thus creating oxygen vacancies (Wang *et al.,* 2010). Once this occurs, the electron in the conduction band is available to reduce materials while the hole in the valence band is available to oxidize materials (Pelaez *et al.*, 2012). This is an essential feature of Titanium (IV) Oxide that is exploited to reduce and oxidize both organic and inorganic molecules (Pelaez *et al.,* 2012). Often the recombination of the electron and hole can happen and heat is given off as illustrated in equation 2 below:

$$TiO_2^-(e^-_{cb} + h^+_{vb}) \xrightarrow{(Recombination)} TiO_2 + Heat \quad \text{…………….} \quad \textit{Equation 2}$$

This is responsible for the low quantum yields of the photo catalyst (Ibhadon and Fitzpatrick, 2013). Several radicals that are responsible for photo oxidation and photo reduction are created in the process of absorbing a photon. The reactions that cause hydroxyl radicals responsible for photo reduction is as shown in equation 3 below:

$$H_2O + TiO_2\,(h^+_{vb}) \longrightarrow OH^- + H^+ \qquad \textit{Equation 3}$$

Equation (3) above illustrates how water molecules together with hydroxyl ion undergoes reaction with photogenerated holes at the top of TiO_2 to form hydroxyl radicals (Yang *et al.,* 2007), whereas adsorbed oxygen at the photocatyst's surface is reduced by the conduction band (Haque and Muneer, 2007). Superoxide radical anions together with hydroxyl radicals are the main (Haque and Muneer, 2007) oxidising species in the photocatalytic oxidation processes (Haque and Muneer, 2007).

The hydroxyl radicals attack organic compounds, which results in various reaction intermediates and produces the final products, as CO_2 and H_2O (Ahmed *et al*., 2011). A summary of the mechanism of photodegradation process is illustrated in Figure 2.5 below (Winzenburg and Faust, 2012).

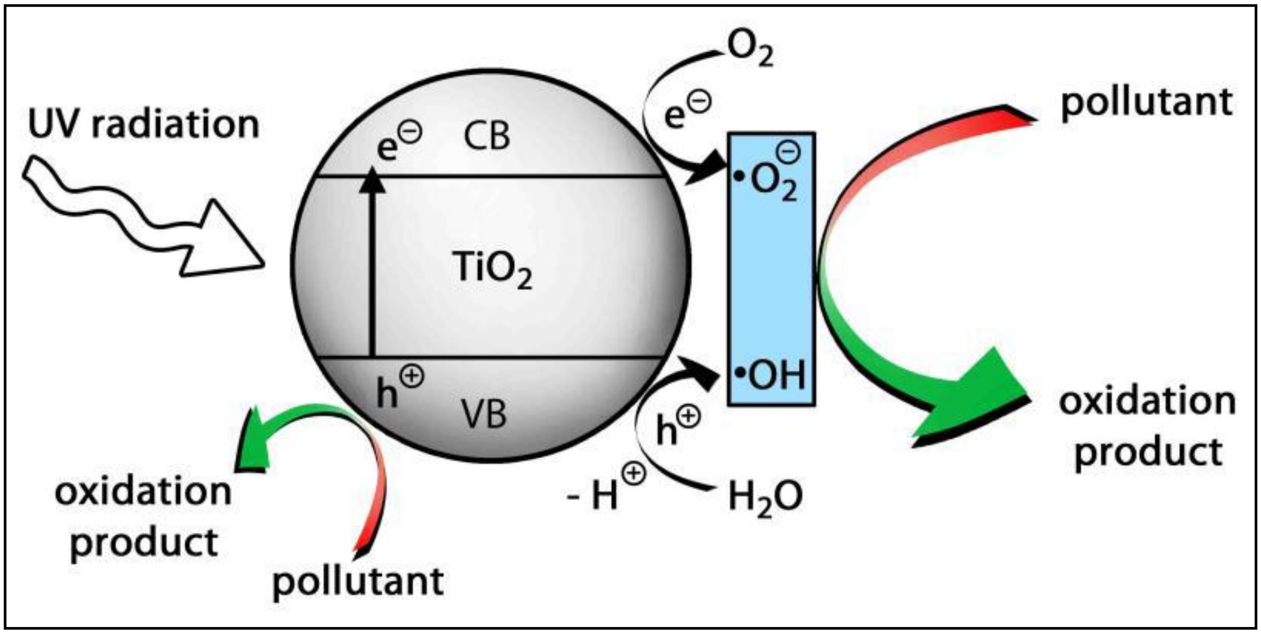


Figure 2.7: Simplified photocatalysis mechanism of pure TiO2 (anatase) upon UV irradiation (Winzenburg and Faust, 2012).

Application of photocatalysis is hampered (Liu *et al*., 2013) by the fact that TiO_2 only absorbs in the UV region (Liu *et al*., 2013) of electromagnetic radiation due to its large bandgap energy (Liu *et al*., 2013). Only 2 to 5% of the solar spectrum (Hupka *et al.*, 2006) (UV fraction of solar light) can hence be utilized by conventional TiO_2-photocatalysis (Hupka *et al.*, 2006). Consequently, when TiO_2 is used as a photocatalyst, UV lamps are required (Hupka *et al.*, 2006) hence an increase in UV/TiO_2 system's costs of operation (Hupka *et al.*, 2006).

Sensitization of the surface of titania (indirect mechanism) or structure modification of TiO_2 to change spectrum's absorptions to visible light region (photocatalysis' direct mechanism) (Hupka *et al.*, 2006) can lead to induced reactions as a result of visible light on TiO_2 (Hupka *et al.*, 2006).

Several attempts of intensification of TiO_2's photocatalytic activity have occurred (Song et al., 2013). They include: extension of absorption of light to the visible range by using dyes to cover the surface, combination of other semiconductors with TiO_2, introduction of metals like Fe, V, Pt, Cr, Nb, and Ru (Anpo, 2000) for doping, introduction of non-metals like B, N, S, or C for doping (Asahi *et al.*, 2001; Sakthivel and Kisch, 2003; Umebayashi *et al.*, 2002) or conversion of TiO_2 to a non-stoichiometric form (Justicia *et al.*, 2002) and partially coating with noble and transition metals (Liu *et al.*,2004).

2.6.4 Visible Light Photocatalysis

The two principle modes by which the activity of TiO_2-based photocatalysts can be extended into the visible region are doping and surface modifications (Chatterjee and Dasgupta, 2005). Doping generally means the insertion of atoms, or group of atoms or ions into a host's crystal lattice. Induction of bathochromic shifts i.e band gap reduction or introduction of states of intra-band is the major reason for doping which results in more visible light absorption (Mital and Manoj, 2011).

Doping of TiO_2 with suitable elements (Chatterjee and Dasgupta, 2005) such as chromium, iron or tin or with non-metallic atoms like sulphur (Ohno *et al.*, 2003), nitrogen (Asahi and Morikawa, 2007) or carbon (Sakthivel and Kisch, 2003) induces inter-band states. Hence, additional absorptions of lower energy (i.e. longer wavelengths) lead to electrons getting excited into the TiO_2's conduction band (Asahi *et al.*, 2001; Chatterjee and Dasgupta, 2005). Figure 2.6 below illustrates a simplified photocatalysis process of doped TiO_2 (Winzenburg and Faust, 2012).

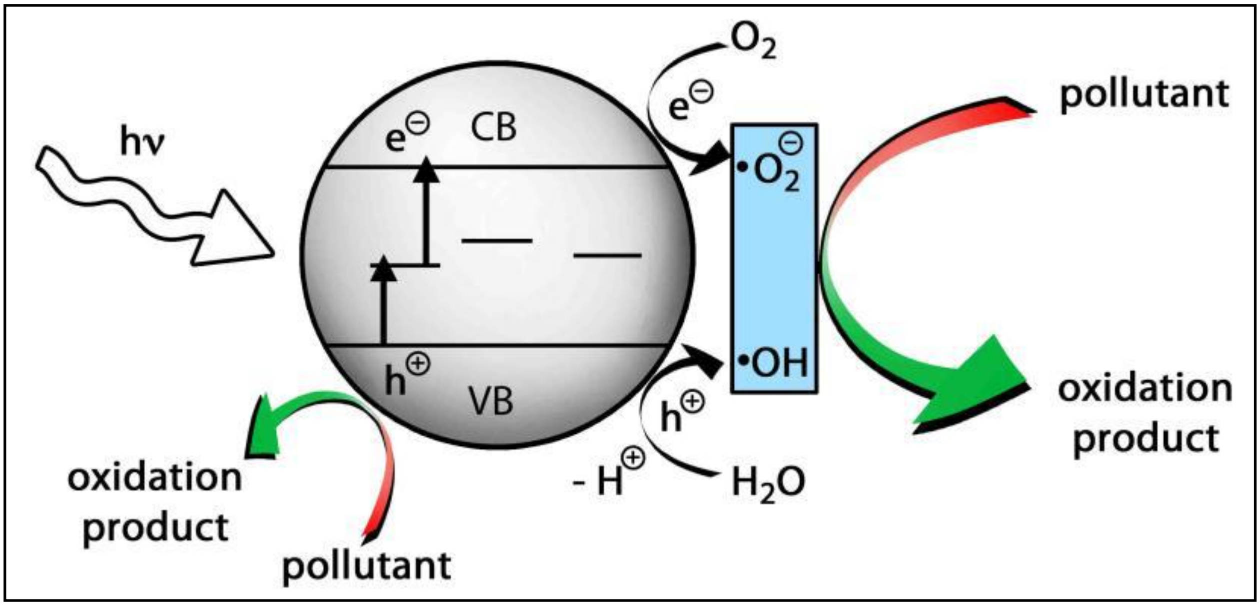


Figure 2.8: Simplified Photocatalysis mechanism of doped TiO2 (anatase) upon irradiation with visible light (Winzenburg and Faust, 2012.)

Response of visible light of N-doped TiO_2 is associated with localized N 2p states which are occupied and located at 0.7 eV which is above the valance band. Visible light can move these electrons in N 2p levels to conduction band. These electrons that have been photogenerated are then bound to the oxygen that has been adsorbed producing anions which are superoxided, leading to photoreaction (Ohama and Van Gemert, 2011).

2.6.4.1 Surface Modifications

Surface modification is a valuable alternative to obtain Vis-active photocatalysts. Suitable modifiers for the TiO_2 surface are secondary semiconductors (SC) such as CdS or Bi_2S_3 (Bessekhouard *et al*., 2004) or organic dyes such as erythrosin B, Rose Bengal, or corbocyanines (Chen *et al.,* 2005). Both semiconductor and surface-bound dyes can act as electron donors, if there is a match between energy of the conducting band of TiO_2 with that of their excited state (Chatterjee and Dasgupta, 2005).

2.6.4.2 Nitrogen Doping

The presence of a large band gap is the main disadvantage of the pure TiO_2 (Pelaez *et al.,* 2012), meaning that activation can only occur upon irradiation with photons of light in the UV domain (387 nm for anatase) (Pelaez *et al.,* 2012). This leads to limitations in solar applications' practical efficiency (Pelaez *et al.,* 2012). Therefore, enhancement of the efficiency of solar for TiO_2 under solar irradiation can be achieved through TiO_2 modification so as to facilitate absorption of visible light (Pelaez *et al.,* 2012).

There has been an extensive investigation of doping in nonmetal anion due to presence of nonmetals' electron states above the valence band edge of TiO_2 compared with pure TiO_2 (Tan *et al*., 2011). Some of the studied nonmetals include Nitrogen (N), Sulphur (S) and Carbon (C). Doping with nonmetal anions broadens the band gap of TiO_2 in its electronic structure (Tan *et al*., 2011) and affects the red-shift in the absorption spectra of nano-doped TiO_2 (Tan *et al*., 2011).

Introduction of nitrogen into the TiO_2 structure can be easier due to nitrogen's small ionization energy, same atomic size with oxygen and high stability (Pelaez *et al.,* 2012). There has been adoption of both wet and dry preparation methods for effective nitrogen incorporation into TiO_2 either as a surface dopant or in the bulk form (Pelaez *et al.,* 2012). Ion-implantation and sputtering are physical techniques which depend on direct energetic nitrogen ions treatment on TiO_2 (Nakano *et al.*, 2005; Pelaez *et al.,* 2012). There has been also successful application of pulsed laser deposition, atomic layer deposition and gas phase reaction methods in N-TiO_2 preparation (Zhao *et al*., 2008; Pelaez *et al*., 2012).

Sol-gel method is a technique which is most versatile for N-TiO_2 nanoparticles synthesis. It permits fine control of nanostructure of the material, porosity and morphology and also requires relatively simple equipment (Pelaez *et al.,* 2012). It is one of the bottom-up approaches used to synthesis nano-scale materials which have notable advantages. It is made up of solutions then lead to a solid phase without a precipitate.

The use of sol-gel method in the latest nano - field is due to its low cost process without involving any expensive machines compared to solid state processing routes using ball milling and RF magnetron sputtering. Besides that, it can be done under ambient temperature which is low temperature processing and it synthesis high homogeneity and purity of the nanostructures. Compared to other fabricated techniques, sol-gel method has many advantages due to its homogeneity, high purity, stoichiometry control, felicity and flexibility during dopants introduction in large concentrations, easily processed, capable in coating area which are large and complex and control over composition (Carp *et al.,* 2004).

Hydrolysis of precursors of titanium alkoxide in the presence of sources of nitrogen results in simultaneous growth of TiO_2 and N doping (Pelaez *et al.,* 2012). There has been a use of typical salts of titanium which include titanium tetrachloride and alkoxide precursors (Pelaez *et al.,*

2012) which includes tetrabutyl orthotitanate and titanium tetra-isopropoxide (Pelaez *et al.*, 2012).

2.6.5 Factors Affecting Photocatalytic Kinetics

Photocatalytic degradation of dyes and other organic matter in wastewaters is affected by:

1) pH of the precursor solution(catalyst's solution during preparation)
2) pH of the degrading solution (Akpan and Hameed, 2009)
3) oxidizing agent (Akpan and Hameed, 2009)
4) calcination temperature (Akpan and Hameed, 2009)
5) dopant content (Akpan and Hameed, 2009)
6) catalyst loading (Akpan and Hameed, 2009)

2.6.5.1 Effect of pH on Photocatalytic Degradation

The effect of pH on the photocatalytic reaction has been vastly studied (Umar and Aziz, 2013) due to the fact that photocatalytic (Umar and Aziz, 2013) water treatment is highly dependent on the pH (Umar and Aziz, 2013). This is because pH affects the charge on the catalyst particles (Prabha and Lathasree, 2014), size of aggregates and the position of conductance and valence bands (Prabha and Lathasree, 2014). The ionization state of the surface of the photocatalyst (Ahmed *et al*., 2011) can also be protonated and deprotonated (Ahmed *et al*., 2011) under acidic and alkaline conditions respectively (Ahmed *et al*., 2011) as shown in the following reactions (Ahmed *et al*., 2011):

$$TiOH + H^{+} \longrightarrow TiOH_2^{+} \quad pH < pH\ zc \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 1}$$

$$TiOH + OH^{-} \longrightarrow TiO^{-} + H_2O \quad pH > pH\ zc \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 2}$$

Hydroxyl radicals can be formed (Akpan and Hameed, 2009) by hydroxide ions reacting with positive holes (Akpan and Hameed, 2009). At low pH level, the positive holes become major oxidation species, whereas at high or neutral pH level hydroxyl radicals are considered predominant species (Akpan and Hameed, 2009). Adsorption on the TiO_2 surfaces by dye molecules can thus be influenced by change in pH which is a significant step in occurrence of photocatalytic oxidation (Akpan and Hameed, 2009).

2.6.5.2 Catalyst Loading

Optimium concentration of a catalyst is generally determined so as to ensure there is no excess catalyst and for total absorption of efficient photons in application of any given photocatalyst (Bibak and Aliabadi, 2014). Excess loading by a photocatalyst will lead to scattering of unfavorable light and reduction of penetrating light into the solution (Saqueeb and Muneer, 2003; Bibak and Aliabadi, 2014).

2.6.5.3 Light Intensity

The extent at which a semiconductor catalyst absorbs light at a given wavelength is the measure of its intensity (Ahmed *et al.*, 2011). High light intensity is important especially in water treatment because it raises the reaction rate in a photocatalytic reaction (Chong *et al*., 2010).

The relationship between the quantum yield (Φ) and the quantity of photon in the system (*Na*) was presented as follows:

$\Phi = \Delta n / Na$……………………………………………………………….*Equation 1*

The quantity of photons from the lamp is related to the lamp power, P and energy per photon, E, as derived from Planck's equation:

$N = PE = \frac{P\,h\,c}{\lambda} = \frac{I\,A\,h\,c}{\lambda}$…………………………………………………………*Equation 2* where, I is visible light intensity or the energy per unit area per unit time (W/m^2) and A is surface area.

2.7 Immobilization of the N-doped TiO_2

Most of the literature studies related to photodegradation have been carried out using the suspension of nanocrystals of the catalyst in aqueous solution. However, the use of aqueous suspension is not suitable for industrial applications due to the inconvenient and expensive separation of nano-particles of titanium dioxide for reuse. Moreover, suspension of fine particles limits the penetration of light leading to reduced efficiency of photodegradation. Therefore, there is a need to immobilize the photocatalyst onto an appropriate inert support in an efficient way, which eliminates the need of filtration of catalyst for reuse.

Immobilization of photocatalyst eliminates the need for the separation of the catalyst particles from the treated liquid and enables the contaminated water to be treated continuously (Mukherjee *et al.*, 2014). The catalyst film is porous and can therefore provide a large surface area for the degradation of contaminant molecules (Mukherjee *et al.*, 2014). If a conductive material is used as the support, the catalyst film can be connected to an external potential source to remove excited electrons to reduce electron-hole recombination, thereby, significantly improving the process efficiency (Mukherjee *et al.*, 2014).

There have been many attempts to immobilize TiO_2 photocatalyst over different structures of supports along with increasing the surface/volume ratio at the same time, which consequently enhances the photocatalytic oxidation efficiency. However, the surface area can only be efficient if it allows efficient absorption of light. There are different kinds of materials that have been used as a support to fix TiO_2, such as cellulose fiber (Goetz *et al*., 2009) glass and borosilicate glass (Zhang *et al.*, 2012) , ceramic, cloth, zeolite and stainless steel (Yanagida *et al*., 2006). Immobilization of TiO_2 can be prepared by many deposition techniques such as sol-gel, atmospheric pressure metal organic chemical vapour deposition, electron beam evaporation, reactive magnetron sputtering, spray pyrolysis, electrophoresis, anodic oxidative hydrolysis of $Ti^{3+,}$ reactive thermal deposition and static-dynamic films compressed method.

2.8 Pesticides

The frequent occurrence of pesticides (Ahmed *et al*., 2011) and phenolic compounds in wastewater (Ahmed *et al*., 2011) and environmental hazards associated has intensified (Ahmed *et al*., 2011) worries over public health due to their bio-recalcitrant structure and high toxicity (Ahmed *et al*., 2011). Over 98% of sprayed insecticides (Vivekanandhan and Duraisamy, 2012) and 95% of herbicides get to destinations other than their target species (Vivekanandhan and Duraisamy, 2012), including non-target species, water, air and soil (Vivekanandhan and Duraisamy, 2012).

2.8.1 Classification of Pesticides

Pesticides can be categorised into 9 major groups, based on their chemical structures:

1) Triazine (N-Containing pesticides): a group of compounds with molecules having unsaturated ring of three carbon and three nitrogen atoms.
2) Carbamates (Cbs): a salt or ester containing the anion $NH2COO^{-}$, derived from compound carbamic acid.
3) Organochloride (OCs): pesticides containing chloride.

4) Organophosphorous (OPs): pesticides containing phosphorus.
5) Chlorophenols (CPs): for example; trichlorophenol, pentachlorophenol, dichlorophenol, 2-chlorophenol.
6) Phenoxy acids (PAs): a group of chemicals associated with the growth hormone indoleacetic acid (IAA).
7) Quaternary ammonium compounds (Q): these are polyatomic ions which are positively charged of the structure NR_4^+ with R being alkyl or aryl groups.
8) Phenylurea (PhUrs): a chemical compound on which relatively nontoxic herbicides are based.
9) Thiocarbamate (ThCbs): a family of organosulfur compounds.

Pesticides pose a major health challenge even in small amounts due to their extreme high potential for endocrine disruption (Nghiem *et al.,* 2004). The WHO guidelines for pesticides are annexed in appendix 8. The environmental fate of pesticides (Navarro *et al.,* 2009) is determined by their tendency to partition into environmental compartments such as air and water and their mobility in soils (Navarro *et al.,* 2009).

In most urban areas, ground-waters are of special interest due to their use as the main source of drinking water and also in irrigation (Okungu *et al*., 2005). Contamination of ground-waters is directly associated with pollutant movement (Grenni, 2011) within the soil column supporting the adjectives and diffusional flow system (Grenni, 2011), ground- water geochemistry, and the general groundwater flow (Grenni, 2011). Despite the fact that the amount of pesticide in the groundwater (Hildebrandt *et al.,* 2007) cannot be directly associated with the agricultural activity right above the well, quality of the ground water can only be evaluated through the same (Hildebrandt *et al.,* 2007).

2.9. Lake Victoria Basin

2.9.1 Geography

Lake Victoria is the Africa's largest and world's second largest freshwater lake with a total catchment of 184,000 square kilometres, of which 68,000 km^2 is the actual Lake surface (UN-HABITAT, 2008). The lake is located in the upper reaches of the Nile River Basin making it possible for its waters to be shared by the three East African Countries with Kenya having (6%) of the share, Uganda (43%) and Tanzania (51%) (UN-HABITAT, 2008). Part of the upper watershed that discharges into the lake is Rwanda and Burundi, they drain into Lake Victoria through the Kagera River and between them, occupy about 18% of the Lake catchment (UN-HABITAT, 2008).

Water levels of Lake Victoria are very sensitive to moderate changes in rainfall over the lake and in the catchment (Okungu *et al.,* 2005).

Lake Victoria drainage basin is affected by the following environmental Issues:

i) Ecological degradation (pollution, contamination, biodiversity degradation, land/forest degradation, an introduction of exotic species).
ii) Extensive poverty
iii) Rapid population growth
iv) Elevated mortality rates (as a result of for example TB and malaria).

These threats have impacted negatively on the socio-economic values and contributing to huge losses. Key among the impacts experienced include:

i) Declining water levels and prolonged droughts in the entire basin (Awange *et al.*, 2006).

ii) Electricity production at Jinja declined by 30% (Okungu *et al*., 2005).

iii) Fish landing structures constructed to ensure good quality of fish have been rendered useless (Okungu *et al*., 2005).

2.10 X-Ray Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

2.10.1 X-Ray Diffraction (XRD) Instrumentation

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of $K_{\alpha1}$ and $K_{\alpha2}$. $K_{\alpha1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha2}$.

The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha1}$and $K_{\alpha2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded.

When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Other applications include:

- Characterization of crystalline materials
- Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- Determination of unit cell dimensions
- Measurement of sample purity

2.11 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample.

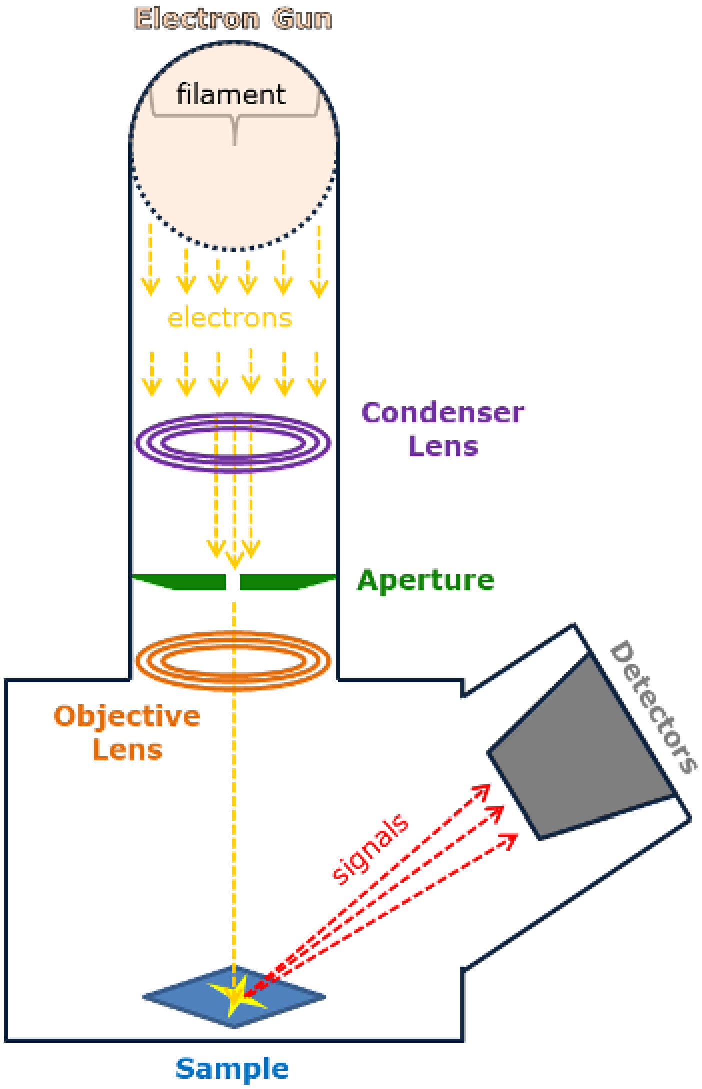


Figure 2.9: Scanning Electron Microscopy (SEM) Instrumentation

CHAPTER THREE

3. METHODOLOGY

3.1 Study Area

Homa Bay County is located in the former Nyanza Province, along the south shore of Lake Victoria's Winam Gulf. To the north and west, the county borders Lake Victoria. It borders Kisumu and Kericho counties to the North- East, Nyamira and Kisii counties to the east, and Migori to the South.

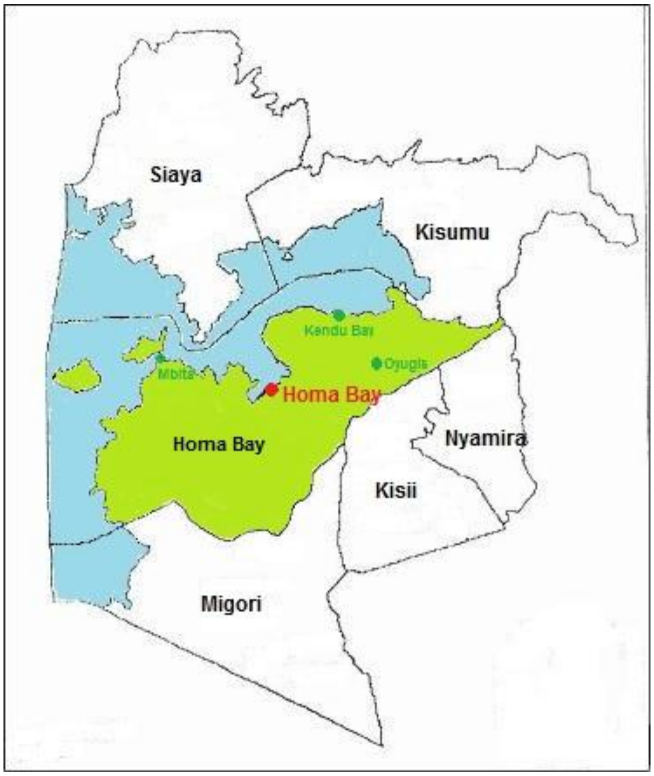


Figure 3.1: Nyanza Counties, Homa_Bay.

Homa Bay County is known to have a semi- arid climatic condition (Ochichi, 2014). It also has a binomial rainy pattern with long rains falling between the months of March and May while short rains falling between the months of September and November with roughly measurements of 1180 millimeters. Its daily temperature falls between 26-28 °C (UN-HABITAT, 2005).

Homa bay county's main water sources include Lake Victoria, dams and pans (UNESCO, 2006). Other sources are piped water, rivers and a few boreholes. These rivers and water pans get polluted through the following: defecation in bushes due to absence of pit latrines, agro-chemicals and waste water discharge that end into water points during surface run off (Bakibinga-Ibembe *et al.*, 2010). The water obtained from the pans is also contaminated by livestock since the pans are not protected.

Some of the water pans were observed to be drying up and their water quality also reducing. As a result of reduction of water quality and/or drying up, some of these pans have been abandoned by households.

Figure 3.2: Water pan at Homa Bay (Yao Kawiti)

3.1.1 Sampling sites with Global Positioning System (GPS) Coordinates

The sampling sites showing their GPS Coordinates.

Site	GPS Location
Yao Kawiti (water pan at Homa hills)	0°22'48.00" N 34°30'0.00" E
Awach Tende (River)	0º28'60" S 34º37'0" E
Oriang’	0º43'0" S 34º16'0" E

3.2 Laboratory measurement apparatus

PerkinElmer Lambda 25 UV-Vis spectrophotometer with 1 cm matching quartz cuvette cells was used for the absorbance measurements for the determination of absorbance of methyl Red and methylene blue photodegradation. The electrical conductivity and the total dissolved solids (TDS) of water was determined using portable TDS/conductivity meter model Mi 306 Conductivity/TDS/NaCl/Temp meter from Martini instruments, while determination of turbidity was done using a turbidity meter model LaMotte TC-3000e.

3.3 Synthesis of the photocatalyst

Sol-gel method was used for N-doped TiO_2 preparation. All the chemicals were used as procured without further purification. Titanium (IV) isopropoxide (97%, Sigma Aldrich) - titania precursor, Ammonia solution (25%) and absolute ethanol (99.8%) in the ratio 2:1:10 was measured and the mixture put in a conical flask. This was then stirred at 250 rpm for 1 hour at room temperature and pressure (r.t.p). Initially there was rapid hydrolysis and condensation reaction causing formation of a gel. The resulting white gel was oven dried at a temperature of 120^oC for 1 hour to eliminate any excess NH_3 and other by-products of hydrolysis. The dried material was taken for calcination at 673K overnight. Calcination was carried out in porcelain crucibles.

3.4 Characterization of the Photocatalyst

Scanning electron microscopy (SEM) was used to determine the morphology of the N-doped TiO_2. Philips XL30 Scanning Electron Microscope was used. X-Ray Diffraction was used to determine the crystal size for the synthesized photocatalyst. X-ray diffraction (XRD) by use of philips X-ray diffractometer (7602 EA Almelo, the Netherlands).

3.5 Collection of water samples

Water samples were collected using amber glass bottles. The bottles were pre-washed and rinsed with weak acid solution and deionised water prior to sampling for analysis of chemical parameters. Water samples were collected from Homaline, Awach Tende and Yao Kawiti (water pan) within the L. Victoria basin into amber bottles and packed in cooler boxes during transportation and immediately delivered to the laboratory for analysis. Analysis of biological samples was conducted immediately upon arrival in the laboratory while chemical samples were stored in the fridge at 4 ^{o}C as they wait for analysis.

3.6 Inactivation of *E. coli*

Initially 1 ml of the raw water was transferred directly onto the 3M Petrifilm. This was then placed in an incubator at 37.5^{o}C for 24 hrs. The resultant *E. coli* and coliform were noted by counting the blue and red colonies formed, respectively. A mixture of 100 ml of the raw water with 0.1 g of the catalyst was then transferred into three clear polypropylene bottles and exposed to sunlight for sixty minutes. In three other polypropylene bottles, 100 ml of the water was added with 0.10 g of TiO_2 and exposed to sunlight for 60 min. In another set of three polypropylene bottles, 100 ml of the water was added without addition of the catalyst and also placed in sunlight for the same duration of time. 1 ml of each solution was pipetted out after every 10 minutes and placed onto the 3M Petrifilms, then incubated for 24hrs after which the resultant *E. coli* and coliform noted by counting the blue and red colonies formed as illustrated in Figure 3.1 below.

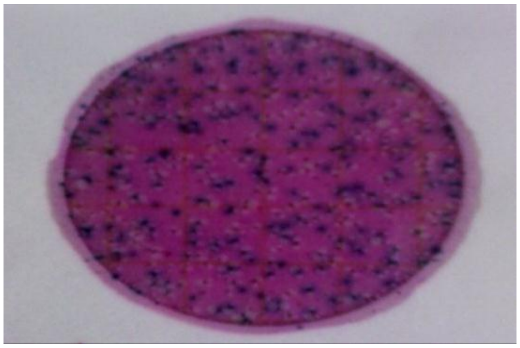


Figure 3.3: 3M Petrifilm after 24 hrs incubation showing blue and red colonies

3.6.1 Application of the Clay Pots in *E. coli* Inactivation

Synthesized N-doped TiO_2 amounting 0.10 g, 0.20 g, 0.40 g, 0.60 g, 0.80 g and 1.00 g were weighed and used to prepare separate pastes. The pastes were then applied in the different clay pots and put in an oven at 90 °C for 3 hrs. 100 ml of raw water was transferred into each pot and allowed to percolate through the pores. From the filtrate, 1 ml was pipetted and placed directly onto the 3M Petrifilm. This was incubated at the temperature of 37.5 °C for 24 hours and the resultant number of *E. coli* and total coliform colonies determined.

3.7 Methylene Blue Degradation

The basic dye used in this study is Methylene blue (MB), A.R. grade. MB in commercial purity was used without further purification. MB is a heterocyclic aromatic compound (M.wt. =319.86, M. formula =$C_{18}H_{18}N_3SCl_3H_2O$, λ_{max}=665 nm Nature= cationic). The accurate weighted quantity of the dye was dissolved in double distilled water to prepare a stock solution. Dye concentration was determined by using absorbance measured before and after the treatment with UV-Visible Spectrophotometer. The solution was obtained by diluting a stock solution of MB dye in accurate proportion in between 0.01 to 0.05 g/L. Stock solution of methylene blue dye was prepared in distilled water. It was further diluted as required.

3.7.1 Effect of Catalyst Weight on Methylene Blue Degradation

Evaluation of photocatalytic activity of N-doped TiO_2 was determined by methylene blue (MB) as a model organic pollutant. 40 ml of aqueous dye solution (0.05 gL^{-1}, pH 7) was put into different vials and 0.05 g, 0.10 g, 0.20 g, 0.40 g, 0.60 g, 0.80 g and 1.00 g of the catalyst added to the vials and stirred in triplicate. Before illumination, the suspensions were mixed for 2 hours in the dark with a magnetic stirrer until the mixture was at adsorption equilibrium. These were then exposed to sunlight for two hours. 0.1 M NaOH solution was used to adjust the pH. Centrifugation process was used to separate the photocatalyst from the solution and the remaining clear liquid absorbance measured using UV-visible spectroscopy at the wavelength of 616.8 nm.

3.7.2 Effect of Time on Methylene Blue Degradation

This was carried out in bright light for 120 min, between 11.00 am and 1.00 pm. 40 ml of aqueous dye solution (0.03 gL^{-1}, pH 7) together with 0.40 g of the catalyst was exposed for 2 hours on the sunlight. 0.10 M NaOH solution was used to adjust the pH. A magnetic stirrer was used to stir the suspension for 2 hours in the dark place before illumination inorder to ensure adsorption equilibrium of the mixture is reached. During the photoreaction process, 6 ml of the solution was removed after every 20 min, followed by separation of the photocatalyst from the solution by centrifugation and the remaining clear liquid absorbance tested by UV-visible spectroscopy at the wavelength of 613.8 nm.

The methylene Blue (MB) degradation was calculated as follows:

$$\text{MB degradation \%} = \frac{(A_0 - A)}{A_0} \times 100$$

Where,

A_0 is the Methylene Blue initial absorbance

A is Methylene Blue absorbance at sampling time.

3.7.3 Effect of Varied pH on Methylene Blue Degradation

Exactly 0.10 g of the photocatalyst was added to the solution in varying concentration ranging between 10 mg/L to 50 mg/L. the initial pH was adjusted by adding HCl and NaOH (0.05M). pH was varied from value of 2 upto 12. Solutions were then placed under sun light for given time interval and the percentage removal measured. The highest percentage was chosen for the study of photocatalysis. The tests were all carried out in triplicate.

3.8 Methyl Red Degradation

The photocatalytic activity of the synthetized photocatalyst was evaluated in the photoelectrodegradation reaction of methyl red (MR) dye (2-(N, N-Dimethyl-4-aminophenyl) azobenzene carboxylic acid, Sigma-Aldrich). Photocatalyst loading and exposure time were explored to determine the optimum working conditions of the photocatalyst for methyl red degradation. 20 ppm Methyl Red solution and varying amounts of 0.025, 0.05, 0.10, 0.20, 0.40, 0.60 and 0.80 g of photocatalyst. This was used to establish the optimum amount of the photo-catalyst. The illumination time was 240 min, and aliquots of the samples were taken at an interval of 30 minutes and absorbance measured at a wavelength of 413 nm to determine change of concentration with time. The percentage degradation of methyl red was determined according to the equation **([Ro-Rt]/[Ro])*100:**

Where, Ro is methyl red initial concentration and Rt the concentration after time, t, in minutes. Degradation percent versus the time for all the variables was plotted for data analysis.

3.9 Pesticide Analysis

To test the photocatalytic efficacy of the synthesized composites against pesticides, 1 ppm of 17 OCP-mixture was used. Into a 5ml sample of the pesticide mixture, 0.10 g photo catalyst was added and mixed for two hours on a magnetic stirred at 150rpm in the dark. The catalyst was filtered off and the pesticides extracted using Solid Phase Extraction procedure. This served as the dark equilibrium adsorption reference.

Aluminium foil was used to cover the reaction vessel to exclude all the light. Into a second volumetric flask, 5 ml of the pesticide mixture was treated with 0.10 g of the photo catalyst and stirred under visible light for two hours. First, the mixture was stirred for 15 minutes in a dark place until the adsorption equilibrium was attained before illumination with Visible light. The catalyst was filtered off. The filtrate was concentrated to near dryness in rotary evaporator and made to a final volume of approximately 1 ml in isooctane and transferred into 20 ml glass vials using Pasteur pipettes. The solution was reduced under a moderate stream of white spot nitrogen gas to a residual volume approximately 1 ml and transferred into auto sampler vials using Pasteur pipettes for GC analysis.

3.10 Water Quality Variables Determination

3.10.1 pH, Total Dissolved Solids (TDS) and conductivity

pH, Total Dissolved Solids (TDS) and Conductivity were determined using Mi 306 Conductivity/TDS/NaCl/Temp meter from Martini instruments. These were determined at the point of sampling.

pH: using buffer solution of pH 4, 7 and 10, calibration of the pH meter was done. pH readings of the samples were taken after rinsing the electrode with distilled water followed by the sample. The tip of the electrode was placed in the water sample and the readings recorded directly.

Conductivity: The conductivity meter was calibrated using the standards of conductivity 84 and 1,413µS/cm conductivity standards. The electrode was initially thoroughly rinsed with distilled water. Conductivity readings were taken after immersing the electrode in the water samples.

TDS: This was determined using a TDS portable meter. The probe of the meter was immersed into the sample and the displayed value of TDS recorded. Mi 306 Conductivity/TDS/NaCl/Temp meter from Martini instruments was used.

Total Suspended Solids (TSS)

Whatman filter paper No. 1 was oven dried at a temperature of 105 °C then transferred into the dessicator after obtaining a constant dry weight. Water samples were shaken until homogenized and 100 ml filtered through the pre-weighed filter paper using a Buchner funnel fitted to a vacuum pump. The residue on the filtrate was oven dried at a temperature of 105 °C to constant weight and TSS was calculated as the weight of the residue per unit volume of the sample filtered. The results were expressed in mg/ L using the equation below:

TSS = (A – B) x 1000/V……………………………………………………..Equation 1

Where:

A- Weight of the filter paper and dried residue in mg

B- Weight of the filter paper in mg

v- sample volume in in ml

CHAPTER FOUR

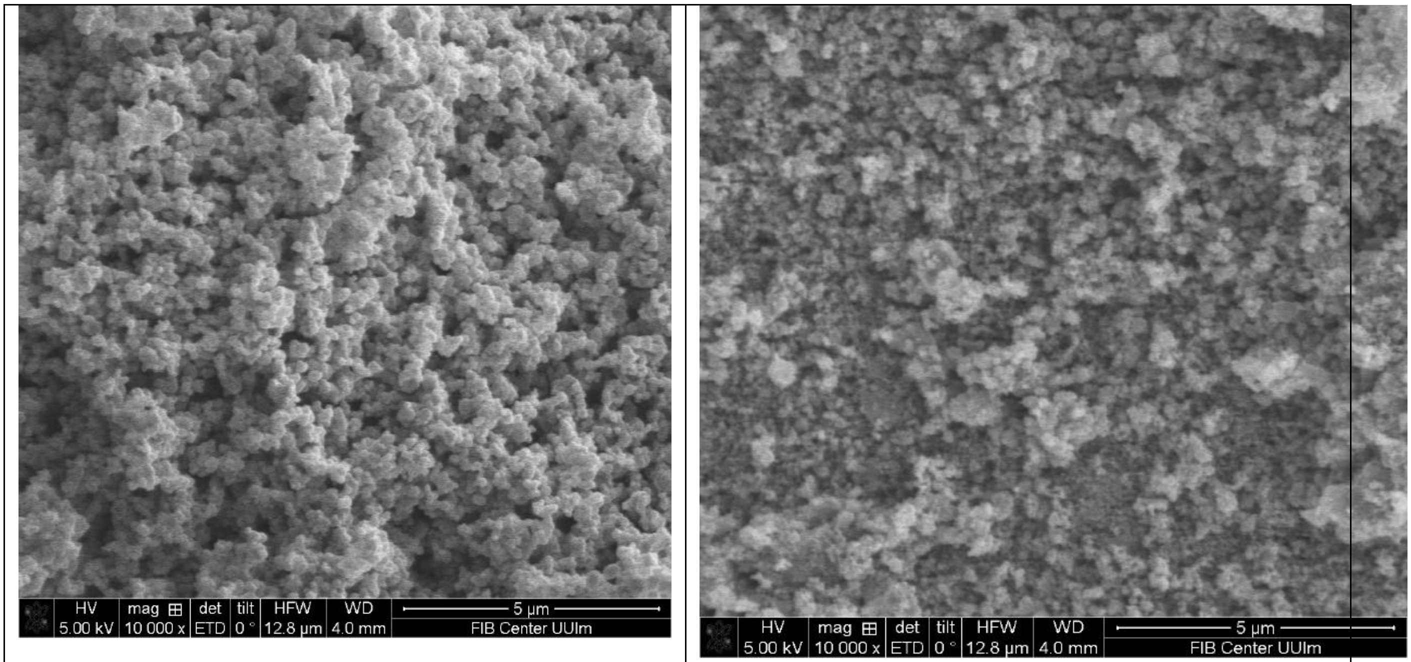
4. RESULTS AND DISCUSSION

4.1 Characterisation of synthesised N-Doped TiO_2

The synthesised N-Doped TiO_2 was characterised using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques.

4.1.1 SEM analysis

Figure 4.1 below shows the SEM micrographs for N-doped TiO_2 and the undoped TiO_2 photocatalysts. The results of SEM revealed that the photocatalyst consist of irregular agglomerated nanoparticles. The images revealed that the morphology and size of the particles were not changed on incorporation of N into TiO_2 by treatment with Ammonia Solution. The Morphology of the TiO_2 particles was not altered on N-doping due to the comparable atomic size of Nitrogen with that of Oxygen (Pelaez *et al.*, 2012). Appendix. 1 shows other SEM micrographs with different magnifications. The surface morphology of TiO_2 show spherical shaped grains with increased porosity after Nitrogen doping.



N-doped TiO_2 SEM Micrograph

TiO_2 SEM Micrograph

Figure 4.1 SEM micrographs for N-doped TiO_2 and TiO_2 photocatlysts

4.1.2 XRD ANALYSIS

Using XRD analysis, N-doped TiO_2 was analysed for determination of both the phase composition and the crystal size. The characterization of products was determined through scanning at the rate of 5°/min in the 2θ range 10°–70° using X-ray diffraction (XRD) by use of philips X-ray diffractometer (7602 EA Almelo, the Netherlands) with Cu Kα radiation (λ = 0.1542 nm).

In Figure 4.2 below, 2θ values of diffraction peaks observed in XRD spectra of pure TiO_2 at 25.5, 38.0, 47.2, 53.5, 54.3, 63.1, 68.90, 70.36, and 75.2. These peaks were assigned to reflections from (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes, which mostly corresponds to anatase phase (Veluru *et al.*, 2011). This indicates that the anatase is the dominant phase and this is beneficial since anatase is reported to be more photocatalytically active than rutile (Ocwelwang and Tichagwa, 2014).

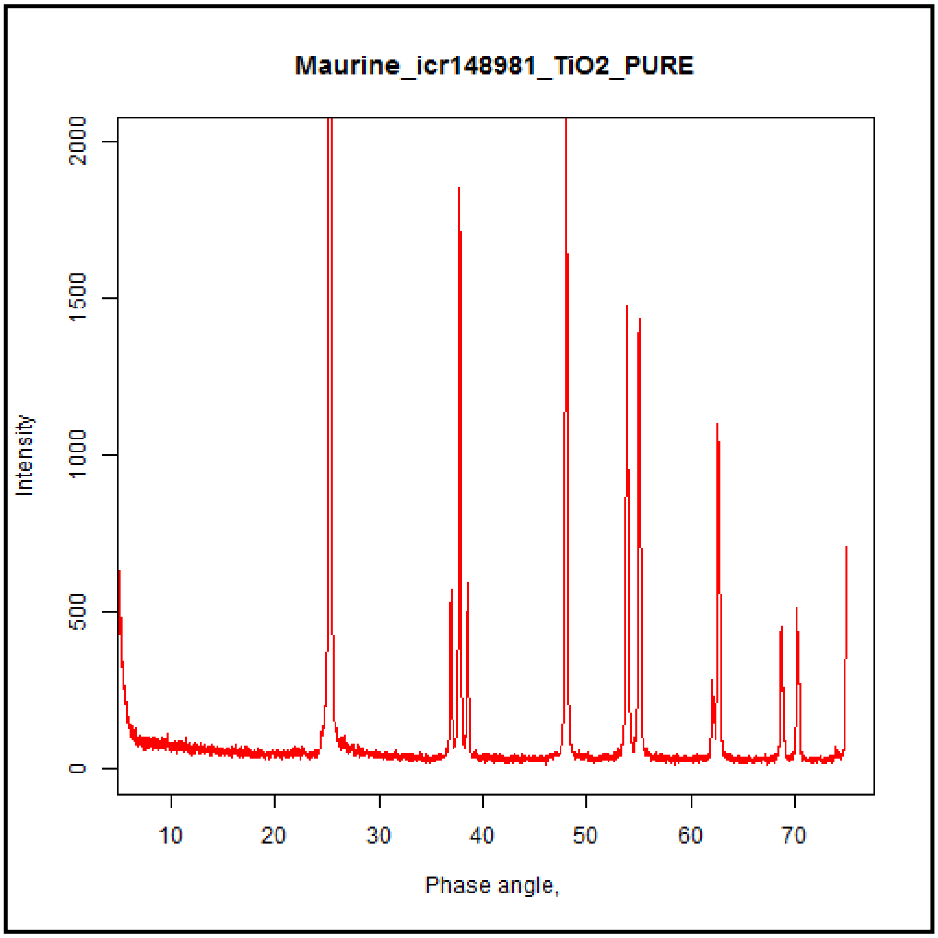


Figure 4.2: XRD Pattern for pure TiO_2

In Figure 4.3 below, 2θ values of diffraction peaks observed in XRD spectra of N-doped TiO_2 at 25.5, 39.2.0, 48.2, 54.5, 65.1, 68.90, 70.36, and 75.2. These peaks were assigned to reflections from (101), (004), (200), (105), (204), (116), (220), and (215) crystal planes, which mostly corresponds to anatase phase (Veluru *et al.*, 2011). The crystallite sizes were estimated from the strongest peaks at 25.5°.

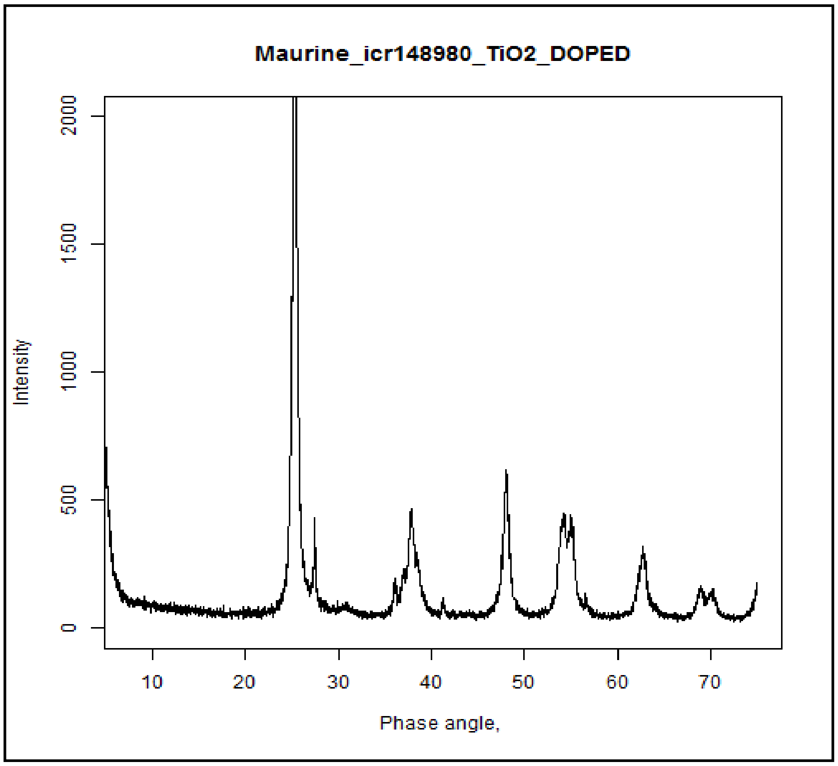


Figure 4.3: XRD Pattern for N-doped TiO_2

Determination of N-doped TiO_2‘s particle size from the results of XRD was done using the Debye-Scherrer’s formula given by the equation:

$$D = K\lambda / (B\cos\theta)$$

Where, B at 2θ is the Full Width at Half Maxima (FWHM) of the base peak (I/I_I=100) in radians with the value of **0.007652.**

K - Scherer constant, =0.89

D- size of the crystal (diameter) in nm

λ - Wavelength of the Cu-Kα X-rays used,= 0.15406 nm

θ - Angle expressed in degrees, 12.750 (2θ=25.500) for the base peak from Fig 4.2, cos**θ =**

0.9753

Crystal size of **18.372nm** was yielded after the above figures were substituted into the Debye-Scherrer equation.

4.2 Photocatalytic Inactivation of *E. coli*

The optimal weight of the photocatalyt for inactivation of *E. coli* was found to be 0.10 g. The weights above 0.10 g did not cause additional inactivation of *E. coli*, whereas the weights below 0.10 g had lower inactivation (Figure 4.4).

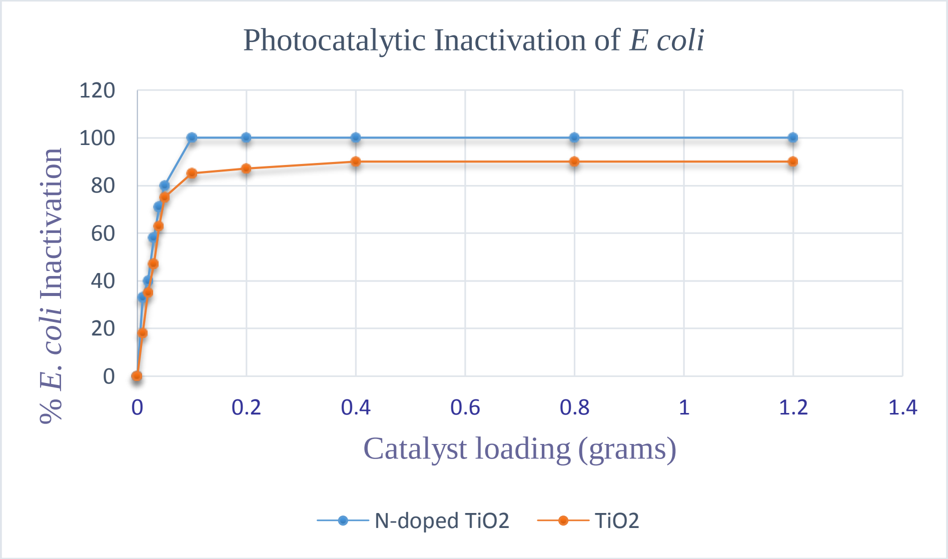


Figure 4.4 Photocatalytic inactivation of E. coli using different catalyst loading

The fact that the mass of the photocatalyst above 0.10 g did not translate into enhancing inactivation of *E. coli* suggested that although the larger catalyst concentration provides more catalytically active centres for the absorption of photons that translate into more electrons and holes are generated, but the excess photocatalyst may also act as an optical filter and impede the further penetration of incident light into the medium. Zhang *et al.* (2012) also reported this effect. The 0.10 g of the photocatalyst was thus taken as the optimal amount used in other experiments on *E. coli* inactivation.

4.2.1Comparison of N-doped TiO_2, $TiO_2$and SODIS in *E. coli* inactivation

Use of N-doped TiO_2 photocatlyst achieved 98.5% inactivation of *E. coli* raw water from the river within 50 minutes compared to TiO_2 which achieved 81.1% and SODIS 76.7% inactivation of the *E. coli* under similar conditions, from the initial *E. coli* concentration of 1,500 CFU/ml. Figure 4.5 below illustrates the results of the experiment.

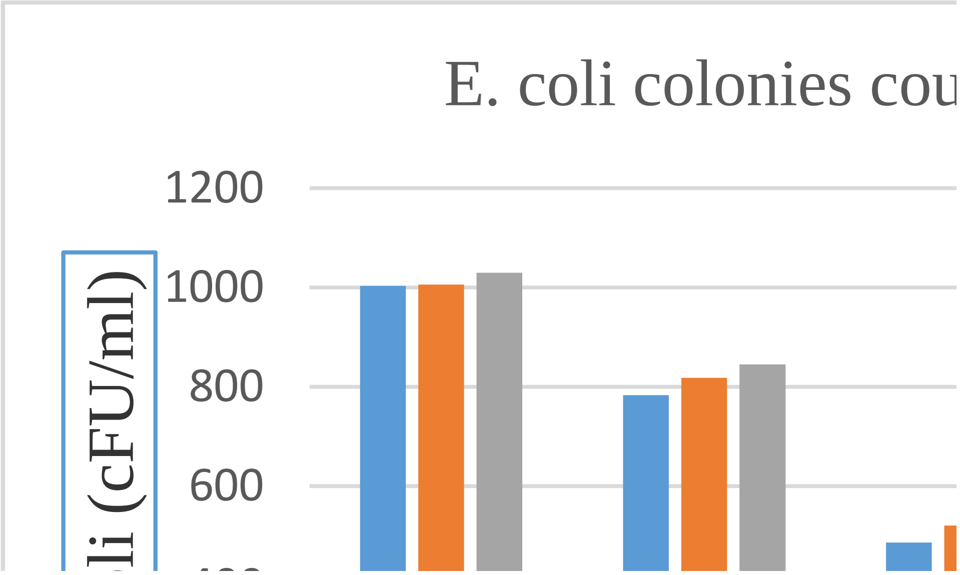


Figure 4.5: Comparison of E. coli inactivation using N-Doped TiO_2, TiO_2, and SODIS

The results revealed fastest inactivation by N-doped TiO_2 than un-doped TiO_2 photocatalyst and SODIS alone. No *E. coli* inactivation was observed in any control bottles.

In SODIS reaction between dissolved oxygen in water and UV-A (wavelength 320–400 nm) produces forms of oxygen which are highly reactive (hydrogen peroxides and oxygen free radicals) also believed to causing damage to pathogens (Naggi, 2009). This depends on time of exposure which varies from 6 to 48 hours (UNICEF, 2008) for complete pathogen inactivation. Inactivation is faster in the application of Advanced Oxidation Processes, the most widely used being the hydroxyl radical, •OH, which can increase a reaction rate by a million to a billion times. This is what is observed in the inactivation of *E. coli* using N-doped TiO_2.

4.2.2 Inactivation of *E. coli* using the clay Pots

The raw water used had *E. coli* concentration of 1,600 CFU/ml. increased concentration of the catalyst for instance from 0.10 g to 0.40 g used as paste on the pots, led to almost complete removal of *E. coli*. On the other hand, the use of the clay pot without addition of the photocatalyst resulted in 99.5% *E. coli* inactivation. There was inactivation of the E. *coli* bacteria from 1600 CFU/ml to 100 CFU/ml with increasing amount of photocatalyst as shown in Table 4.1 below. The 100 CFU/ml was above the recommended standard for *E. coli* concentration for potable water according to WHO and KEBS that require *E. coli* concentration to be nil. Clogging of the pores of the clay pot filters due to increased amount of photocatalyst inhibited inactivation of E. *coli* to nil.

Table 4.1: Effect of Filtering raw water with E. coli using clay pots with the photocatalyst paste

Water sample	***E. coli*(CFU/ ml)**
Raw	1,600
Filtered with just the clay pot	240
Filtered with 0.10 g photocatalyst	180
Filtered with 0.20 g photocatalyst	160
Filtered with 0.40 g photocatalyst	100
Filtered with 0.80 g photocatalyst	100
Filtered with 1.20 g photocatalyst	100

4.3 Methylene Blue (MB) Degradation

There was a decrease in concentration of MB at the initial hour of the test of the MB degradation under dark conditions but after the second hour, there was no change in concentration. From the results it can be concluded that the dye's adsorption equilibrium on the surface of the photocatalyst had reached within the initial hour. In the presence of titania films, there was a constant decolourisation of methylene blue with the widely described photocatalytic properties of TiO_2 (Fisher *et al.*, 2012). Figure 4.6 below illustrates the effect of irradiation time on Degradation of Methylene Blue

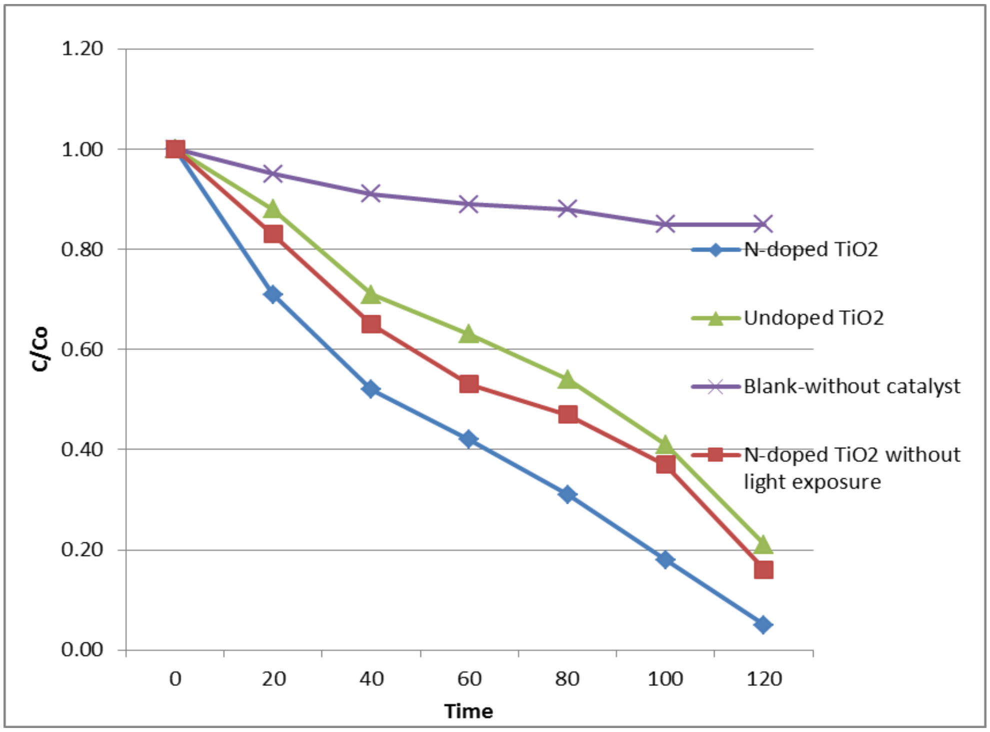


Figure 4.6: Plot of C/Co of Methylene Blue with time

The graph shows a linear plot of C/Co for methylene blue photo-degradation after 100 min of illumination under visible light. In the absence of light irradiation, the use of N-doped TiO_2 photocatalyst achieved only 83.7% degradation. However, in the presence of light irradiation and photocatalyst, 91.01% degradation of Methylene Blue was achieved under similar conditions.

The results suggested that under irradiation light, N-doped TiO_2 catalyst had higher photocatalytic activity. At Increased irradiation of the solution that contained catalyst upto 120 min resulted in 99.6% methylene blue degradation. Under similar conditions, the un-doped TiO_2 was able to degrade 78.7% of methylene blue.

The rate of photodegradation of methylene blue under visible light was evaluated by plotting the natural log of the ratio of the remaining concentration of methylene blue against exposure time to the photocatalyst under irradiation. Figure 4.7 below shows the findings of the plot of the concentration of methylene blue In (C_t/Co) against exposure time.

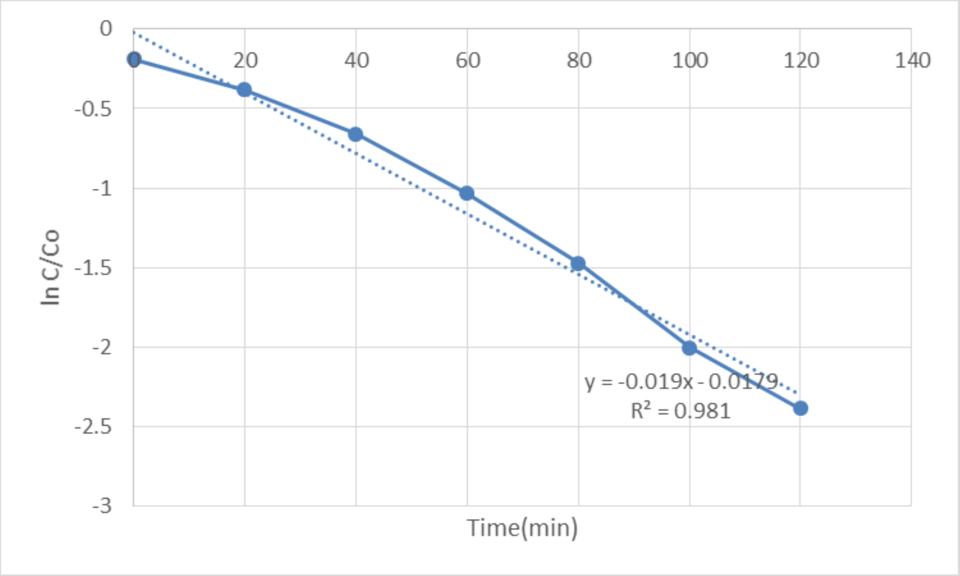


Figure 4.7: Linear plot of ln (C/CO) for degradation of methylene blue under light irradiation after 120 min

The data agreed best with the Langmuir-Hinshelwood kinetic model whereby reaction rate is directly proportional to the concentration of the initial reactant.

$$r = dC/dt = kKC/(1 + KC)$$

Where, r is the oxidation rate of the blue dye in (mg/l min),

C is the concentration of dye in (mg/l), *T* is the time of illumination, *K* is the adsorption coefficient of the reactant (L/mg) and *k* is the reaction rate constant (mg/l min). The equation is simplified to an apparent first-order equation when the initial concentration is taken to be *C*o:

$dC/dt = kKC$

$\int dC/C = kK\int dt$

When the equation is integrated and boundary conditions of C taken to be C_o

at t = 0, then

$Ln\ (C_0/C_t) = kKt = k_{app}t$

In otherwise

$C_t = C_0e^{-kt}$ **…………….** first order rate equation.

Rearranging the equation one gets:

$lnC_t = -kt + lnC0$

whereby

C_t = concentration of Dye at time, t

t = time in minutes,

k = apparent first order reaction rate constant,

Co = the concentration of the original dye (ppm).

The equation obtained is in y =mx + c form. A straight line is obtain when ln(Ct) versus t is ploted, upon linear regression of the slope, equals the apparent first-order rate constant *k*app which is $1.9x10^{-2}$ min^{-1}.

4.3.2 Effect of dosage of the photocatalyst on methylene blue degradation

Figure 4.8 below shows results of methylene blue degradation after application of different amounts of the photcatalyst. The data revealed that phodegradation increased initially with increasing amount of the photocatalyst up to 0.60 g. This suggests that with increasing amount of the photocatalys initially, both the quantity of dye molecules adsorbed and the photons absorbed increased hence promoting degradation. However, turbidity increases with increase in catalyst solution concentration reducing penetration of light into the solution and consequently decreasing photo-degradation. Similar findings were reported by Franco and co-workers (2009).

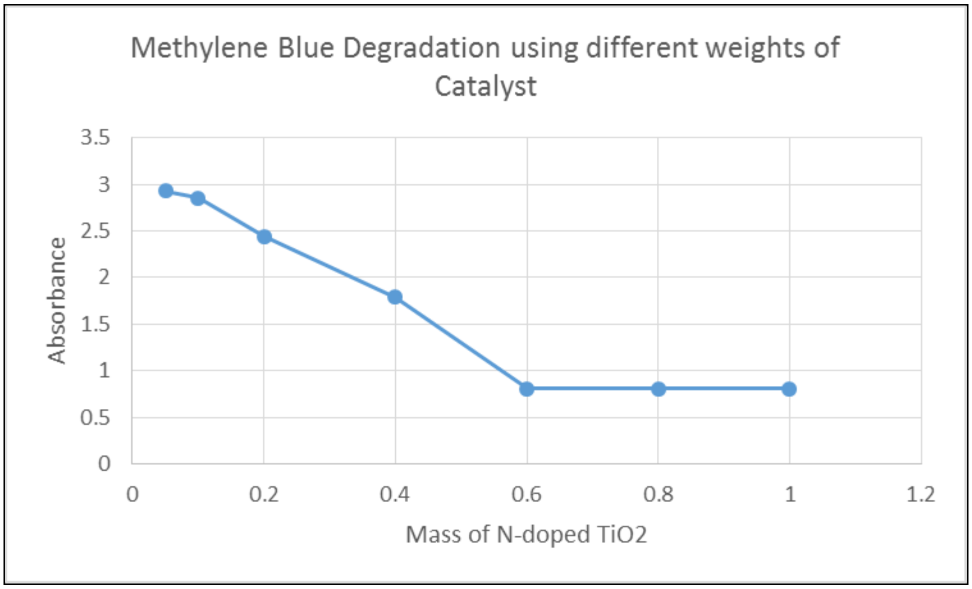


Figure 4.8: Plot of Absorbance of Methylene Blue against Catalyst loading

The optimal amount of the photocatalyst on degradation of methylene blue was 0.6 g. The N-doped TiO_2 phtocatalyst has got good adsorption capability because of large surface area which enables the diffusion of the methylene blue molecules freely into the N-doped TiO_2. However, rapid recombination formed by irradiation from many pairs of hole-electrons leads to reduced photocatalytic degradation of MB molecules (Mohapatra & Parida, 2006).

4.3.3 pH effect on degradation of methylene blue

An increase in pH of the reaction mixture from 2 to 7 was found to increase photo-degradation of methylene blue from 23 to 97.1 %. On the other hand, the rate of degradation decreased from 97.1 to 77 % as the pH increased from 7 to 11 (Figure 4.9).

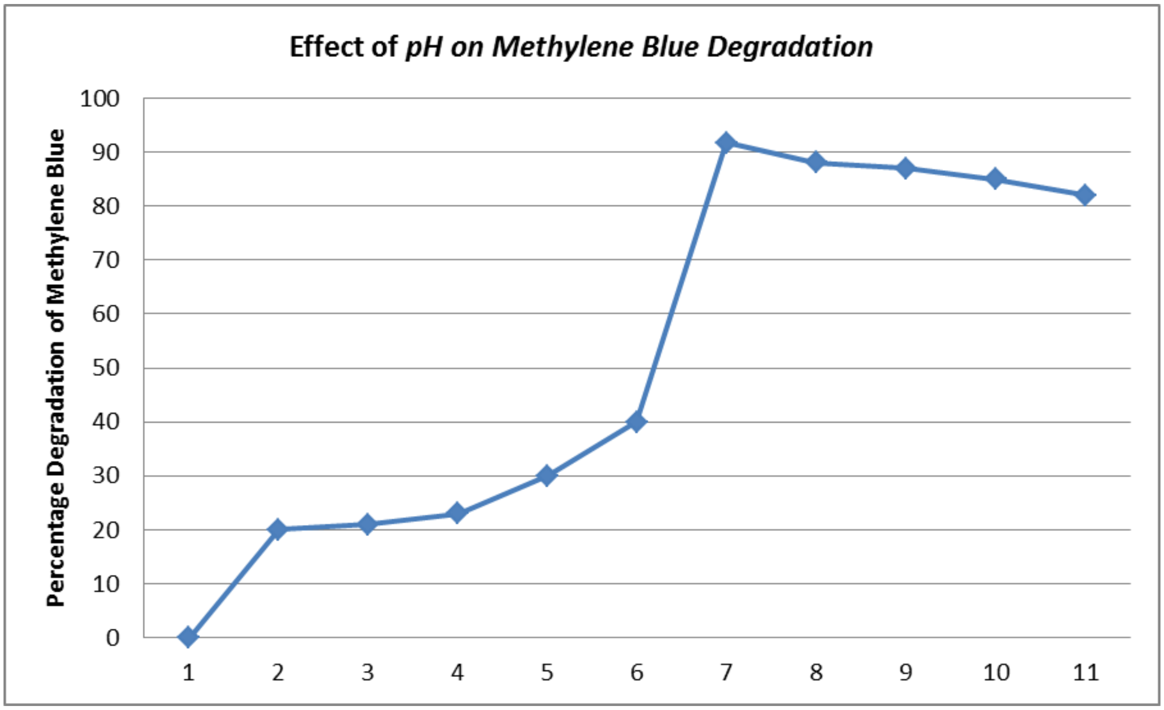


Figure 4.9: pH effect on Methylene Blue Degradation

The highest percent rate of photo-degradation (97.1%) was recorded at pH of 7.0. Consequently, pH 7 was selected as the optimal pH condition for methyl blue photodegradation experiments. The reduction in photodegradation rate at increased pH could be due to the effective scavengers of hydroxyl ions from carbonate ions formation thus reducing the degradation rate (Akbar and Onar, 2003) At increased pH values, the hydroxyl radicals are rapidly scavenged lacking the chance to react with the dye molecules (Madhu *et al.*, 2009).

4.4 Degradation of Methyl Red

4.4.1 Degradation of methyl red using varying amounts of the photocatalyst

Figure 4.10 below shows the effect of increasing amount of N-doped photocatalyst on methyl red. The results revealed that increasing the amount of photocatalyst in the solution up to 0.70 g increased degradation of methyl red. The highest photodegradation achieved was 97.8% obtained at the loading of 0.70 g of the photocatalyst, beyond which photodegradation reduced tremendously. The observed decrease in photo-degradation of methyl red after 0.70 g loading of the photocatalyst could be due to agglomeration of catalyst particles that reduced the catalyst surface area available for photon absorption. In addition, increasing the concentration of photocatalyst increased turbidity of the solution that also inhibits light penetration into the photoreactor, hence reducing photocatalytic degradation (Saqueeb and Muneer, 2003; Tang and Chen, 2004).

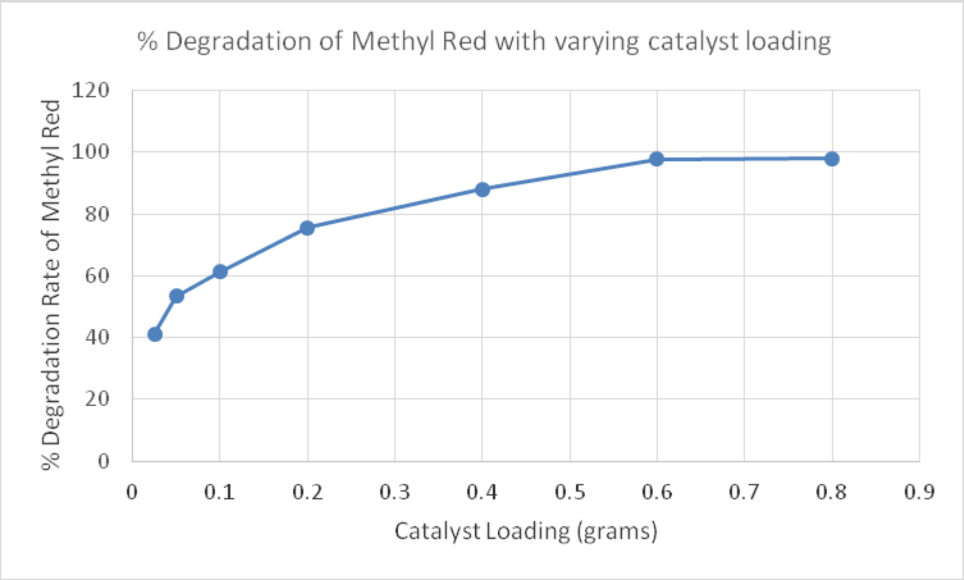


Figure 4.10: Percentage degradation of Methyl Red with varying Catalyst loading

4.4.2 Degradation of Methyl Red under Varying Irradiation Time

Figure 4.11 illustrates the plot of percentage degradation of methyl red when exposed to visible light for a period of 240 minutes. It was established that the percentage photo-degradation increased with increasing irradiation time. Irradiation of upto 150 min resulted in 97% reduction in the amount of methyl red dye in the solution with photo-catalyst loading of 0.7 g·L^{-1}.

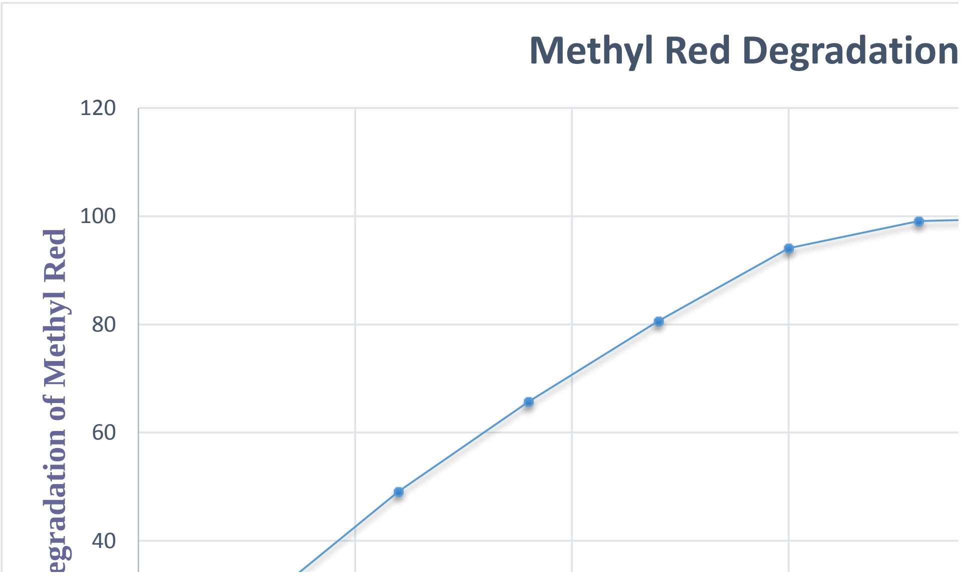


Figure 4.11: Percentage degradation Methyl Red with given time

Figure 4.12 below shows the plot of C/Co of methyl red dye in the solution with the N-doped TiO_2 and TiO_2 only exposed to light irradiation. There was quick loss of colour of azo dyes solution which is associated with dye molecules linkage to the azo cleavage. The double bonds formed from nitrogen- nitrogen bonding (-N=N-) are characteristic of azo dyes molecules and the azo bonds determines the colour. In Azo dye molecules, the azo bonds are the most active bonds and also easily oxidized by either positive holes or hydroxyl radicals (Feng *et al.*, 2000; Karkmaz *et al.*, 2004).

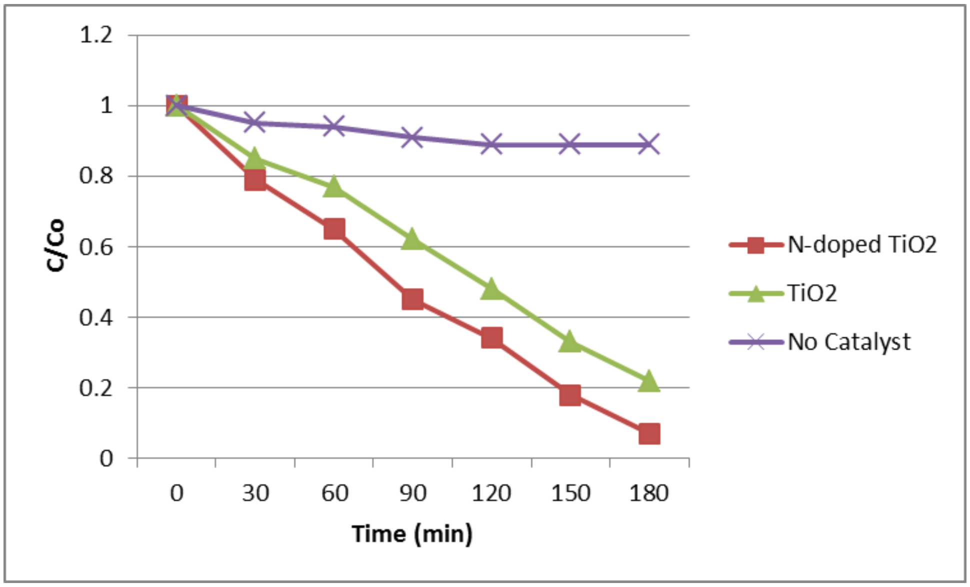


Figure 4.12: Plot C/Co of Methyl Red in solution with varying time

The linear fitting for the batch test are shown in Fig. 4.13. The kinetic constant value calculated was 4.14x 10^{-2} min^{-1}. The increase on the constant value indicates an increment on the methyl red degradation, which is consistent with the degradation profile.

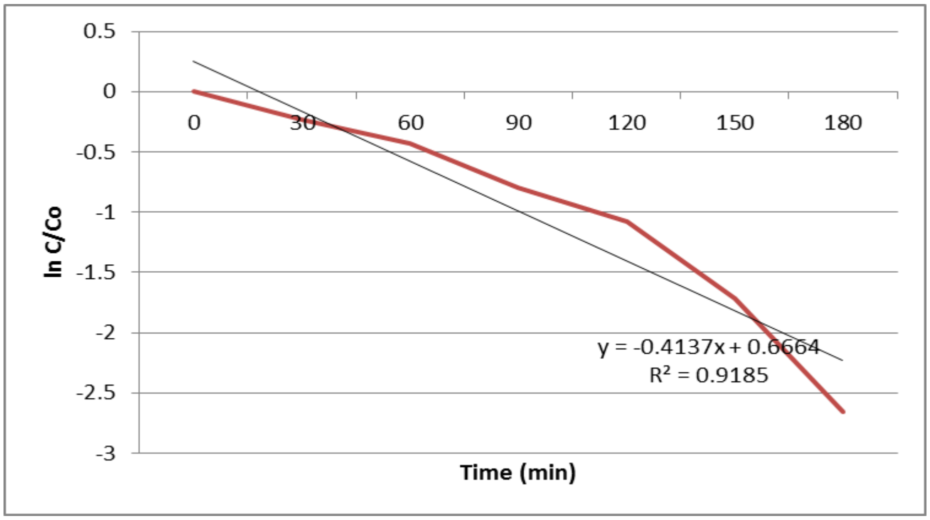


Figure 4.13 Kinetic constant for Methyl Red Degradation

4.5. Pesticide Degradation

Photocatalytic experiments were prepared in triplicates. Table 4.2 below shows the mean concentration of each pesticide studied in the initial sample and the final concentration after the photocatalytic treatments. Additionally, pesticides blank tests-solution containing N-doped TiO_2 with no irradiation of light together with the one with irradiation of light but with no catalyst were conducted. The irradiation time was 120 min.

Table 4.2: Concentrations of Pesticides in sample before and after photocatalytic treatment.

Pesticide	Concentration (ng/ml)		% Degradation
	Initial	After irradiation with N-doped TiO2	
α-HCH	1834.58	1824.64	0.50
β-HCH	840.83	530.35	36.00
ɣ-HCH	942.85	942.25	0.06
ẟ-HCH	2083.95	1441.09	30.00
Aldrin	1435.77	932.51	35.00
Heptachlor	1407.03	674.90	52.00
Heptachlor Epoxide	847.59	355.01	58.00
Endosulphan I	1670.89	770.16	53.90
pp’ DDE	1190.78	449.85	62.00
Dieldrin	1607.39	719.15	55.20
Endrin	1610.08	612.00	61.90
Endrin Aldehyde	366.89	117.57	67.90
Endosulphan II	1692.59	594.44	64.80
pp’ DDT	121.86	44.39	63.60
Endosulphan Sulphate	590.96	289.60	50.90

The pesticides that were effectively removed by the photocatalytic treatment, attainment yields greater than 50%, were heptachlor, endosulphan I, endosulphan II, *p,p'*- DDE, dieldrin, endrin, endrin aldehyde, *p,p'*- DDT, endosulphan sulphate and heptachlor epoxide.

The degradation percentages obtained after the photocatalytic treatment were lowest for α-HCH and δ-HCH, that is 0.5 and 0.06, respectively.

In the case of heptachor, *p,p'*-DDE, *p,p'*-DDT and aldrin, a significant degradation of N-doped TiO_2 radiation was shown in blank experiments. Therefore, their degradation is as a result of photocatalytic treatment together with radiation only. This is illustrated in Table 4.3

Table 4.3 Pesticides degradation in blank experiments

Pesticide	% Degradation by N-doped TiO_2	% Degradation by visible light
Heptachlor	43	18
p,p'-DDE	40	27
p,p'-DDT	24	29
Aldrin	50	21

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Doping of nitrogen into TiO_2 matrix and the study of the activity of the photocatalyst for the methylene blue and methyl red degradation under visible light was successfully done. Nitrogen doping caused visible light response.

These results indicate that N-doped TiO_2 photocatalyst has a greater photocatalytic property because of the response range of the visible light extension, and elevated photo-generated intensity of current different from un-doped TiO_2. In the degradation of methyl red together with methylene blue, the synthesized of N-doped TiO_2 proved to be successful. The photocatalyst degraded Methylene blue upto 99.6% with 0.6g being the optimum catalyst loading. The highest photodegradation achieved for Methyl Red was 97.8% obtained at the loading of 0.70 g of the photocatalyst, beyond which photodegradation reduced tremendously.

The photocatalytic efficiency varied with amount of photocatalyst, in terms photocatalyst's active sites on the surface where, the catalyst dosage increases with the total active surface area. However, continued increase of dosage increases turbidity thereby decreasing light penetration through scattering effect.

The pesticides residues were effectively removed through treatment by photocatalyst resulting to greater 50% reduction. These included: heptachlor 52%, endosulphan I 53.9%, endosulphan II 64.8%, pp' DDE 62%, dieldrin 55.2%, endrin 61.9%, endrin aldehyde 67.9%, *p,p'*- DDT 63.6%, endosulphan sulphate 50.9% and heptachlor epoxide 58%. Use of the photocatalyst for *E. coli* removal from water infested with bacteria reduced the *E. coli* load from 1600 CFU/ml to 100 CFU/ml.

The Ceramic water filter coated with N-doped TiO_2 is a cost effective method for improving the potable water quality, especially water that is contaminated with microbial contaminants. In all the experiments carried out, proved that the synthesized N-Doped TiO_2 worked better compared to just using TiO_2.

Choosing the optimum degradation parameters was critical in order to attain high rates of degradation, which is important in any photocatalytic oxidation process practical application.

5.2 Recommendations

It is recommended that further studies should be done on the synthesis of N-doped TiO_2 since from the time the study was being conducted only one precursor of Titania was used, that is Titanium (IV) isopropoxide ($C_{12}H_{28}O_4Ti$). Ammonia Solution was the only source of Nitrogen. Other precursors can be used as well as different methods other than Sol-gel.

Since the tested POU was found to be effective in improving water quality, communities without access to potable water should be encouraged to use it in treating their water. Local communities such as Oriang' Women Pottery can be trained on how to incorporate the photocatalyst into the pots that they are making so that they improve on what they already have in the market.

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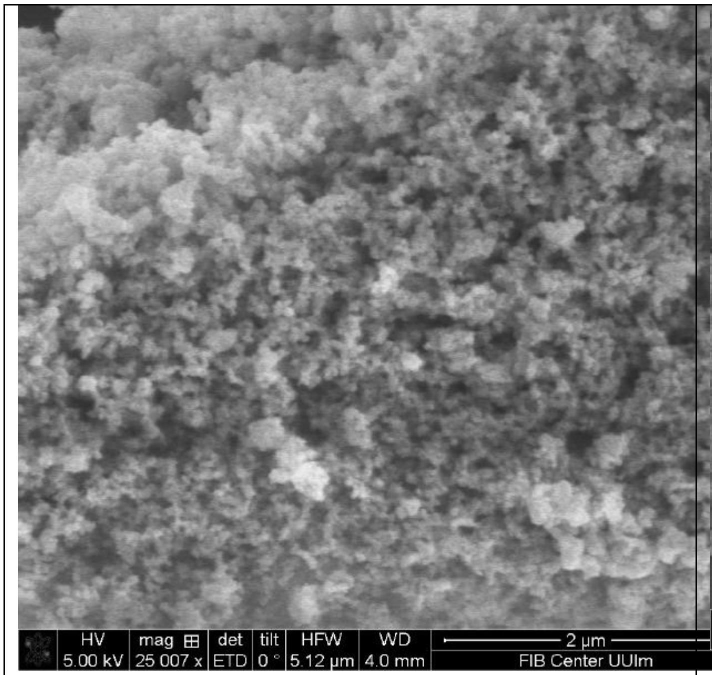
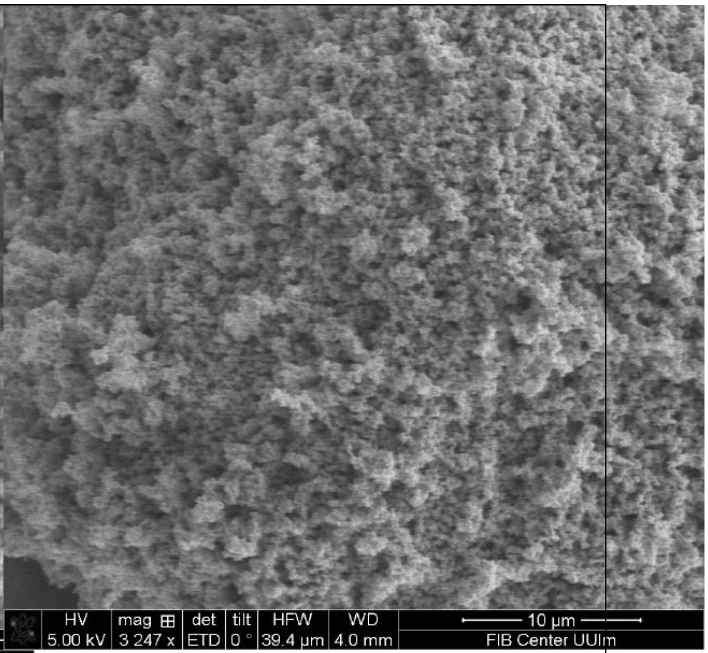
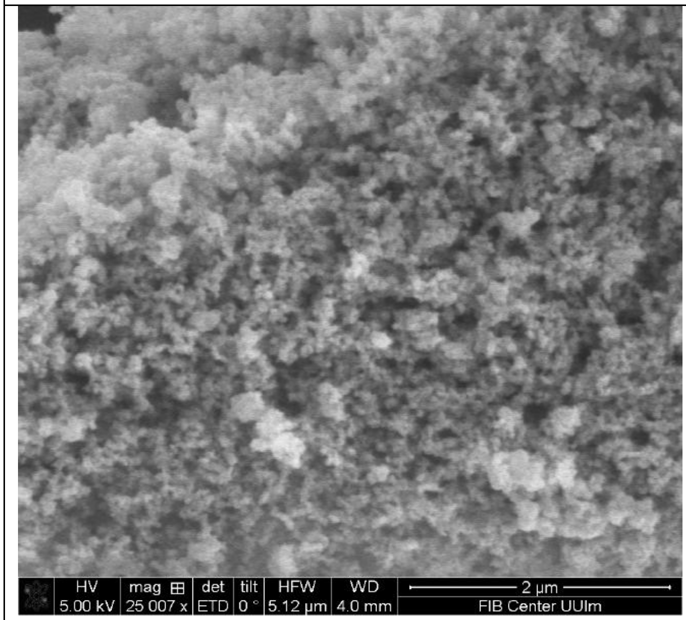
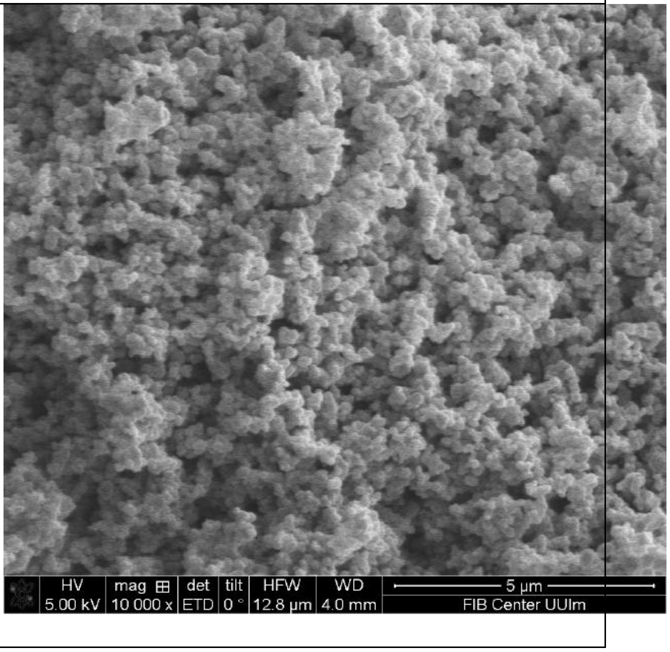
APPENDICES

Appendix 1: SEM IMAGES FOR N-DOPED TIO_2 AND TIO_2









Appendix 2: WHO GUIDELINES FOR PESTICIDES

Substance		**Formula**	**Health based guideline by the WHO**
Alachlor		$C_{14}H_{20}ClNO_2$	20 µg/l
Aldicarb		$C_7H_{14}N_2O_4S$	10 µg/l
Aldrin and dieldrin		$C_{12}H_8Cl_6$/ $C_{12}H_8Cl_6O$	0.03 µg/l
Atrazine		$C_8H_{14}ClN_5$	2 µg/l
Bentazone		$C_{10}H_{12}N_2O_3S$	30 µg/l
Carbofuran		$C_{12}H_{15}NO_3$	5 µg/l
Chlordane		$C_{10}H_6Cl_8$	0.2 µg/l
Chlorotoluron		$C_{10}H_{13}ClN_2O$	30 µg/l
DDT		$C_{14}H_9Cl_5$	2 µg/l
1,2-Dibromo-3-chloropropane		$C_3H_5Br_2Cl$	1 µg/l
2,4-Dichlorophenoxyacetic acid (2,4-D)		$C_8H_6Cl_2O_3$	30 µg/l
1,2-Dichloropropane		$C_3H_6Cl_2$	No guideline
1,3-Dichloropropane		$C_3H_6Cl_2$	20 µg/l
1,3-Dichloropropene		$CH_3CHClCH_2Cl$	No guideline
Ethylene dibromide (EDB)		$BrCH_2CH_2Br$	No guideline
Heptachlor and heptachlor epoxide		$C_{10}H_5Cl_7$	0.03 µg/l
Hexachlorobenzene (HCB)		$C_{10}H_5Cl_7O$	1 µg/l
Isoproturon		$C_{12}H_{18}N_2O$	9 µg/l
Lindane		$C_6H_6Cl_6$	2 µg/l
MCPA		$C_9H_9ClO_3$	2 µg/l
Methoxychlor		$(C_6H_4OCH_3)_2CHCCl_3$	20 µg/l
Metolachlor		$C_{15}H_{22}ClNO_2$	10 µg/l
Molinate		$C_9H_{17}NOS$	6 µg/l
Pendimethalin		$C_{13}H_{19}O_4N_3$	20 µg/l
Pentachlorophenol (PCP)		C_6HCl_5O	9 µg/l
Permethrin		$C_{21}H_{20}Cl_2O_3$	20 µg/l
Propanil		$C_9H_9Cl_2NO$	20 µg/l
Pyridate		$C_{19}H_{23}ClN_2O_2S$	100 µg/l
Simazine		$C_7H_{12}ClN_5$	2 µg/l
Trifluralin		$C_{13}H_{16}F_3N_3O_4$	20 µg/l
Chlorophenoxy herbicides (excluding 2,4-D and MCPA)	2,4-DB	$C_{10}H_{10}Cl_2O_3$	90 µg/l
	Dichlorprop	$C_9H_8Cl_2 0_3$	100 µg/l
	Fenoprop	$C_9H_7Cl_3O_3$	9 µg/l
	MCPB	$C_{11}H_{13}ClO_3$	No guideline
	Mecoprop	$C_{10}H_{11}ClO_3$	10 µg/l
	2,4,5-T	$C_8H_5Cl_3O_3$	9 µg/l

Appendix 3:LIST OF CONTAMINANTS AND THEIR (MCLS) USEPA

MICROORGANISMS

Contaminant	MCLG (mg/L)	MCL or TT (mg/L)	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Cryptosporidium	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Giardia lamblia	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Heterotrophic plate count (HPC)	n/a	TT	HPC has no health effects; it is an analytic method used to measure the variety of bacteria that are common in water. The lower the concentration of bacteria in drinking water, the better maintained the water system is.	HPC measures a range of bacteria that are naturally present in the environment
Legionella	zero	TT	Legionnaire's Disease, a type of pneumonia	Found naturally in water; multiplies in heating systems
Total Coliforms (including fecal coliform and *E. Coli*)	zero	5.0%	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present[5]	Coliforms are naturally present in the environment; as well as feces; fecal coliforms and *E. coli* only come from human and animal fecal waste.
Turbidity	n/a	TT	Turbidity is a measure of the cloudiness of water. It is used to indicate water quality and filtration effectiveness (such as whether disease-causing organisms are present). Higher turbidity levels are often	Soil runoff

Appendix 3:LIST OF CONTAMINANTS AND THEIR (MCLS) USEPA

MICROORGANISMS

Contaminant	MCLG (mg/L)	MCL or TT (mg/L)	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
			associated with higher levels of disease-causing microorganisms such as viruses, parasites and some bacteria. These organisms can cause symptoms such as nausea, cramps, diarrhea, and associated headaches.	
Viruses (enteric)	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste