



UNIVERSITY OF NAIROBI

**AN INVESTIGATION OF THE SYNERGYSTIC EFFECTS OF TITANIUM (IV)
OXIDE MODIFIED CLAY IN DISINFECTION AND PURIFICATION OF
WATER**

By

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DECLARATION

This thesis is the original work of the author except where due references are made. It has not been submitted partially or wholly for the award of degree to this or any other institution of learning.

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This thesis has been submitted with our approval as university supervisors

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ABSTRACT

Access to potable water is a problem facing developing countries worldwide. This water problem is expected to worsen with the population increase in the developing countries. It is in view of the water crisis that a series of research studies have been conducted with sole aim of alleviating the problem and coming up with a cost effective point of use water treatment method. This study was carried out to assess the effectiveness of titanium (iv) oxide (TiO_2) modified clay in water purification. Clay soils were collected from Kenyatta University, department of ceramics and Got Ramogi, in Thika and Bondo sub-counties respectively. Chemical compositions of the two clay samples were determined by X-ray fluorescence (XRF) machine. Titanium (iv) oxide (TiO_2) used was DEGUSSA P25 and calcination was done in an oven. The calcination temperature was 600°C . Methyl orange was degraded by TiO_2 to determine its photocatalytic activity. The residual concentration of the degraded methyl orange was determined using UV spectrophotometer, model Shimadzu pharmaspec UV 1700. The ceramic filter was coated with TiO_2 . Water samples used in the analysis of physico-chemical parameters and E. coli were collected from Usenge beach in Bondo sub-county and Nairobi River in Nairobi county. Triple distilled water was spiked with different concentrations of copper and lead salts then filtered. A measured concentration of organochlorine pesticides mixture was spiked in triple distilled water then filtered. Analyses of various parameters were done on the water samples before and after ceramic filtration to determine the efficiency before subjecting the filters to field sample analysis.

Parameters analyzed include turbidity, pH, TSS, TDS, E. coli, pesticides and heavy metals. E. coli analysis was done by transferring the sample to a 3M test kit, then incubating at 37.2°C for 24 hours. Heavy metal analysis was done using Atomic Absorption Spectroscopic machine model Spectra AA.10. Labtec. Pesticide extraction was done using Solid Phase Extraction cartridge from Superlco Analytical TM U.S.A and analysis was done by gas chromatography mass spectroscopy machine of model Varian Cp 3800 GC/MS.

Results showed that TiO_2 modified clay filter reduced turbidity from 24.667 ± 0.0577 NTU to 0.0212 ± 0.0016 NTU. TSS in water were reduced by filters from 276 ± 14.730 mg/L to 1.00 ± 0.328 mg/L. The filtered water had E. coli colonies reduced from 4310.83 ± 15.718 c.f.u/100ml to 0.00 c.f.u/100ml, the modified clay filters reduced up to 1000ppm of lead and copper to below detection level. OCP pesticides in water were all reduced by the filters to below detection levels except δ -HCH which had residual 390 ± 108.45 ng/l out of the initial 2512.479 ng/l. Improved efficiency of the TiO_2 modified filters was noted in their enhanced ability to reduce the contaminant levels in water.

DEDICATION

This study is dedicated to my dear wife Trezah Owuor and my children (Daddy's girls); Vera, Yvonne, Olive ("Zawadi") and Lesley for the sacrifice they made during my long absence from home.

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TABLE OF CONTENTS

DECLARATION	ii
ABSTRACT	iii
DEDICATION	iv
ACKNOWLEDGEMENT	v
LIST OF TABLES	viii
LIST OF FIGURES	x
CHAPTER ONE	1
1.0 INTRODUCTON.....	1
1.1. Background Information.	1
1.2. Water treatment at household level	2
1.3. Treatment of Water Using Photocatalyst.	3
1.4 Problem Statement.	3
1.5 Objectives.....	4
1.5.1 Main Objective	4
1.5.2 Specific Objectives were to:	4
1.6 Justification	4
CHAPTER TWO	6
2.0 LITERATURE REVIEW	6
2.1 Water Borne Pathogens.....	6
2.3 Water Purification and Disinfection Methods.....	10
2.3.1 Clay Filtration.....	10
2.3.2 TiO ₂ Photocatalyst	11
2.3.4 Photocatalytic Inactivation of Bacteria in Water	14
CHAPTER THREE.....	16
3.0 MATERIALS AND METHODOLOGY	16
3.1 The Study Area.....	16
3.1.1 Description of Lake Victoria	16
3.2 Water Collection and Analysis.....	18
3.3 Soil Collection and Characterization.....	18
3.4 Materials and Chemicals	18
3.4.1 Materials	18
3.4.2 Chemicals	19

3.5 Clay Filters	19
3.5.1 Clay and Sawdust Processing	19
3.5.2 Clay Mixing	19
3.5.3 Filter Making	19
3. 5. 4 Filter Drying and Kilning Process	20
3.5.5 Flow Rate Testing	20
3.5.6 Calcinations of Titanium (iv) Oxide Powder.....	20
3.5.7 Coating of filters using TiO ₂	20
Figure 3.2: Summary of clay filter making process.	21
3.5.9 Testing the photocatalytic activity of TiO ₂	21
3.6.1 pH Measurement.....	22
3.6.2 Turbidity	23
3.6.3 Total dissolved solids	23
3.6.4 Total suspended solids.....	23
3.7 <i>E. coli</i> analysis.....	23
3.8 Heavy metals analysis	24
3. 8. 1 Copper Analysis.....	24
3. 8. 2 Lead Analysis	24
3.9 Pesticide Analysis.....	25
4.0 RESULTS AND DISCUSSION	26
4.1 Soil Characterization	26
4.1.1 Clay Mixing	28
4.2 Clay Filters	28
4.3 Flow Rates Analysis	30
4.4 Testing the photocatalytic effectiveness of titanium (iv) oxide.	31
4.4.1 Determination of the optimum amount of titanium (iv) oxide for reduction of methyl orange dye.....	32
4.5 <i>E. coli</i> analysis.....	35
4.6 Coating the filters with TiO ₂	36
4.7 Levels of the physico- chemical parameters in the filtered water samples	36
4.7.1 pH	37
4.7.2 Turbidity.	38
4.7.3 Total dissolved solids (TDS)	39
4.7.4 Total Suspended Solids (TSS)	39

4.7.5 <i>E. coli</i> Analysis	40
4.7.6 Heavy Metal Analysis.....	40
4.7.7 Pesticides	43
4.8 Results for the analysis of the water sample from Lake Victoria	45
4.9 DISCUSSION	47
5.0 CONCLUSION AND RECOMMENDATIONS.....	50
5.1 Conclusion.....	50
5.2 Recommendations	51
REFERENCES.....	52
APPENDIX.....	64

LIST OF TABLES

Table 4.1: Percentage chemical composition of Kinangop and Got Ramogi clays.....	31
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Table 4.2: Percentage ratios of clay to sawdust.....	32
Table 4.3: Weight and percentage shrinkage of clay filters.....	32
Table 4.4: Natural and modified clay filters flow rates.....	34
Table 4.5: Percentage reduction of methyl orange by varying amounts of Titanium (iv) oxide.....	36
Table 4. 6: levels of physico – chemical parameters in the filtered water sample.....	41
Table 4.7: Levels of copper in the filtered water samples from natural and modified clay filters..	46
Table 4.8: Levels of lead in the filtered water samples from natural and modified clay filters.....	47
Table 4.9: Results of the 17 mixtures of OCP pesticides in the filtered water sample.....	50
Table 4.10: Physico-chemical parameters and heavy metals in the filtered water from Lake Victoria.....	48

LIST OF FIGURES

Figure 2.1: The chemical structure of some of clay soil.....	10
Figure 3.1: Map of Bondo district showing the sampling site.....	18
Figure 3.2: Flow chart summary of the filter making process.....	23
Figure 4.1: Natural Kenyatta University unmodified and TiO ₂ modified clay filters.....	33
Figure 4.2: Natural Got Ramogi unmodified and TiO ₂ modified clay filters clay filters.....	33
Figure 4.3: Colour change of methyl orange during the degradation process by suspended TiO ₂ photocatalyst.....	35
Figure 4.4: Determination of the optimum amount of TiO ₂ to be used in degrading Methyl orange.....	36
Figure 4.5: Degradation of 15ppm and 20 ppm methyl orange at pH 7.....	37
Figure 4.6: Degradation of 15 ppm and 20 ppm methyl orange at pH 3.....	38
Figure 4.7: Degradation of 20 ppm methyl orange at both pH 7 and pH 3	38
Figure 4.8: Degradation of 15 ppm methyl orange at pH 7 and pH 3	39
Figure 4.9: Degradation of 15ppm at pH 7 methyl orange in 60 minute intervals.....	40
Figure 4.10: Graph showing reduction of E. coli in a suspension of TiO ₂	40
Figure 4.11: OCPs concentrations in the water samples collected from Lake Victoria.....	52

LIST OF ABBREVIATIONS.

AAS	Atomic absorption spectroscopy
BDL	Below detection Level
BHC	Benzene hexachlorine
CB	Conduction band
CWP	Ceramic water purifier
CFU	Colony forming unit
DBP	Dibenzophenyl
DCM	Dichloro methane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenylchloroethane
DDT	Dichlorodiphenyltrichloroethane
DEAP	District environment action plan
DO	Dissolved oxygen
EPA	Environmental protection agency
eV	Electron Volts
GC/MSD	Gas chromatography/Mass spectrometry detector
HAA	Halo acetic acid
HCH	Hexa-chloro hexane
HPLC	High performance liquid chromatography
h ν	Light photon
KEBS	Kenya Bureau of Standards
KWAHO	Kenya Water for Health Organisation
LOI	Loss on ignition
mA	Milli amperes
MO	Methyl orange

NGO	Non-governmental organisation
nm	Nanometres
NTU	Nephelometric turbidity units
OCP	Organochlorine pesticides
PAH	Polycyclic aromatic hydrocarbons
PET	Polyethylene
PFP	Potters for peace
POP	Persistent organo pesticides
POU	Point of use
PPM	Parts per million
PVC	Polyvinyl Chloride
SPE	Solid phase extraction
THM	Trihalomethanes
TDS	Total dissolved solids
TIC	Total ion current
UN	United Nations
UN/GEMS	United Nations/ Global Environmental Monitoring System
UNDP	United Nations Development Programmes
UNEP	United Nations Environmental Programmes
UNICEF	United Nations Children Education Fund
USEPA	United States Environmental Protection Agency
USA	United States of America
UV	Ultra violet rays
UV-A	Region within UV spectrum
VB	Valence band
% Wt.	Percentage weight

WHO World Health Organisation

XRF X- Ray Fluorescence

CHAPTER ONE

1.0 INTRODUCTION.

1.1. Background Information.

Lack of clean water for household use has become a global problem. Report from WHO (2004), shows that close to 1.8 billion people lack access to safe drinking water, while 2.6 billion either have little or no sanitation. Montgomery and Elimelech reported that 3,900 children die daily from water borne diseases (Montgomery and Elimelech, 2007).

Lima *et al* (2000) and Behrman *et al* (2004) reported that the leading causes of health disability are intestinal parasitic infections, diarrhoea causing water borne bacteria and enteric viruses. According to WHO (2004) estimate, around 4.0% of the global deaths and around 5.7% of the global diseases are caused by inadequate water, poor sanitation and hygiene, while around 4.2% of the disability adjusted years worldwide is attributed to other water-related diseases such as ascariasis and schistosomiasis. In addition, many countries especially in Africa experience the highest water disparities with over 50% of the water resources concentrated within a single basin (UN Water/Africa, 2011).

By 1995, already 10 African countries including Kenya, Algeria, Burundi, Cape Verde, Djibouti, Egypt, Libya, Malawi, Rwanda and Tunisia experienced water scarcity (UN Water/Africa, 2011). According to the report from the UN, the water situation is expected to get worse by 2025 (UN Water/Africa, 2011).

It is now evident that sickness related to drinking contaminated water is among the leading causes of human mortality and morbidity (Shannon *et al*, 2008). At the moment, about 75% of Africa's water resources come from ground water, whereas the surface and rain water constitutes 25% (Shannon *et al*, 2008). The greatest challenge is that, most of the water resources are heavily contaminated by high load of sediments, chemicals and microbiological pollutants.

Sobsey 2002, in a paper presented at the UN meeting in Geneva, on water management at home, observed that it would take decades before effectively treated conventional piped water system was connected to most households. He further suggested that people should collect water from the source and organise for its treatment at the consumption site (Sobsey, 2002). The shortfall in the service provision has been addressed in the recently passed UN Sustainable Development Goals (UN, 2015) and the concluded Millennium Development Goals, which aimed at reducing the

percentage of people who could access safe water by 2015 (UN, 2000). Cases of waterborne diseases caused by drinking unsafe water are very high among the poor in developing countries (UN, 2009). The most affected are the children, the elderly and immuno-compromised individuals, whose immunities cannot resist waterborne infectious diseases (Brown, 2007).

The data available from the International agencies (World Bank, 2009), and local research activities (Getenga *et al*, 2004), show that the water resources in Africa have elevated levels of microbiological pathogens like bacteria, viruses, protozoa as well as chemical contaminants such as pesticides, heavy metals and persistent organic pollutants among others (Wandiga, 2001). Kenya is one of the African countries grossly affected by water quality and scarcity challenges. Currently, the country is categorized as chronically water scarce with a water supply of less than 647m³ / person per year, compared to the global benchmark of 1000m³ / person per year. Statistics projects a drop to 235m³ / person per year in Kenya by 2025 (WHO, 1998). Singh and Bengtson 2005 predicted an increase in demand which will be catalysed by the increased population growth. They further observed that the population increase is likely to exert more pressure on the existing water sources (Singh and Bengtson, 2005). The challenges facing water quality and water quantity are great and of equal measure. Out of the total Kenyan population of 40 million (Kenya CBS, 2009), urban population constitutes 32.3%, whereas the rural population constitute 67.7%. Kenya CBS (2009) also reported that only 13.4% and 38.4% of the rural and urban populations, respectively, are using piped water while more than 86% of the rural communities have no access to clean water (KWAHO/UNDP, 2007).

1.2. Water treatment at household level

New strategies for providing clean water have been devised to control the persistent waterborne diseases. These strategies include a system where water is treated at the consumption level to minimise the possibilities of ingesting pathogenic microbes. In trying to control the increasing water shortage and the rising figures on water related diseases, Sobsay (2006) reported that several methods have been used worldwide to treat contaminated water, either from the point of collection or at the consumption point. These methods include filtration, solar disinfection, adsorption, ozonation, reverse osmosis and chlorination (Sobsay, 2006). Padmanabhan *et al* (2006) observed in their publication that the available technologies for treating water like adsorption are not effective since they only concentrate and transfer pollutants to another phase without completely destroying them. Gaya and Abdullah (2008) observed that the conventional water treatment methods such as sedimentation, filtration, membrane technologies and chemical treatment are

quite expensive and they also release toxic by-products into the environment. According to the publication by Lu *et al* (2009) and Coleman *et al* (2005), chlorination has been noted to generate bi-products which are mutagenic and carcinogenic. The effectiveness of ceramic filters in reducing bacteria, viruses, protozoa and helminthes loads in water was reported by Brown and Sobsey in their publication dated 2006.

1.3. Treatment of Water Using Photocatalyst.

Esplugas *et al* (2002) and Pera-titus *et al* (2004) proposed a purification principle which is based on the in situ generation of highly reactive species (H_2O_2 , $OH\cdot$, $O_2\cdot^-$, O_3) for the mineralisation of refractory organic compounds and pollutants, pathogens and disinfection by products. Among these AOPs, titanium dioxide (TiO_2) photocatalyst has demonstrated its wide applicability in the oxidation of persistent organics into biodegradable compounds and their mineralisation into carbon dioxide and water (Chong, 2010). Generation of hydroxyl radicals can be harnessed to kill bacteria and fungus (Fujishima and Hashimoto, 1996; Chen, 2009). Chong *et al* (2009) commented on the way in which natural clay has been used as a support for TiO_2 . This, according to Chong *et al* (2009), has been because they are inexpensive and also have high adsorption capacity. Chong *et al* (2009) also reported that several clay types such as bentonite, zeolite, sepiolite and montmorillonite have been investigated to find a suitable photocatalytic support and it was found out that all these clays have superior capacity to increase adsorptive surface contact during photocatalysis. These clays, according to Chong *et al* (2009), were found to be catalytically inactive and they also have superior adsorption capacities which were quite ideal for increasing surface contact during photocatalysis. The superior adsorption capacities of clay soil have been found attractive for increasing the surface contact during Photocatalytic reaction (Chong *et al*, 2009).

1.4 Problem Statement.

Water of Lake Victoria is the main source of water used for drinking, industrial processes, irrigation and domestic use, food, transport, recreation, biodiversity conservation, hydroelectricity power generation, navigation, fisheries production, forestry and livestock production to the surrounding communities (Getenga *et al*, 2004). Various studies carried out in Kenya have shown levels of contamination by pesticides. Getenga *et al* (2004) found in Nyando River the level of α -Benzene hexachlorine (α -BHC) to be 0.219 ± 0.091 mg/L, lindane concentration in water was 1.240 mg/L. The levels of benzene hexachlorine (BHC) and lindane were considered to be very high. Research study conducted by Mwakio and Shitsama, (2003) to determine the concentrations of lead, arsenic, cadmium and selenium in Lake Victoria water showed that lead had average

concentration of 0.199 ppm, cadmium 0.018 ppm, arsenic 0.82 ppm and selenium 0.825 ppm. All these concentrations were found to be well above the WHO (1998) recommended guidelines on the minimum level of heavy metals in drinking water. This should be a cause for concern, especially for rural communities. KWAHO/UNDP (2007) report indicated that most of the communities living around Lake Victoria basin drink contaminated water in their homes since they cannot access safe drinking water. USEPA (2006) report showed that chlorine is ineffective in controlling water-borne pathogens such as *Cryptosporidium parvum* and *Mycobacterium avium*. Therefore, alternative disinfection methods are needed. The above findings provide a springboard for this study which aims at providing locally sustainable novel water purification system to eradicate water borne diseases and reduce levels of pesticides and heavy metals.

1.5 Objectives

1.5.1 Main Objective

To determine the synergistic effects of modified titanium (iv) oxide clay in purification and disinfection of water.

1.5.2 Specific Objectives were to:

1. Study the chemical and physical characteristics of different types of clay to be used in making filters for disinfection and purification of water.
2. Compare disinfection and purification capacities of natural and TiO₂ modified clay filters with respect to water, physicochemical parameters, pesticide residues, heavy metals and E. coli.
3. Correlate the disinfection and purification capacities of TiO₂ modified clays with their physicochemical characteristics.

1.6 Justification

Most households in developing world will still have to wait for some years before they receive clean piped water systems treated using modern water treatment technologies. These people are therefore forced to collect untreated water from the source, treat it at the household level and ensure that the water is stored in a way that will minimise recontamination (Sobsay, 2002). This water problem was one of the issues addressed in the Millennium Development Goals whose target was to reduce the number of people who could not access safe water to half by 2015 (UN 2000).

Studies on water purification and disinfection have already provided some leads for point of use methods in Cambodia, Nepal, Brazil, India and Sierra Leone. Researches have been done on Clay / tile purification (Dies, 2003), TiO₂ impregnated tiles purification method (Azzaryatul, 2008) and indigenous charcoal purification method and solar disinfection. A lot of work has also been done on TiO₂ coated PET bottles for solar disinfection (Williams, 2009). In Kenya there is no publication of research work on the water purification using TiO₂ coated on local clay.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Water Borne Pathogens

Sobsay (2002) reported that most of the infant deaths in developing countries are associated with diarrheal illness because these infants are very susceptible to malnutrition, dehydration and other ailments which are connected to these infections. He (Sobsey) also added in the same report that most of these diarrheal illnesses are caused by drinking contaminated water, insufficient sanitation and poor hygiene (Sobsay, 2002).

Lima *et al* (2000) reported, in the research which he conducted among the children in northern Brazil that malnutrition is mostly as a result of intestinal infections and diarrheal infections which are caused by waterborne bacteria and enteric viruses. Similar observation was also made by Behrman *et al* (2004).

Pitman (2002) reported that public health in developing countries in the sub-Saharan Africa and South East Asia are greatly ravaged by water borne pathogens. According to the report by the WHO (2003), the pathogens responsible for these infections include helminthes, protozoa, fungi, bacteria and viruses. The WHO report also mentioned the emergence of resistant pathogen strains which pose a serious challenge to water disinfection (WHO, 2003). Curtis *et al* (2000) pointed out that diarrhea causing organisms which are generally found in faeces are transmitted through oral ingestion. WHO (2006) reported that drinking water, food, hand, clothing and utensils are the main transmission routes of diarrhea causing organisms in poor sanitation and hygienic conditions.

Some bacterial water borne pathogens like *Mycobacterium avium* are known to be resistant to free chlorine. *M. avium* in particular forms a chlorine resistant cyst in water supply systems at high pH and low temperature of natural water (USEPA, 2006). USEPA (2006) further pointed out that halogenated water treatment methods also produce disinfection by-products such as trihalomethanes (THM) and haloacetic acid (HAA) which are toxic (USEPA, 2006). It is therefore important that an effective method of controlling waterborne pathogens in drinking water be developed. The developed method should involve a combination of approaches which could result into cost effective and efficient physico-chemical removal, photon based chemical and micro- organism inactivation.

EPA (2009) report shows that the presence of bacteria such as *E. coli* and faecal coliform in water indicates that the water is contaminated with human or animal wastes. Results from the research conducted indicate that microbes in these wastes can cause diseases like diarrhoea, cramps, nausea and headaches (EPA, 2009). WHO and UNICEF (2004) report listed bacteria as one of the major contaminants to be removed from drinking water since they are linked to the larger fraction of deaths which resulted from drinking unsafe water.

The use of photocatalysts to destroy bacteria and viruses was cited by Mills and LeHunte in 1997. The two scientists also reported on the ability of the photocatalysts to completely destroy bacteria such as *Streptococcus cricetus*, *Streptococcus mutans*, *Streptococcus mitis*, *Escherichia coli*, *Saccharomyces cerevisiae*, *Lactobacillus acidophilus* and poliovirus. Report by Shepherd *et al* (2002) proved that immobilised TiO₂ can degrade microcystin toxins and a green algae species (which has a thick wall) called *Chlorella vulgaris*.

2.2: Types of clay pots and their application in Kenya.

Clay pots have been used by various communities in Kenya over the years for cooking fetching and carrying water from its point of collection and storage. Mutagaywa (1995) classified traditional Kenyan pottery into three forms: (1) A simple open pot which is in two sizes, smaller one which is used for storing and serving meat and vegetables. Larger size is used for brewing and serving beer or fermenting and serving porridge. (2) A simple restricted pot was used to cook fish. It was also used to store grains. (3) This pot with a neck was used to brew and store traditional beer. It was also used to carry and store water.

Users in the Nyanza Province of Kenya frequently carry water from some distance or purchase vended water and traditionally store this water in their homes in clay pots (Young, 2005). In western Kenya, pottery making has exclusively been done by women (Mutagaywa, 1995). However, only a small proportion of the women in any potting community are involved in the trade, and those women who do make pottery usually undertake this craft part-time in combination or alternating with other household tasks (Wandibba, 2003).

Women produce various types of clay pots and pans mainly for household use in food processing, preparation, and storage and for water carriage and storage (Wandibba, 2003).

People in the Nyanza Province of Kenya, located along the shores of Lake Victoria, traditionally store their water in wide-mouth clay pots (Bovin and Morohashi, 2002). These people prefer using clay pots because of the evaporative cooling effect such vessels have on water and because the

clay makes the water palatable (Bovin and Morohashi, 2002). However, the wide mouths encourage the drawing of water with cups, and the hands holding the cups are often contaminated (Young, 2005). So, even pristine water stored improperly can be easily contaminated, leading to incidences of diarrheal disease, mainly in children under the age of five (Bovin and Morohashi, 2002).

Examination of different pottery forms produced suggests that variation in size within form classes relates to differential function, such that potters distinguish these differences with terminological distinctions (Wandibba 2003). However, sometimes distinct forms have the same terminology. One specific example of this is described by Wandibba (2003).

2.2.1: The chemical structures of clays.

According to the observation by Grimshaw (1971), clays are chemically aluminosilicate minerals and they have numerous industrial uses (Murray, 2002). The importance of chemical composition of clay in pottery and ceramic making is explained in detail by Amethyst (1996). Cement manufacture, where the amount of MgO in the soil must always be below 5 % require chemical composition of the clay Clays are also an important source of aluminium (Troxell *et al*, 1968).

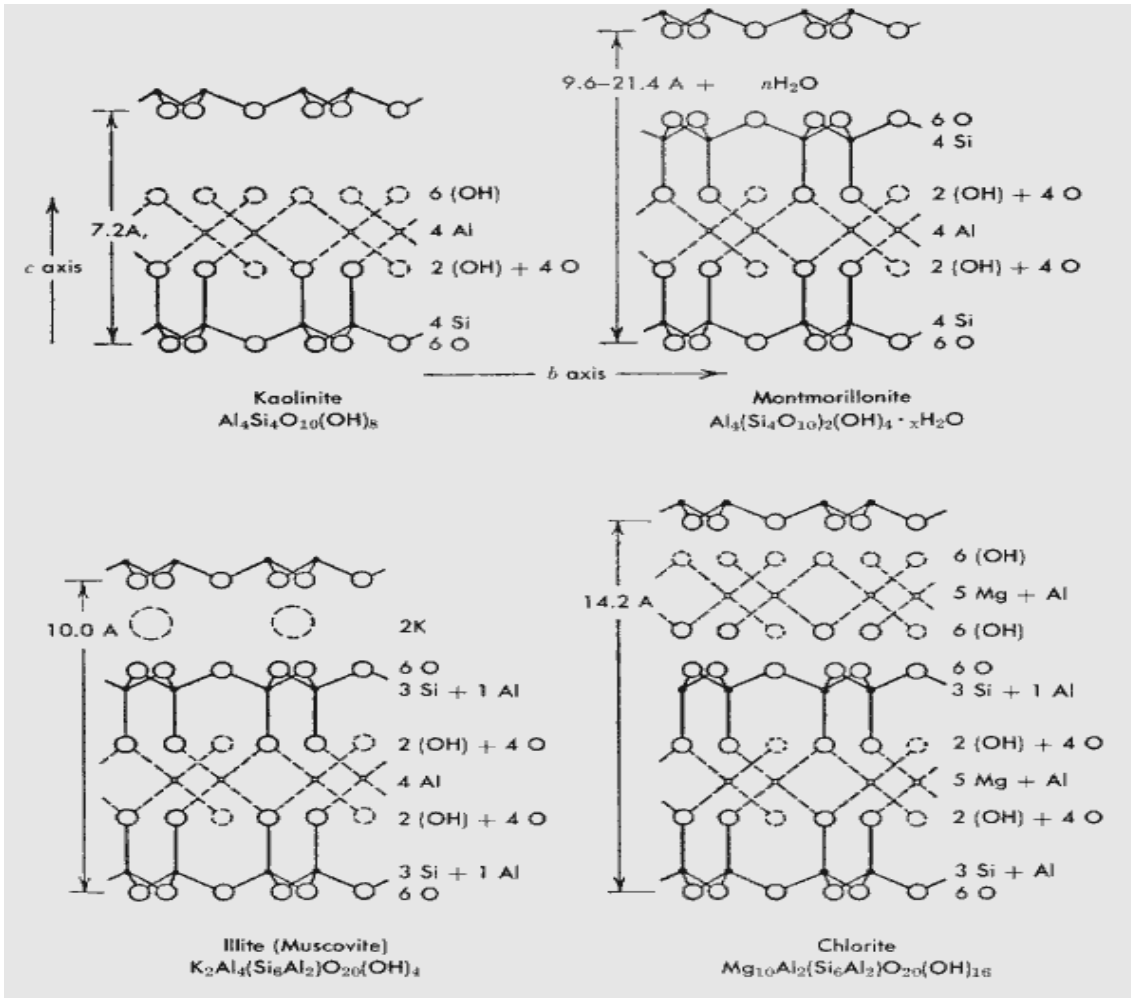


Figure 2.1: Chemical structure of some clay minerals.

Source: (Anthoni, 2000)

Kaolinite group have the general formula $Al_4Si_4O_{10}(OH)_8$. Kaolinite structure is composed of alternate silicate sheets (Si_2O_5) and aluminium oxide/ hydroxide sheets ($Al_2(OH)_4$), gibbsite sheets (Sarwenaj, 2008).

The montmorillonite are classified as minerals of general formula $(Ca, Na, H)(Al, Mg, Fe, Zn)(Si, Al)_4O_{10}(OH)_2 \cdot xH_2O$. (Sarwenaj, 2008).

Illites / Micaceous have an numerous cations between the layers to balance lattice charges. They have the general formula $KHA_{12}(Si, Al)_4O_{10}(OH)_2 \cdot xH_2O$ (Sarwenaj, 2008).

Gaboriaud et al (2005) reported that chlorite group are 2:1 silicates and their general formula are $X_{4-6}YO_{10}(OH,O)_8$ where X can be Al, Fe, Li, Mg, Mn, Ni, Zn and Y can be Al, Si, B or Fe.

2.3 Water Purification and Disinfection Methods

Several research studies conducted by Clasen *et al* (2006, 2005, 2004b and 2004a) showed that ceramic filter technology has been used to effectively remove microbial pathogens from water and has also resulted into the notable improved health condition of the ceramic filter users. Clasen *et al* also dwelt on the convenience and availability of these filters because of their simplicity, affordability and the fact that they are made using local knowledge and material. Brown (2007), however, observed that locally produced ceramic filters have not been subjected to thorough evaluation in field studies to determine their microbiological effectiveness, their ability to reduce diarrheal disease and the duration they take before replacement.

2.3.1 Clay Filtration

This is a process where porous fired clay is used to remove pollutants from water. Lantagne (2001b, 2001a and 2001) identified two categories of clay filters; (i) those filters which are made using advanced technologies in developed countries are made to specifications, high quality and are very costly, and (ii) those made in developing countries with varying effectiveness but are mostly made using local materials. The products in the second category are always affordable and are locally available. The example of the second category is the filtron project by Potters For Peace (PFP), a non-governmental organization (NGO) that promotes the technology in Cambodia, Nepal and Sierra Leone (Lantagne, 2001b ; 2001a; 2001).

Both Cheesman (2003) and Dies (2003) reported on the diversity of low cost Ceramic filtration in developing countries in terms of their overall design, method of production, clay, quality assurance and quality control procedures, burn out materials used, firing temperature and methods of chemical modification .

The advantages of locally produced filters, as enumerated by Roberts *et al* (2001), are that they are light, portable, cheap and have low maintenance cost. Cheesman *et al* (2001) further observed that ceramic filters can greatly reduce turbidity without altering the taste of the water as is the case with chemical and thermal disinfection.

Ceramic water purifier's average pore size range of up to 3 μm results in the possibility of some viruses and bacteria passing through with the permeate and in some cases, some natural organic matter, specifically humic acid as well as Polycyclic Aromatic Hydrocarbons (PAH) can pass through the filter pores unless fouling level increases resulting in the blocking of pores of the membrane (Vernabets, 2009). Brown, (2007) studied the effectiveness of Ceramic Water Purifier (CWP) and found that CWP reduce E-coli bacteria by 99.9%. Field and testing resulted in

approximate mean reduction of 99%. Brown (2007) also found that CWP can be used to reduce diarrhea outbreak by around 40% and that filter effectiveness can be maintained for up to 44 months in field use.

Results of studies conducted by Yauvz *et al* (2003) and Battacharyya and Gupta (2008), on different types of clays, showed that kaolinite and montmorillonite have good adsorbance which could be used to remove toxic heavy metals from water. Similar research was also conducted by Veli and Alyuz (2007) and they also reported on the suitability in removing heavy metals from water through adsorption process. Kamel *et al*, (2004) proposed Cu>Fe>Pb>Mn>Zn to be the order for ion sorption affinity to Egyptian kaolinitic clay.

2.3.2 TiO₂ Photocatalyst

The first contribution to understanding the heterogeneous photo catalytic process was in 1972 with the pioneering research of Fujishima and Honda (1972). The possibility of water getting split by a photochemical cell was revealed by the two authors, using a rutile TiO₂ photo anode and a platinum counter anode. This finding opened the frontiers of titanium photo catalysis for other types of applications. Four years later, Carey *et al* (1976) published a report on the photo catalytic degradation of organic molecules, biphenyl, and chlorophenyl derivatives, by TiO₂.

Gaya *et al* (2008) reported that the multifaceted properties and photo catalytic performance of titanium dioxide had generated increased interest due to its photo stability, low cost and non-toxicity.

Dalrymple (2007) reported that the successful uses of TiO₂ photocatalysts to photo degrade resistant organic contaminants in water which include several complexes, endocrine disruptors and dyes have been well documented.

Titanium dioxide has been widely used to remove toxic chemicals from waters. Naiya *et al* (2009) reported that inorganic solid adsorbents, such as Al₂O₃, SiO₂, ZrO₂, and TiO₂ are preferred because of their high mechanical properties and strong resistance to thermal degradation, as compared to other bio- sorbents or organic adsorbents. Bourikas *et al* (2001) argued that TiO₂ is a preferred photocatalyst because it has many advantages when used as adsorbent for heavy metal removal from wastewater. TiO₂ is also an extensively studied oxide and has high chemical stability and negligible solubility over a wide pH range. Bourikas *et al* (2001) further added that, TiO₂ presents ideal point of zero charge (at around pH 6). This makes it possible to study adsorption on positively and negatively charged surfaces of TiO₂ over a broad pH range

(Vandenborre *et al.*, 2007; Olsson *et al.*, 2003; Tel *et al.*, 2004). According to Henrich and Cox, (1994), TiO₂ exists in two major forms, anatase and rutile. He further stressed that anatase powder is preferred in most applications because of its greater surface area as compared to rutile.

However, Bhattacharya *et al* (2004) reported on the aggregation challenges that are met when using bare TiO₂ in photo catalytic reactors. Bhattacharya *et al* (2004) attributed the nano size (about 4-30 nm) of TiO₂ to be the cause of its rapid aggregation in suspension which lead to loss of its surface area and catalytic activity. Torimoto *et al* (1997) observed that aggregated photocatalyst also do not adsorb pollutants because of its lost porosity. XUY *et al* (1999) observed that it was the search for the solution to the challenge posed by bare TiO₂, that led to recent attempts to immobilize nano sized TiO₂ on porous adsorbent material like activated carbon (Yoneyama and Torimoto 2000) alumina (Sapath *et al* 1994) clay and zeolites (Anderson and Bard 1995) to produce composite adsorbent / catalyst. Takeda *et al* (1997) chose sol-gel route as the best preparation method for TiO₂ based materials because it is well established and produce excellent results. Takeda *et al* (1997) also noted that TiO₂ mounted on an adsorbent material has a bigger specific surface area and more effective adsorptive sites than loose TiO₂. Takeda reported that TiO₂ are very reactive and chemically stable when exposed to ultra violet light with energy band gap which is equal to or more than 3.2 eV, in the anatase crystalline phase (Takeda *et al*, 1997).

2.3.2.1. Mechanism of TiO₂ degradation of pollutants

Chong (2010) observed that photocatalytic mechanism is initiated by TiO₂ absorbing light photon (hv) with the band gap energy of 3.2 eV. The band gap energy produces electron-hole pair on the surface of the titanium nanoparticle. The activated electron is promoted to the conduction band (CB) leaving behind a positive electron hole at the valence band (VB). The electrons at the excited state and the electron holes can either recombine then the activation energy dissipates as heat or react with electron donors and electron acceptors adsorbed on the semiconductor surface. Furube *et al* (2001) reported that the presence of oxygen prevents the recombination of the electron and electron hole pair, while allowing the formation of super oxide radicals (O₂^{·-}). This radical, according to Furube *et al* (2001), can further be protonated to form the hydroxyl radical (HO₂[·]) and subsequently H₂O₂. The H₂O₂ radicals formed, reported Chong (2010), have scavenging properties and these properties can prolong the recombination time of the excited electrons to the electron hole in the entire catalytic reaction. Chong (2010) attributed the occurrences of the photocatalysis to the presence of both dissolved oxygen (DO) and water molecules. It is the

presence of the water molecules which is responsible for the formation of the highly reactive hydroxyl radicals (OH[•]). Chong (2010) noted that aromatic hydrocarbons can be hydroxylated by the reactive OH[•] radical which leads to successive oxidation/addition reactions and eventually ring opening. Chong (2010) further observed that the resulting intermediates from the degradation of the aromatic hydrocarbons, mostly aldehydes and carboxylic acids, are further decarboxylated to produce carbon dioxide and water.

According to Zhao and Yang (2003), the activation of TiO₂ by ultra violet (UV) light can be written as:



Here, h⁺ (holes) and e⁻ (electrons) are powerful oxidizing and reductive agents, respectively. These photo-generated holes react with water attached on TiO₂ and the photo-generated electrons react with oxygen in water to form reactive oxygen species (ROS) such as OH[•], HO₂[•] and H₂O₂ in the following photocatalytic reaction as was proposed by Huang *et al.*, (1998):

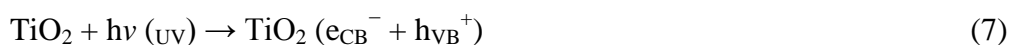


Equation (2) is an oxidative reaction while Equations (3-6) are reductive reactions. According to Rincon and Pulgarin (2003), the generated [•]OH radicals are highly participative in the oxidation of organic substances, as well as the inactivation of bacteria. Ibanez *et al* (2003) observed that the inactivation of bacteria by heterogeneous photocatalysis using ultra violet ultra violet (UV-A) light (320-400 nm) with TiO₂ is one of the most effective disinfection technologies since the degradation products are not carcinogenic, mutagenic or malodorous.

2.3.3. Degradation Process for Methyl Orange by Titanium (iv) Oxide Photocatalyst

Chen and Liu (2007) observed that chemical stability of modern dyes make them resistant to the commonly used conventional biological methods used to treat industrial wastewater; this has resulted in the emission of coloured discharge from the treatment plants. Dalton *et al* (2001) also

supported the use of inorganic photocatalysts as cheap and effective way of removing organic compounds and pollutants. Marinas *et al* (2001), Tanaka *et al* (2002) and Konstantinou and Albanis (2004) also supported the use of TiO₂ photocatalyst as an effective alternative means of removing organic pollutants from wastewater. According to the reaction mechanism proposed by Vinodgopal and Khamat (1994), methyl orange dye is degraded by conduction band electrons (e⁻) and valence band holes (h⁺) which are generated when light energy which is equal or greater than its band gap energy (E_g=3.2 eV) radiates TiO₂ suspended in aqueous solution. The photo-generated electron holes can react with the dye leading to its complete degradation through reduction process, react with O₂ adsorbed on the Ti-surface or dissolved in water reducing it to superoxide radical anion O₂^{•-}. Rashed and El- Amin (2007) used Hoffman *et al* (1995) illustration to explain that the photo generated electron holes can oxidize the organic molecule to form R⁺, react with OH⁻ or H₂O to form OH • radicals, which together with peroxide radicals are responsible for the TiO₂ photodecomposition of organic substrates. Given below is a complete mechanism proposed by Hoffman *et al* (1995), showing the relevant reactions at the TiO₂ semiconductor surface causing the degradation of dyes.



According to observation made by Hoffman *et al* (1995), the resulting OH• radical, can oxidize most of methyl orange dye to the mineral end-products.

2.3.4 Photocatalytic Inactivation of Bacteria in Water

Brown (2007) justified the use of, *E. coli*, as surrogate for bacterial pathogen as test microbe by explaining that they are potentially present in most drinking water sources. Brown (2007) further stressed that since *Escherichia coli* are gram negative, rod-shaped bacterium measuring 1–2 μm in length and 0.1–0.5 μm in diameter, which is similar to other disease causing bacteria found in drinking water. It was therefore chosen as a model for the reduction of bacterial pathogens in water through the primary physical separation process of ceramic filtration.

Ibanez *et al* (2003) tested the bactericidal heterogeneous photocatalysis on *Enterobacter cloacae* and on Gram-negative bacteria, *Pseudomonas aeruginosa* and *Salmonella typhimurium* and

reported that sub-lethal ultra violet (UV-A) rays provoked an important lethality with the presence of TiO₂. After 40 min of ultra violet (UV-A) irradiation, 99.9% of viability was lost in all the studied strains and an exponential decrease in the viability was observed. Cho *et al* (2004) concluded that the ·OH radicals produced during the heterogeneous photocatalysis is the one responsible for *E. coli* inactivation.

The findings above are the cognitive tools for our study on modified titanium oxide in clay filters.

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

3.1 The Study Area

3.1.1 Description of Lake Victoria

Lake Victoria is the world's second largest fresh water lake with surface area of 69,000 Km² and has the world's largest freshwater fishery (LVEMP, 2003). It is located at an elevation of 1134m above sea level, between longitudes of 0° 21`N and 3° 00`S and between latitudes of 31°39`W and 34°53`E. It has a total volume of 2,760 Km³ and catchment area of 251,000Km² which is distributed among the East African countries (UN GEM/Water, 2008). This water supports over 38 million people, which constitutes approximately 4% of the population of the continent of Africa, which directly or indirectly depend on the lake's resources. Bondo sub-county lies on the Lake Victoria drainage basin.

3.1.2 Description of Bondo sub- county

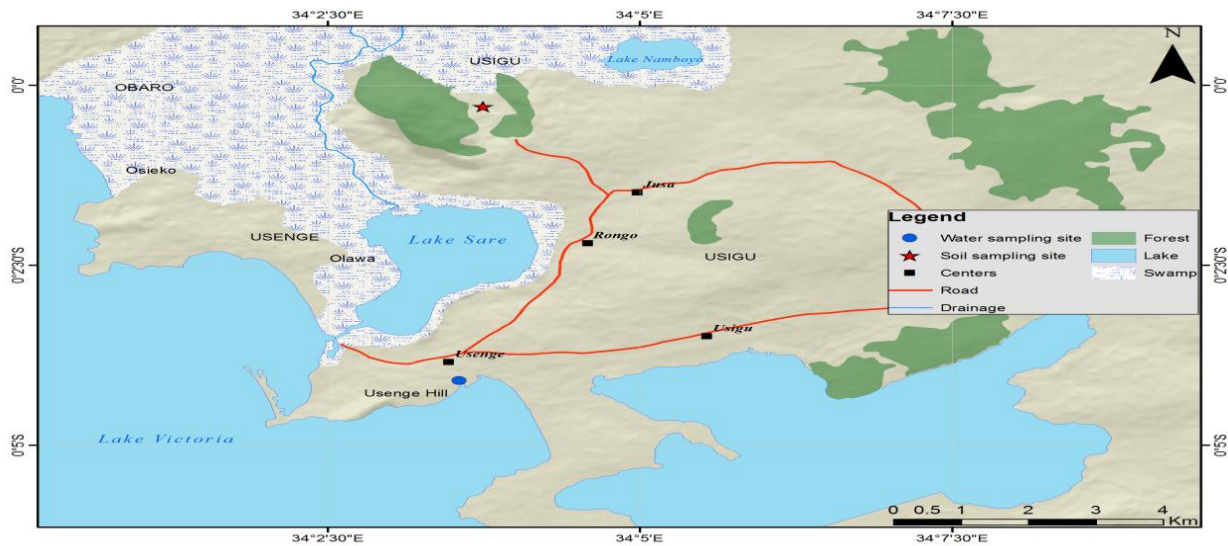


Figure3.1: Map showing the sampling site in Bondo sub-county

The project was intended to assist communities living along the shores of Lake Victoria in Bondo Sub-county, (Siaya County). Bondo Sub-county (Figure 1) lies between longitudes 0° 26' N to 0° 90' S and from latitudes 33° 58' W to 34° 35' E. DEAP (2007) report shows that the sub-county was carved out of the former Siaya District, as a new district, in May 1998. It borders Siaya sub-county to the North, Kisumu sub-county to the East and Homa Bay and Suba sub-counties across the Winam Gulf to the South East and South respectively. To the West is Uganda. The sub-county has a total area of 1,972 Km² out of which 972Km² is landmass while the rest 1000Km² is under water of Lake Victoria. According to the DEAP (2007) report, the sub-county has three administrative divisions; Maranda, Nyang'oma and Usigu.

Bondo sub-county falls within the former Nyanza Province region where only 0.6% of her population have access to clean, piped water (KWAHO/UNDP, 2007). Data obtained from the Kenya National Bureau of Statistics in Bondo sub - county show that around 35% of the people in Bondo have access to clean water while the rest rely on water from Lake Victoria, dams and pans (DEAP, 2007). The annual average rainfall of the sub-county is 1000 mm the mean temperature is 22.5 °C while evaporation rate ranges between 2000 mm and 2,200 mm annually. DEAP (2007) report also show that the types of soil in Bondo sub-county range between black cotton, sandy loams and laterites including red volcanic soils in the North.

3.2 Water Collection and Analysis

Triplicate water samples for the determination of heavy metal and pesticide residues were collected from a sampling site at Nairobi River next to Pesticide analytical lab in Chiromo campus and Usenge beach on the Bondo side of Lake Victoria, by grab sampling method in labelled 2.5 litre amber glass bottles, while the samples for pH, turbidity, total dissolved solids (TDS), total suspended solids (TSS), copper and lead analyses were collected in 1.0 L plastic containers. Water samples for faecal coliform analysis were collected in triplicate and sterilized 1.0 L glass bottles. All the water samples were then temporarily stored in polyurethane cool boxes containing dry ice and taken to the laboratory for analyses.

3.3 Soil Collection and Characterization

The soil samples used for filter making were obtained from Got Ramogi in Usigu location, Bondo Sub-county and from the Ceramic Department at Kenyatta University (the area of collection for the Kenyatta University soil was not availed to the researcher). Soil samples (from 15-30 cm) were collected from five different points in Got Ramogi area and combined to make composite sample. The five sampling points were randomly selected within sampling site. A soil core was dug using a hoe and scooped using a spade down to the depth of 30 cm from the five different locations within the site and approximately 500 g of the scooped core taken. The cores were thoroughly mixed to give a composite sample. Triplicate samples of approximately 500 g were taken from the composite sample. Each sample was wrapped in a sterilized aluminium foil, labelled and placed in a black plastic bag before transferring to a labelled self-sealing polythene bag and placing in a plastic container with lid. The samples were stored temporarily in polyurethane cool-boxes containing dry ice prior to transportation to the laboratory for analysis and further storage. In the laboratory, samples were taken for characterization while the rest were stored at ≤ -19 °C and analysed within 7 days.

Soil types, which were to be used for making filters, were sent to the Department of Mines and Geology (Ministry of Mining) in industrial area, Nairobi for XRF analysis.

3.4 Materials and Chemicals

3.4.1 Materials

The following instruments were used: UV Spectrophotometer model Shimadzu - Pharmaspec UV 1700, pH meter model IQ Scientific Inc. Turbidity meter model LaMotte Tc-3000e, Furnace model ELSKLO DESNA J.V. Type LNT-20. Serial No. 30, Atomic Absorption Spectroscopic (AAS) machine used was of model SpectrAA. 10. Labtec, GC/MS machine model VARIAN CP

3800. Other apparatus used were: Solid Phase Extraction cartridges from Superlco Analytical™, Whatman filters paper No. 1, 3M microfilm test kits, Magnetic stirrer, 100ml Pyrex beakers, sampler vials and Pasteur pipettes.

3.4.2 Chemicals

TiO₂ powder used was DEGUSSA P25, triple distilled water, lead nitrate (PbNO₃)₂ 99.5% purity, copper powder, nitric acid (HNO₃) analar grade of 97% purity, a mixture of 16 organochlorine pesticides (OCP) HPLC grade, hexane HPLC grade 99.7% purity from Sigma Aldrich, Germany, dichloromethane (DCM) standards HPLC grade 99.7% purity from RFCL India and methanol HPLC grade 99.7% purity from RFCL India.

3.5 Clay Filters

3.5.1 Clay and Sawdust Processing

Got Ramogi is known to produce soil which is suitable for clay moulding. The soil from Kenyatta University was used by the Department of Ceramics to make various types of earthen wares. The collected clays were first dried under shade for one week, before they were homogenized using a pestle and mortar. The soil samples were sieved using a 600 µm mesh size sieve. Hagan *et al* (2009) in his findings, pointed out that the particle size should not be emphasised as long as the soil to be used in filter making, is in powder form.

Saw dust was collected from Industrial Area in Nairobi County, dried at the roof top of the Department of Chemistry, University of Nairobi, for 3 days and then sieved using a sieve of 600 µm mesh size.

3.5.2 Clay Mixing

Various percentage volume ratios of clay to saw dust were used and these were as follows; 50: 50, 55: 45, 60: 40 and 65: 35. Dry mixing was thoroughly done for 30 min before water was added. This was to ensure that saw dust and clay were uniformly mixed. After addition of water, the mixture was properly kneaded then wedged to remove air which might have been lodged between the clay particles. The clay was then divided into six equal pieces and the weight of each piece taken and recorded.

3.5.3 Filter Making

Filters were made on the potter's wheel under the guidance of a ceramic technician at Kenyatta University. 50: 50 and 55: 45 ratios were moulded with difficulty on the potter's wheel, since the

two clays had lost most of their plasticity due to the presence of high percentage of sawdust in the mixtures. All sets of the clay filters were made in triplicates.

Clay filters were labelled while, still wet as GR1, GR2 and GR3 for natural clay filters, while TGR1, TGR2 and TGR3 for modified clay filters made of clay from Got Ramogi (GR) in Bondo sub-county. KN1, KN2, KN3 were labels for natural clay filters while TKN1, TKN2 and TKN3 were for the TiO₂ modified filters made from clay from Kenyatta University (KN).

3.5.4 Filter Drying and Kilning Process

The twelve filters were air dried for 6 days in the shade. Their dry weights were taken and recorded. Filters were then kilned in a furnace model ELSKLO DESNA J.V. Type LNT-20. (Serial No. 30) stationed at the Ceramic Department, Kenyatta University. The kilning was done at 850°C for 5 hours. After the kilning, the filters were soaked in 10 litres of distilled water for 16 hours to remove air and ash that were lodged in the pore spaces.

3.5.5 Flow Rate Testing

The filters were filled with water then placed on top of 1 litre Pyrex beakers into which water drained. All the water was allowed to drain into the beaker through the filter pores. The time which water took to drain into the beaker was recorded. The amount of water collected in the beaker was measured using a measuring cylinder then expressed to one hour.

3.5.6 Calcinations of Titanium (iv) Oxide Powder

Titanium (iv) Oxide (TiO₂) powder used was DEGUSSA P25 (a Titania photo catalyst) from London Drug House. The photo catalyst was used without further purification. 50g TiO₂ was put in a crucible then calcined in a furnace at 600°C for 1 hour, the ramp rate was 5°C/min.

3.5.7 Coating of filters using TiO₂

Coating was done on filters labelled TKN1, TKN2, TKN3, TGR1, TGR2 and TGR3. 0.08g of TiO₂ powder was placed in a 200ml beaker containing 100ml water then stirred on a magnetic stirrer for 1 hour to make the suspension homogeneous. The mixture was then poured in the clay filters. The mixture was then gently rolled on the inner surface of the filters to ensure that TiO₂ was uniformly spread on the inner surface of the filter. This also gave the photo catalyst enough time to penetrate into the pore surfaces. The filter was then dried under shade for two days, to allow TiO₂ to adsorb onto clay particles, before heating in an oven at a temperature of 600°C for one hour. Calcination was meant to make the photo catalyst to be photocatalytically active. After

heating, the filters were then left to cool before they were soaked in water for 24 hours to remove air and ash from the pore spaces.

3.5.8. Summary of TiO₂ modified filter making process.

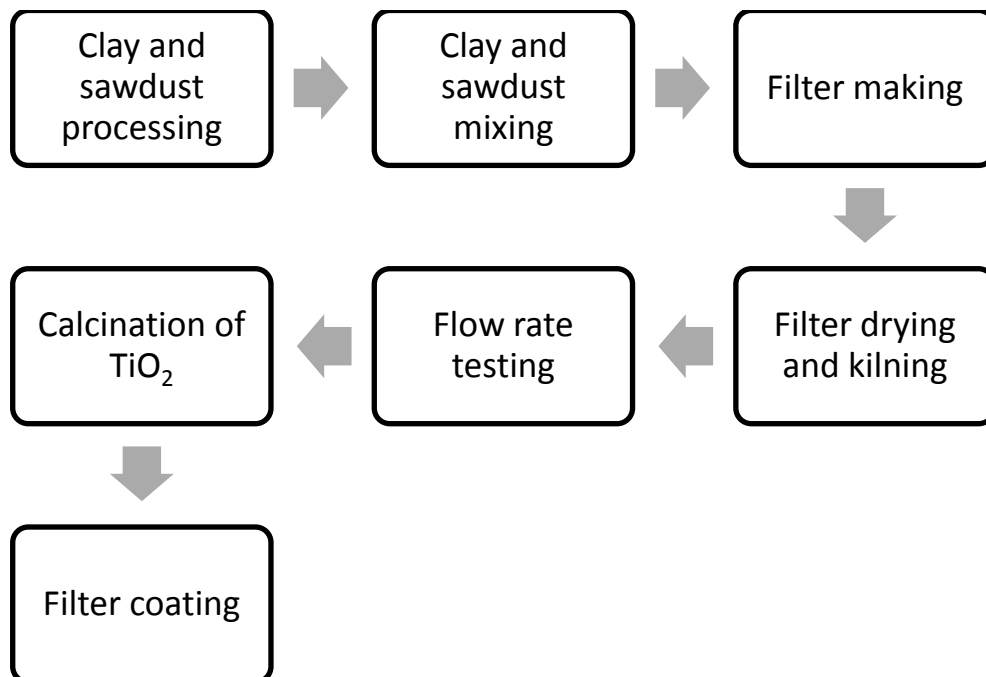


Figure 3.2: Summary of clay filter making process.

3.5.9 Testing the photocatalytic activity of TiO₂

The initial intention of this research project was to use chromium doped Titanium (iv) oxide to shift its photocatalytic activation spectrum from ultra violet light to visible light since UV represents only 5% of the solar irradiation reaching the earth. Doping was also expected to lower the activation energy of the photocatalyst. However the project could not take off because the doping procedures which were available required the use of an autoclave which was to be set at a pressure of 15 psi and average temperature of 121 °C for 48 hours but the available autoclaves which I got could not accommodate the above temperature and pressure. When I carried out the procedure at 90 °C and 10 psi pressure, the photocatalyst lost its photocatalytic ability, hence the decision to use the undoped TiO₂.

3.5.9.1 Methyl Orange photocatalytic degradation

The effectiveness of TiO₂ photo catalyst was tested by using it to degrade methyl orange (MO) under solar radiation. 0.08 g of TiO₂ was put in a 100ml water sample containing 15 ppm and 20 ppm MO. The mixture was first stirred in darkness on a magnetic stirrer for 30 minutes then under solar radiation for up to 180 minutes. An aliquot of the mixture was drawn from the sample after

20 minutes interval, filtered using a glass wool inserted in a funnel, centrifuged, and analysed using UV spectrophotometer Shimadzu-pharmaspec UV 1700 model to determine the residual concentration of methyl orange at wavelength of 471nm. The samples analysed were of pH 3 and pH 7. Further tests were done on the methyl orange degradation to determine hourly reduction of the concentration of the dye. The above procedure was repeated using 0.03 g, 0.05 g, 0.10 g and 0.12 g of TiO₂ separately to determine the optimum amount which would effectively degrade high percentage of methyl orange. The percentage degradation of MO by different masses of TiO₂ was calculated using the following formula:

$$\text{Percentage reduction} = \frac{(C_o - C_f)}{C_o} \times 100$$

Where C_o = initial concentration of the MO and C_f = the residual concentration after a given time.

3.5.9.2. *Escherichia coli* (*E. coli*) test

This was done using 3M Petrifilm *Escherichia Coli* (*E. coli*) Count Plate. The bottles containing the water samples were first shaken thoroughly before an aliquot of raw water was drawn from the bottles using Pasteur pipette then carefully poured onto the 3M Test Kits. The kits were then placed in an incubator at a constant temperature of 37.2 °C for 24 hours to enable the *E. coli* colonies to grow. The initial test was done to determine the *E. coli* load in the water samples.

0.08 g of TiO₂ was stirred in 100 ml of the water sample using a magnetic stirrer under solar radiation. An aliquot of the sample was drawn from the beaker then transferred to the 3M test kit at an hourly interval. The kit was then incubated in the same condition as used for the initial test and the results noted.

3.6 Analysis of physico-chemical parameters

All the analyses were done at the Chemistry department, University of Nairobi at an ambient temperature. The analyses of all the physico chemical parameters were done in triplicates. All the analyses were first done prior to filtration to determine the state of the sample then after filtration to check on the efficiency of the filters.

3.6.1 pH Measurement

The pH test was done in the Pesticide Analytical Laboratory, using pH meter model IQ Scientific Instruments, Inc. San Diego, CA, U. S. A. The pH calibration was done with pH 4, 7 and 10 buffers.

3.6.2 Turbidity

Turbidity test was carried out in the laboratory using turbidity meter model LaMotte TC-3000e and recorded.

3.6.3 Total dissolved solids

TDS measurement was done by shaking thoroughly the water samples, and filtering 100 ml of the samples through pre-weighed Whatman filter paper No.1. The filtrate was then transferred into a clean pre-weighed glass beaker and heated in an oven at temperature of 103° C for 24 hours to evaporate the water. The temperature of the oven was then adjusted to 180 ° C for 8 hours. The beaker was removed from the oven, cooled in a desiccator then weighed and the weight recorded. TDS was calculated using the following formula and the result expressed in mg/L;

$$\text{TDS} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{(\text{mass of dry beaker (mg)} + \text{Residue(mg)} - \text{mass of dry beaker (mg)})}{\text{Volume of the sample (L)}}$$

3.6.4 Total suspended solids

100 ml of the water sample was measured, poured into a flat bottomed flask then shaken thoroughly. The 100 ml was then filtered using a pre weighed Whatman filter paper No.1. The residue on the filter was dried to a constant weight in an oven at 105⁰ C, cooled in a desiccator then weighed. TSS was calculated as the weight of the residue per volume of the sample filtered, using the formula shown below and the result was expressed in mg/L.

$$\text{TSS (mg/L)} = \frac{(A)-(B) \times 1000}{\text{Volume of the sample (L)}}$$

Where:

A = weight of filter paper + dried residue (mg).

B = weight of filter paper (mg).

3.7 *E. coli* analysis

This was done using 3M Petrifilm *Escherichia Coli* Count Plate.

Water used for the analysis was collected from Lake Victoria and Chiromo River in 1.0L sterilized glass bottles then taken to the Pesticides Analytical Laboratory for analysis.

An aliquot of water sample was drawn from the bottle using Pasteur pipette and carefully transferred into the 3M test kit. The kit was then put in an incubator at 37.2° C for 24 hours to enable the *E. coli* colonies to grow.

3.8 Heavy metals analysis

3.8.1 Copper Analysis

1 g copper powder was dissolved in 50 ml of 5M HNO₃ analytical grade made to 1litre, with distilled water, to make a concentration of 1000 ppm as a stock solution. From the stock solution, concentrations of 1 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm, 100 ppm and 500 ppm were prepared. The samples were first filtered by the clay filters before being taken for AAS analysis.

Water sample from Lake Victoria was prepared for analysis as follows; 100 ml of the water sample was digested with a mixture of 14M HNO₃ and 10ml of 11.9M HCl in a ratio of 3:1 in a 500 ml digestion flask on a hot plate at 100 °C until the volume was reduced to 30 ml. The samples were allowed to cool, filtered before being taken for AAs analysis.

The prepared solutions were filtered then taken for analysis using atomic absorption spectroscopic machine, model Spectr AA. 10. Labtec. The lamp current used for the analysis was 3 mA, a wavelength of 324 nm and slit width was 0.5 nm. The fuel used on the machine was acetylene and air was the oxidant.

3.8.2 Lead Analysis

1.5980 g of lead nitrate Pb (NO₃)₂ analytical grades was dissolved in 100 ml deionised water then diluted to 1000 ml to obtain 1000 ppm stock solution. The following concentrations were prepared from the stock solution: 1 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm, 100 ppm and 500 ppm. They were then filtered before being taken for AAS analysis.

Water sample from Lake Victoria was prepared for analysis by digesting 100 ml of the water sample using a mixture of 14M HNO₃ and 10ml of 11.9M HCl (3:1) in a 500 ml digestion flask on a hot plate at 100 °C until the volume was reduced to 30ml. The samples were allowed to cool, filtered before being taken for AAs analysis.

The analysis for both copper and lead were done at the Department of Geology and Mines, Ministry of Mining. The machine used was SpectrAA.10. Labtec model and was set at the working condition: Lamp current was 8 mA, wavelength was 217 nm, slit width was 1.0 nm, and the flame used was acetylene while air was the oxidant.

3.9 Pesticide Analysis

To test the effectiveness of photo catalyst coated clay filters against pesticides 0.5 ppm mixture of 16 organo- chlorine pesticides (OCP) were dissolved in 100 ml water. The pesticides mixture was first dissolved in acetone then dissolved in water. The OCP pesticide mixture contained α -HCH, β -HCH, δ -HCH, gamma-HCH, Heptachlor, Aldrin, Heptachlor epoxide, Endosulphan, pp-DDE, Dieldrin, Endrin, pp-DDD, Endrin aldehyde, pp-DDT and methoxychlor was used. Photocatalytic activation was done using solar radiation. 100 ml of the water sample was filtered then taken through pesticide extraction process. Another similar amount of water was used as a control and therefore was not taken through filtration process. 100 ml water spiked with the pesticide mixture, was filtered through each of the moulded clay filters, another 100 ml of spiked water was taken for extraction without being taken through the filtration process for validation purposes. The pesticides were extracted from the filtered water using Solid Phase Extraction procedure. Solid Phase Extraction (SPE) was performed using 1 cm 18' packed super clean cartridges from Superlco Analytical™, U.S.A., with silica between two polyethylene layers. The SPE cartridges were first conditioned with 10 ml 99.7% HPLC grade hexane from Sigma Aldrich Germany, 10 ml 99.7% HPLC grade DCM from RFCL Ltd India and 10 ml 99.7% HPLC grade methanol also from RFCL Ltd, India. This was followed by flushing with 10 ml distilled water. The filtered water samples (spiked and Lake Victoria water) were run through the SPE cartridges and eluted with 30 ml 99.7% HPLC grade hexane from Sigma Aldrich Germany.

The eluate was concentrated to near dryness in rotary evaporator and made to a final volume of approximately 1 ml in iso-octane and then transferred into 20 ml glass vials using Pasteur pipettes. These concentrates were blown down under white spot nitrogen gas to a residual volume approximately 1 ml and transferred into auto sampler vials using Pasteur pipettes ready for GC injections. Actual volumes in the auto sampler vials were determined gravimetrically using mass and density of iso-octane. Analyses of all samples were conducted in splitless mode. VARIAN CP 3800 GC/MS for total ion current (TIC) chromatograph instrument was used for the analyses of the residual concentration of the pesticides with time. The instrument was equipped with a DB5 MS capillary column of dimensions 30M x 0.25 mm x 0.25 μ m and a temperature program with initial temperature of 80 °C for 3 minutes, ramped to 250 °C at 10 °C/ min with a hold time of 23 minutes. High purity helium gas (99.999%) was used as a carrier gas whereas white spot nitrogen was used as a makeup gas. A carrier gas constant flow rate of 1ml/min was maintained throughout all the analyses, whereas the makeup gas was maintained at a constant flow of 30 ml/min.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Soil Characterization

The results of chemical composition by weight of SiO_2 were 57.8 % for the Kenyatta University soil and 56% for Got Ramogi soil (Table 4.1). The percentage weight given as oxides are composed of slightly higher percentage composition of SiO_2 but lower composition of Al_2O_3 in Kenyatta University clay than in Got Ramogi clay (Table 4.1). Kenyatta University clay had percentage weight of 15.37% while that from Got Ramogi had 20.51% Al_2O_3 values. The losses on ignition for the two clays were 10.75% and 9.11% for Kenyatta University and Got Ramogi clays, respectively. The loss on ignition generally entails the removal of water of crystallization and carbonaceous material through the application of heat (Amaakaven *et al*, 2014). Kenyatta University had highest loss on ignition (LOI) value.

Table 4.1: Percentage chemical composition by weight for Kenyatta University and Got Ramogi clay soils.

	Kenyatta University soil	Got Ramogi soil.
Metal oxide	Percentage weight	
SiO ₂	57.8	56
Al ₂ O ₃	15.37	20.51
CaO	1.11	0.36
MgO	1.9	0.18
Na ₂ O	2.34	1.59
K ₂ O	0.49	0.47
MnO	0.1	0.13
Fe ₂ O ₃	7.62	6.19
LOI	10.75	9.11

Marina and Benea (2002) observed that the presence of negative charges in clay particles influence its surface energy. Meanwhile, molecules inside the structure maintain their neutral charge. Practically, when establishing the suitability of clays for filter making, the ceramic mass composition, their chemical composition, their mineralogy, particle size distribution and their correlation with the technological characteristics are important (Marina and Benea, 2002). According to Weitkamp and Puppe (1999), Si in the structure is in oxidation state +4 making the SiO₂ tetrahedra neutral, while the Al₂O₃ tetrahedra are negatively charged because Al has an oxidation state +3, creating a Brönsted acid site due to the resulting charge imbalance in the framework structure, which imparts exchangeable sites to the zeolite structure. Therefore, according to report by Weitkamp and Puppe (1999) chemical composition of the zeolites determines their ion exchange capacity. The specific ion exchange capacity depends on the zeolite structure, the Si/Al ratio and the exchangeable ions (Weitkamp and Puppe, 1999). The Si/Al ratios from Table 4.1, for Kenyatta University and Got Ramogi clays are 3.8 and 2.7, respectively. From these ratios, it was noted that Got Ramogi clay with lower Si/Al ratio of 2.7 has higher ion exchange capacity than the Kenyatta University clay with Si/Al ratio of 3.8 (Weitkamp and Puppe, 1999).

4.1.1 Clay Mixing

Plasticity increases with the reducing portion of sawdust in the mixtures (Table 4. 2).

Table 4.2: Plasticity levels of clay soil to saw dust v: v ratio mixtures used in filter making

Soil.	Sawdust	Level of plasticity
50	50	<< plastic
55	45	< plastic
60	40	> plastic
65	35	>> plastic

The less plastic soils which had soil to sawdust ratios of 50:50 and 55:45 mixtures were not molded due to their lower plasticity and high porosity values.(Table 4.2)

4.2 Clay Filters

During the molding process, filters which had clay to saw dust ratios of 50:50 and 55: 45 could not be molded since the clay in the mixtures had lost their plasticity due to the high percentage of saw dust. Clay filters which had the mixture ratio of 60: 40 and 65: 35 were molded with ease (Table 4. 2).

Table 4.3: Weight and percentage shrinkage of molded clay from Kenyatta University and Got Ramogi

Site	Weight (kg)		Fired weight	% shrinkage	
	wet	dry		before firing	after firing
Kenyatta University	1.67	1.433	1.42	14.2	15
Got Ramogi	1.67	1.495	1.489	10.48	10.78

The weight of each filter made of clay from Kenyatta University was 1.67 kg while wet and 1. 433 kg when dried under a shade for 6 days (Table 4. 3). Weight of each filter made of clay from Got

Ramogi was 1.67 kg while wet and 1.495 kg when dried under a shade for 6 days. Kenyatta University moulded clay had the highest shrinkage before firing 14.2% and 15% after firing filters than Got Ramogi clay which had 10.48% and 10.78%, respectively. The high values of shrinkage lead to the occurrence of hidden fissures (cracks or splits) and decrease of mechanical resistance. The shrinkage and mechanical resistance are correlated with the mineralogical composition (Benea and Gorea, 2002).



Figure 4.1: Kenyatta University unmodified and modified clay filters



Figure 4.2: Got Ramogi unmodified and TiO₂ modified clay filters.

According to Hagan *et al* (2009), drying under shade was meant to remove the excess water which was used to mould the clay. The initial drying enables the filters to hold their shape although they could still get wet when placed in water (Hagan *et al* 2009). Hagan *et al* (2009) reported that firing process removed the excess water while further heating was to remove water which was chemically bonded to the clay's alumina and silica molecules.

4.3 Flow Rates Analysis

This was done on the selected filters 60:40 and 65:35 respectively and results recorded in ml per hour. Filters made from clay soil to saw dust ratios of 65:35 recorded very low flow rates of 30.6 ml hr⁻¹ during the pre-test session and were not included in the further analysis. Filters made from clay soil to saw dust ratios of 60: 40 were used for further analysis. The flow rate results are shown in table 4. 4.

Table 4.4: Flow rates of natural and modified clay filters

Sites and filters nature	Filter labels	Filter flow rate (ml/hr)
Kenyatta University clay filters		
natural filter	KN1	146
	KN2	144
	KN3	142
modified filters	TKN1	144
	TKN2	141
	TKN3	145
Got Ramogi clay filters		
natural clay	GR1	117
	GR2	120
	GR3	116
modified filters	TGR1	114
	TGR2	115
	TGR3	112

According to Kabegambe *et al*, (2011) filters with moderate flow rate are the most suitable for use, since filters which recorded very low flow rates cannot collect enough water for domestic use while those with very high flow rate may not filter all the contaminants. Kabegambe *et al*, (2011) observed that high flow rate is also a sign of micro cracks on the filter. Got Ramogi clay was selected for modification according to Kabegambe *et al*, (2011).

4.4 Testing the photocatalytic effectiveness of titanium (iv) oxide.

4.4.1 Methyl orange degradation.

The initial ultra violet (UV) spectrophotometer absorbance of methyl orange in suspended TiO_2 mixed with water was 0.81, but after successive hourly intervals, the absorbance kept on reducing until we reached 4 hour mark when it was 0.183 (Figure 4.9). At the absorbance of 0.183 the methyl orange (MO) solution was almost colourless meaning that most of the methyl orange in the solution had been degraded by TiO_2 .

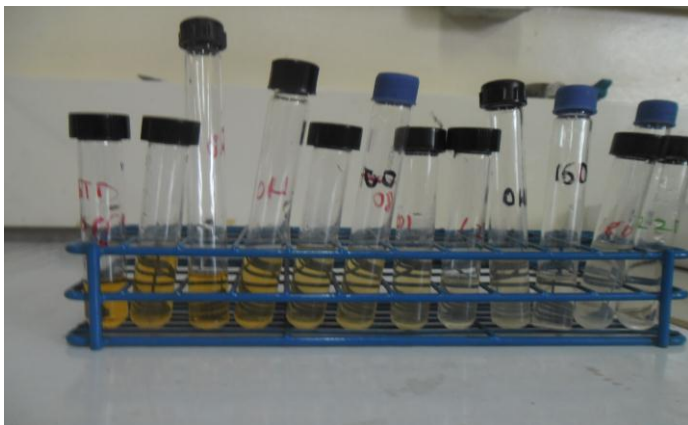


Figure 4. 3: The colour change of methyl orange during degradation process by

TiO_2 photocatalyst.

The detailed mechanism of methyl orange dye catalysed degradation is similar to the one proposed by Hoffman et al (1995) where conduction band electrons (e^-) and valence band holes (h^+) are generated when aqueous TiO_2 suspension is irradiated with light energy greater than its band gap energy which is 3.2 eV. The photo-generated electrons could reduce the dye or react with electron acceptors such as O_2 adsorbed on the TiO_2 surface or dissolved in water reducing it to superoxide radical anion O_2^- . The photo generated holes can oxidize methyl orange molecule to form R^+ or react with either OH^- or H_2O oxidizing them into OH^\bullet radicals. Together with other highly oxidant species (peroxide radicals) they are the ones responsible for the heterogeneous TiO_2 photodecomposition of methyl orange dyes (Hoffman *et al*, 1995).

4.4.1 Determination of the optimum amount of titanium (iv) oxide for reduction of methyl orange dye.

The Photocatalytic effectiveness in the reduction of organic pollutant (methyl orange dye) by TiO_2 was tested, but the optimum amount of titanium (iv) oxide which could degrade greatest percentage of the pollutant was first determined (Table 4.5). Weight of 0.03 g TiO_2 recorded the lowest level of reduction of methyl orange dye (MO). The weight of 0.08 g of titanium (iv) oxide was chosen as the optimum weight for use (Table 4. 5) because it recorded the highest percentage reduction level.

Table 4. 5: The percentage reduction of methyl orange (15 ppm) by varying amounts of titanium (iv) oxide.

Mass of TiO_2 (grams)	% reduction of methyl orange (MO)
0.03	76.67
0.05	87.21
0.08	97.23
0.1	92.88
0.12	82.34

0.08 g of titanium (iv) oxide degraded the largest amount of methyl orange. The results show that the percentage reduction of methyl orange increases as the amount of the photo catalyst is increased until 0.08 g then the amount degraded start decreasing (Table 4.5). Konstantinou and Albanis, (2004) observed that increasing the photocatalyst amount increases the active sites. They also observed that collision of the activated photocatalyst with the inactivated molecules result into the decreased photocatalytic activity. Reduced light penetration and shielding of titanium (iv) oxide by the increased amount of the photocatalyst was also responsible for the reaction rate of the photocatalysts on the methyl orange. The experimental research conducted by Rashed and El Amin (2007) deduced that photocatalytic reactions mostly follow Langmuir-Hinshelwood kinetic rate model, where all the active sites of the photocatalyst are occupied by methyl orange (pollutant) molecules. A further increase in the amount of the photocatalyst may result in decreased rate of reaction and observed rate constant (Konstantinou and Albanis, 2004). Gomes da Silva (2008) added that intermediates generated during the photocatalytic process also affect the rate constant of their parent compounds.

4.4.1 Determination of the optimum concentration and time for methyl orange to be used in the degradation experiment

Figure 4.5, below shows that 15 ppm realised faster degradation rate within 240 minutes than 20 ppm at pH 7.

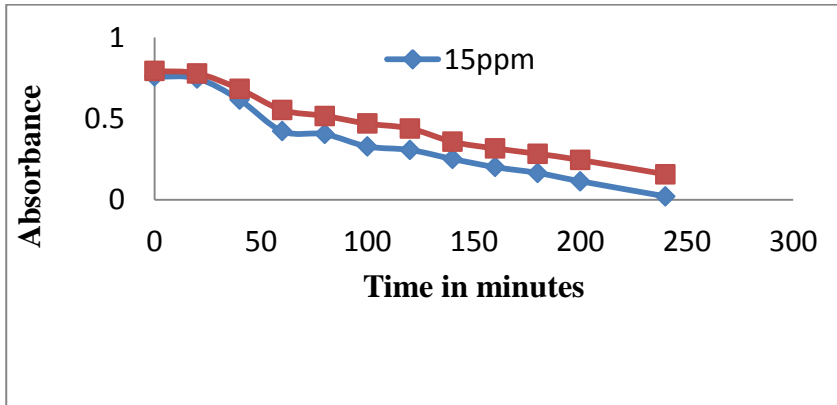


Figure 4.5: Degradation of 15 ppm and 20 ppm methyl orange dye at pH 7

Figure 4.6 below shows that 15 ppm was degraded more at 240 minutes than 20 ppm at pH 3.

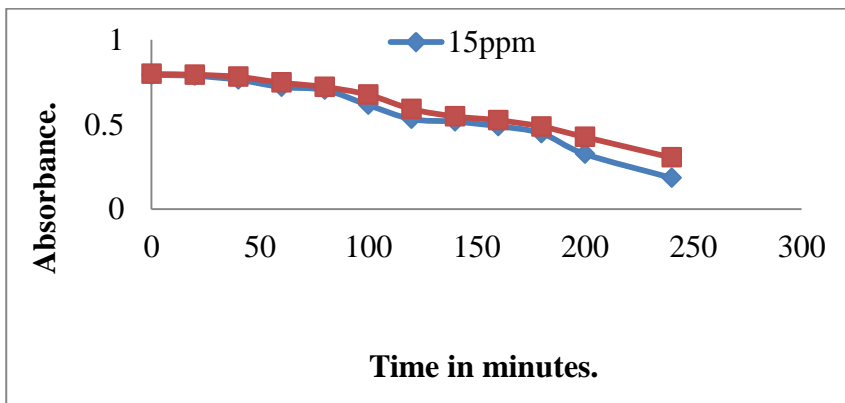


Figure 4.6: Degradation of 15 ppm and 20 ppm methyl orange dye at pH 3

Figures 4.5 and 4.6 show that 15 ppm methyl orange is degraded at 240 minutes at both pH 7 and pH 3, respectively.

4.4.2: Determination of the optimum pH and time of methyl orange use in the degradation experiment.

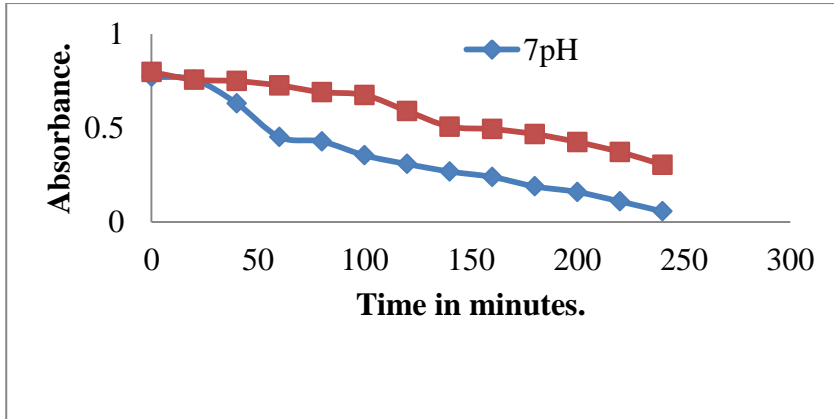


Figure 4.7: Degradation of 20 ppm methyl orange at both pH 7 and pH 3

In Figure 4.7 the concentration of 20 ppm shows the highest degradation at the pH 7 than at pH 3 at 240 minutes

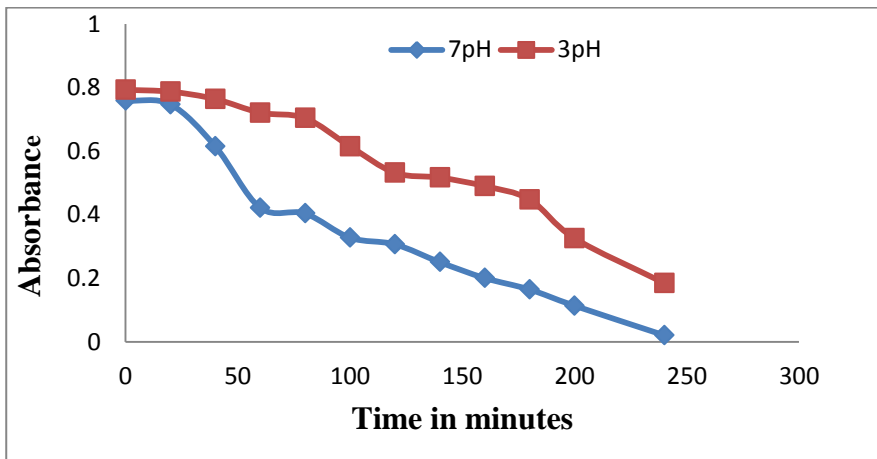


Figure 4.8: Degradation of 15 ppm methyl orange at pH 7 and pH 3

Figure 4.8 indicates that the rate of degradation of 15 ppm MO was highest at pH 7 than the pH 3. Figures 4.7 and 4.8 show that pH 7 is the optimum pH. This is appropriate since the pH 7 falls within the WHO recommended range of between pH 6.5-8.0. (see appendix A)

Working with the samples 15 ppm at pH 7 gave the best degradation results as shown in Figures 4.5, 4.7 and 4.8. Therefore 15 ppm and pH 7 were selected for the degradation process. The optimum methyl orange degradation time was 240 minutes as indicated in figures 4.5 and 4.8.

4.4.3: Determining the optimum time for methyl orange degradation process

Figure 4.9 shows the best degradation values for methyl orange at 15 ppm, at pH 7 in 240 minutes. 1 hour shows the least degradation level followed by 2 and 3 hours while 4 hours is the best degradation time (Figure 4.9). Therefore 15 ppm MO at pH 7 in 4 hours is the optimum concentration, pH and time for methyl orange to be completely degraded from the water sample.

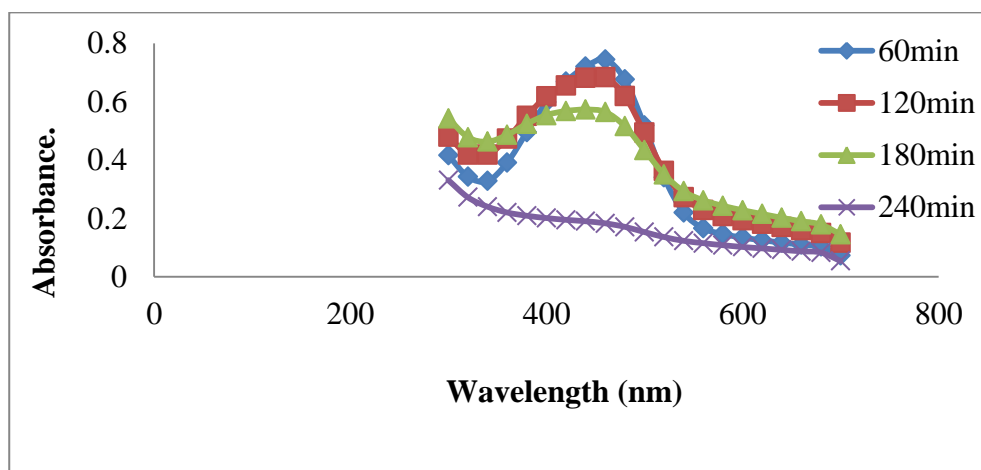


Figure 4.9: Degradation of 15 ppm, pH 7 methyl orange at 60 minutes interval

pH 7 is very appropriate because it fall within the pH range of drinking water and water for household use.

4.5 *E. coli* analysis

The results showing how *E. coli* was deactivated by suspended TiO_2 are as shown in Figure 10. After 3 hours, there were no *E. coli* colonies detected on the 3M test kit.

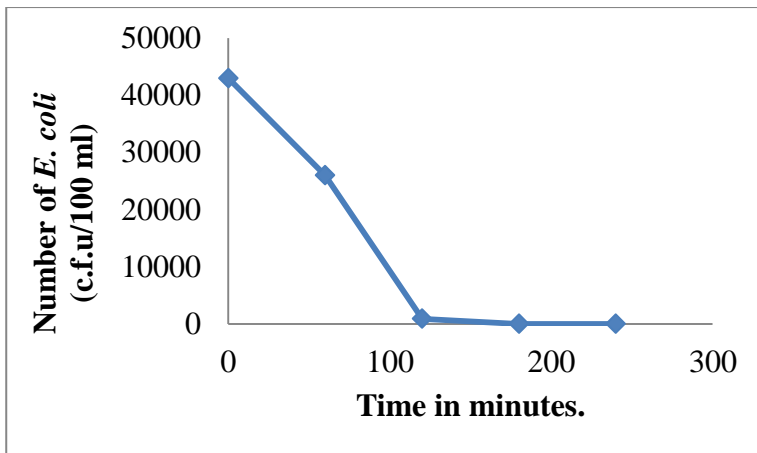


Figure 4.10: Graph showing the reduction of *E. coli* in a suspension of TiO_2

Figure 4.10 shows that suspended TiO_2 is able to completely degrade all the *E. coli* from the water sample at 120 minutes. This shows that the calcined TiO_2 was photo catalytically active.

4.6 Coating the filters with TiO_2

TiO_2 particles were firmly adsorbed onto clay particles in the filters. When water sample was poured into the filters, TiO_2 particles were not dislodged from the clay surface. This ensured that the coated filters could be used for filtration without dislodging TiO_2 particles from the clay surface.

4.7 Levels of the physico- chemical parameters in the filtered water samples

The analytical results for pH, turbidity, total dissolved solids, total suspended solids and *E. coli* in the filtered Nairobi River water sample are shown in the table below. All the filters which were used for the analysis were made using clay to sawdust ratio of 60:40. Filters made using only clay and sawdust are referred to as natural clay filters while those filters which were made using clay, sawdust and TiO_2 are referred to as TiO_2 modified clay filters.

Table 4.6: Levels of physico - chemical parameters in the filtered Nairobi River water samples

Parameter	Unfiltered water	Filters				WHO guidelines
		KN	TKN	GR	TGR	
pH	7.517±0.058	7.517±0.058	7.100±100	7.477±0.015	6.773±0.051	6.5-8.0
Turbidity (NTU)	1.761±0.6629	1.761±0.6629	0.870±0.295	0.395±0.048	0.0212±0.0016	5
TDS (mg/L)	334.222±3.372	334.222±3.372	332.890±0.214	296±5.321	291±8.320	1000
TSS (mg/L)	1.665±0.578	1.665±0.578	1.493±0.578	1.527±0.598	1.00±0.328	Nil
<i>E. coli</i> (c.f.u/100 ml)	Nil	Nil	Nil	Nil	Nil	Nil

Source; WHO, (1996), (See appendix A)

Here KN refers to natural clay filter made using Kenyatta University clay, TKN is the TiO₂ modified Kenyatta University clay filter, GR is the natural Got Ramogi modified clay filter and TGR is the TiO₂ modified clay filter made from the soil from Got Ramogi.

4.7.1 pH

The pH of the water sample from Nairobi River was 7.930 ± 0.058 . pH of the water filtered by natural clay filter (KN) from Kenyatta University was 7.570 ± 0.058 while for the one filtered by the modified clay filters (TKN) from the same region was 7.1 ± 0.100 . Table 4.6 gives a comparison of the reductions of the pH by the four clay filters. Results for the pH of water filtered by Got Ramogi natural clay filter (GR) was pH 7.099 ± 0.009 . Modified clay filter (TGR) from the same region had pH 6.773 ± 0.0511 . The filtration by TGR reduces the pH of water. Table 4.6 shows a reduction of pH by both the GR and KN filters. (pH 7.5 and 7.4, respectively). Table 4.6 show that, TKN and TGR reduced pH better than KN and GR. The reduction of water pH by the

modified clay filter did not alter the water pH value which is within the WHO and KEBS range of 6.5- 8.5 (WHO 1996; KEBS 1996).

The marginal change in pH of the water samples filtered by natural clay filters, KN and GR was occasioned by the presence of H^+ ions in the water sample. The slight increase of H^+ was caused by competition between metallic ions and dissolved salts, for the binding sites on clay structure (Awan *et al*, 2003). There is OH^- on the clay structure surface giving it a negative charge when the dissolved salts get into contact with the clay surface, the cation would be preferred to the H^+ ion. The released H^+ is partly responsible for the reduced pH in water (Kohlmann, 2003).

When it comes to the pH of the water sample which had been filtered by modified clay filters, additional process involving photocatalysis comes into play (Chong *et al*, 2010).

The water molecule split during the photocatalytic reaction, produce OH^- cation and H^+ ions. (Kabra *et al*, 2004). Some of the H^+ produced participates in further reactions producing hydrogen peroxide H_2O_2 and hydroperoxyl HO_2^- radicals while the excess remain in water.

Reduction in the pH (Table 4. 6) in the sample was attributed to the presence of excess H^+ ions in the sample. H^+ ions were generated by splitting of water molecules by the photoinduced TiO_2 to produce OH^- which has scavenging effect (Chong *et al*, 2010).

The pH levels of water filtered by KN, TKN, GR and TGR clay filters fall within the range set by WHO and KEBS for drinking water which is 6.5- 8.5 (WHO 1996; KEBS 1996).

4.7.2 Turbidity.

Viessman Jr and Hammer (1998) described turbidity as caused by the insoluble particles that are present in water. The turbidity of the water sample was 24.667 ± 0.0577 Nephelometric turbidity unit (NTU). After sample was filtered by the natural clay filters, the turbidity reduced to 1.761 ± 0.6629 NTU by natural Kenyatta University clay filters (KN) while those filtered by TiO_2 modified one (TKN) had a turbidity of 0.870 ± 0.295 NTU. The turbidity of water samples filtered by natural clay filters (GR) made from Got Ramogi clay was 0.395 ± 0.0481 NTU and those filtered by TiO_2 modified clay filters (TGR) from the same place was 0.0212 ± 0.0016 NTU (Table 4 6). The analysis result figures are in line with WHO set standard for maximum turbidity level (Appendix A) for domestic water of 5 NTU (WHO 1996). The results show that Got Ramogi modified clay filters have higher turbidity reduction capacity than the Kenyatta University clay filters.

Gelover *et al* (2006) reported that filtration helps in reducing turbidity to below 5 NTU for maximum UV light utilization and photo catalytic reaction. The results in Table 6 indicated that all the filters recorded turbidity of less than 1 NTU which are well below World Health Organisation maximum turbidity level of 5 NTU (Appendix A). High turbidity, according to the observation made by Rincón and Pulgarin (2004), would affect negatively the rate of photocatalytic disinfection. Tang and Chen (2004) noted that turbidity affects the optical properties and reduces the UV light penetration by scattering and absorbing the light rays. Therefore it is necessary to filter water first before subjecting it to photocatalytic treatment.

4.7.3 Total dissolved solids (TDS)

TDS in water include soluble salts that yield ions such as sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), or chloride (Cl^-) (Crittenden *et al*, 1996). The total dissolved solids in the water sample were 344 ± 8.7178 mg/L.

The total dissolved solids (TDS) in water filtered using natural clay filters from Kenyatta University were 332.889 ± 3.372 mg/L (Table 4. 6). Water samples filtered by modified clay filters, had the total dissolved solids of 330.889 ± 3.372 mg/L. The total dissolved solids in the water filtered using natural Got Ramogi clay was 296 ± 5.321 mg/L modified clay filters from Got Ramogi had TDS of 291 ± 8.320 mg/L. The results show clearly that, Got Ramogi natural and modified clay filters had higher potential to reduce TDS than the Kenyatta University clay filters for water samples.

4.7.4 Total Suspended Solids (TSS)

TSS in the unfiltered water sample was 276 ± 14.730 mg/L. The total suspended solids in the water sample filtered by natural Kenyatta University clay filter were 1.667 ± 0.578 mg/L (Table 4.6). TSS in the water filtered by the modified clay filters from the same region was 1.493 ± 0.598 mg/L. Total suspended solid in the water sample filtered by Got Ramogi natural clay filter was 1.527 ± 0.33 mg/L, while modified clay filters from the same region had TSS of 1.00 ± 0.328 mg/L. Results shown in Table 4.6, show that Got Ramogi modified clay (TGR) has better sample filtration for the TSS than the other three filters.

The analysis done showed a slight variation in the amount of suspended solids removed by natural clay and TiO_2 modified clay. Chong (2010) had observed that suspended solids shield target pollutants from oxidation reactions, as a result lower the efficiency of the photocatalyst. It is therefore advisable that the water intended for photocatalytic treatment be filtered first.

The analysis done showed that there was slight variation in the amount of suspended solids removed by natural clay and TiO_2 modified clay. The suspended solids in this case, refer to the

non-filterable residue that is retained on the filter medium after filtration. These residues lower the efficiency of the photocatalyst. It is therefore advisable that the water intended for photocatalytic treatment be filtered first.

4.7.5 *E. coli* Analysis

The *E. coli* colonies in the water sample which was initially recorded at 4310.83 ± 15.718 Colony forming units (c.f.u/100 ml) were reduced to 0.0 c.f.u/100 ml after filtration by all the three sets of filters. Table 4.6 show the colonies of the water sample after filtration. Dark blue dots were not observed on the 3M test kit and this was an indication that the filtered water was *E. coli* free.

The results for all the filters showed no *E. coli* colonies in the filtered water meaning that clay filtration was effective (Table 4.6). However when an aliquot of the residues was removed from each of the filters and transferred to 3M petrifilm test kit then incubated, *E. coli* colonies developed on the test kit with samples from natural clay filters (KN and GR) while samples from modified filters (TKN and TGR) had no *E. coli* colonies. This showed that *E. coli* were not only filtered out by the modified filters but were also destroyed. Huang *et al.* (2000) illustrated that TiO₂ photocatalysis caused initial oxidative damage to the *E. coli* cell wall, although the cells were still viable. Wei *et al* (1994) added that photocatalytic action gradually increased the cell permeability by eliminating the protective cell wall of the *E. coli* and the damage on the underlying cytoplasmic membrane. In addition, if free TiO₂ particles entered into membrane-damaged cells, cell death could be accelerated. Cho *et al* (2004) concluded that the ·OH radicals produced during the heterogeneous photocatalysis is the main reactive species responsible for *E. coli* elimination.

4.7.6 Heavy Metal Analysis

Results of copper and lead analysis in the water samples filtered by KN, TKN, GR and TGR filters are shown in table 4.7. The calibration curves that were used to determine the residual concentrations of lead and copper in the filtered water samples are found in appendix B. Results from the table show that filter KN removes copper and lead from concentrations in the range of 1 ppm- 50 ppm to undetectable level. TKN and GR filters were able to reduce copper and lead from concentrations range of 1ppm- 100 ppm down the level that could not be detected by the AAS. Filters TGR reduced the metals concentrations of up to 1000 ppm to below detectable levels in the water samples. Filters KN and GR are natural clay filters while filters TKN and TGR are TiO₂ modified filters.

4.7.6.1 Copper analysis

Table 4.7: Levels of copper in the filtered water samples from natural and modified clay filters`

	Concentration of copper in the filtered water.			
Concentration in ppm	KN	TKN	GR	TGR
1	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	BDL
10	BDL	BDL	BDL	BDL
20	BDL	BDL	BDL	BDL
50	0.0116±0.0029	BDL	BDL	BDL
100	0.0200±0.0000	BDL	BDL	BDL
500	0.4367±0.0208	0.233±0.0306	0.2317±0.0198	BDL
1000	0.8867±0.0451	0.430±0.01	0.3527±0.0146	BDL

*BDL- below detection limit.

Detection limit was set at the hundred thousandth place value.

From Tables 4.7 and 8, KN clay filter was not able to filter samples with ≥ 50 ppm (0.023% Cu) while TKN and GR did not filter ≥ 500 ppm (0.046%) of copper. There was no amount of copper detected in the filtration of ≤ 1000 ppm of copper sample using the modified clay filter TGR. Modified Got Ramogi clay (TGR) gave the best filtration levels for copper and lead concentrations.

4.7.6.2 Lead analysis

Table 4.8: Levels of Lead in the filtered water samples from natural and modified clay filters

Concentration in ppm	Concentration of lead in the filtered water			
	KN	TKN	GR	TGR
1	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	BDL
10	BDL	BDL	BDL	BDL
20	BDL	BDL	BDL	BDL
50	0.0110±0.0017	BDL	BDL	BDL
100	0.0233±0.0025	BDL	BDL	BDL
500	0.394±0.0309	0.3135±0.0153	0.3667±0.0208	BDL
1000	0.9356±0.0222	0.3533±0.0153	0.3667±0.0208	BDL

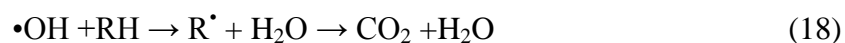
*BDL- below detection limit

Chemical analysis done on the soil indicated that SiO₂ and Al₂O₃ form a large proportion of the chemicals found in the soil (Table 4.1). Heavy metals are mainly removed from water by ion exchange and chemisorption (Mozgawa and Bajda, 2005). Godelitsa (1999) reported the formation of stable inner complexes because the OH⁻, which is the functional group, forms strong chemical bonds with metal ions outside the hydration envelopes of the metal. Elevated concentrations (≥50 ppm) of heavy metals in water were not totally removed by natural clay filters. This is probably due to the fact that the natural clay filter had attained its absorptive saturation level, (Mozgawa and Bajda, 2005). Murray (1994) reported that it is the functional groups which provide chemisorption surface sites for transition and heavy metals. The specific ion exchange capacity depends on the structure of the clays, the Si/Al ratio and the ions to be exchanged (Weitkamp and Puppe, 1999). Dean and Robins (1947) reported that the presence of Al₂O₃ in the soil leads to

rapid adsorption of heavy metals from water. Dean and Robins (1947) wrote that the hydroxyl groups on clay surface dissociate in water serving as Lewis bases towards metal cation. The deprotonated sites, according to Murray (1994) report, forms complexes with the heavy metal ions.

Abd-Allah *et al* (2007) reported that the excellent adsorption capacity of clay is due to its large surface area and its ability to hold water in the clay interlayer sites. Dean and Rubins (1947) reported that the Al-OH groups at the crystal edges are the ones responsible for the quick adsorption of ions from water. This explains the higher efficiency that Got Ramogi clay filter displayed over Kenyatta University clay filter.

Heavy metals removal from water using modified clay filters is explained by the mechanism which was proposed by Chen and Ray (2001) and Serpone and Pelizzetti (1989). Solar illumination on TiO₂ leads to the production of electron and electron holes which can either recombine to produce heat, or can be used to reduce or oxidize species in solution at the TiO₂ surface as indicated by equations (15 – 19).



In equations (15) to (19), M is the metal ions; R represents an organic pollutant or dissolved organic matter and *n* is an integer (Serpone and Pelizzetti, 1989). From the mechanisms and the available literature, it is clear that TiO₂ offers additional adsorption and chemisorption sites to the heavy metals on top of those on the clay structure.

Studies conducted by researchers such as Salim *et al* (1992), Cheung *et al* (2000), Sen *et al* (2002), Khilar *et al* (2006) and Gurses *et al* (2006) show that adsorption at the solid / liquid interface depends on the system pH, the initial concentration of the metal, amount of the adsorbent and the temperature.

4.7.7 Pesticides

The analytes were first calibrated and the calibration curves which were used to calculate the residual concentration of the pesticides are contained in appendix D.

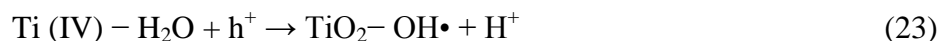
Table 4.9: Organochlorine pesticide residue levels in filtered water sample.

Pesticides	Concentrations in ng/L (validation results)	Pesticides residue levels in water sample filtered by TGR filters
α -HCH	91.2048	BDL
β -HCH	910.5147	BDL
δ -HCH	2512.479	BDL
Heptachlor	1098.245	BDL
Aldrin	657.2004	BDL
Heptachlor epoxide	531.139	BDL
Endosulphan 1	475.7729	BDL
PP-DDE	559.5298	BDL
Dieldrin	350.0299	BDL
Endrin	284.5042	BDL
PP-DDD	247.501	BDL
Endosulphan 2	269.896	BDL
Endrin aldehyde	366.2792	BDL
PP-DDT	451.2727	BDL
Endosulphan sulphate	BDL	BDL
Methoxychlor	60.47903	BDL

Table 4.9 shows the results of a mixture of 16 organochlorine pesticides (OCP) levels in water samples filtered by TGR filter. TGR filter is able to filter completely all the 15 OCP except Delta-HCH (Table 4.9).

Mills and LeHunte (1997) reported that oxidation processes of the organic pollutants, by the generated reactive hydroxyl radicals ($\cdot\text{OH}$) using UV/TiO₂ and UV/H₂O₂ methods, can lead to degradation or mineralization of most pesticide contaminants.

Sepone and Pelizzetti (1989) reported that the electrons could either react with the organic substrate or react with adsorbed O₂ on the TiO₂-surface or dissolved in water, to form superoxide radical anions O₂^{•-}. Konstantinou *et al* (2002) reported that the created electron holes can either oxidise the organic molecule directly, or react with the OH⁻ ions and the H₂O molecules adsorbed at the TiO₂ surface, to form OH[•] radicals which together with other highly reactive oxidant species (peroxide radicals) are reported to be responsible for the heterogeneous TiO₂ photodecomposition of organic substrates (Sepone and Pelizzetti, 1989; Bahnemann *et al*, 1994). The reaction mechanism at semiconductor surface causing the degradation of pesticides, which was proposed by Hoffman *et al* (1995), can be expressed as follows:



The OH[•] radical formed is a very strong oxidizing agent which can oxidize most of organic pesticides to the mineral end products. Substrates which are not reactive to hydroxyl radicals are degraded by TiO₂ photo catalysis whose rates of decay are highly influenced by the semiconductor valence band edge position (Viona *et al*, 1999).

4.8 Results for the analysis of the water sample from Lake Victoria

Analysis of all the samples collected at Usenge beach lake water were done using modified clay filters which were made using clay from Got Ramogi (TGR). TGR clay filter was chosen because all the previous laboratory analysis showed that it has superior ability in removing pollutants from water compared to TiO₂ modified clay filter made using clay soil from Kenyatta University (Tables 4.6, 4.7 and 4.8).

The results for the physico-chemical analysis done on the water samples collected from Lake Victoria are contained in table 4.10.

Table 4.10: The selected physico-chemical parameters and heavy metals in the filtered water from Lake Victoria.

Parameter	Unfiltered water	Filtered water	WHO Values
pH	7.890±0.057	7.44±0.009	6.5-8.0
Turbidity (NTU)	14.067±0.115	0.379±0.031	5
TDS (mg/L)	122±14.574	116.876±6.00	1000
TSS (mg/L)	55.00±1.528	0.052±0.002	Nil
E. Coli (c.f.u/100ml)	2686.667±30.55	Nil	Nil
Copper (mg/L)	0.015±0.007	BDL	2
Lead (mg/L)	0.018±0.0113	BDL	0.01

Analysis done on the water sample collected from the same site had the following levels of organochlorine pesticides;

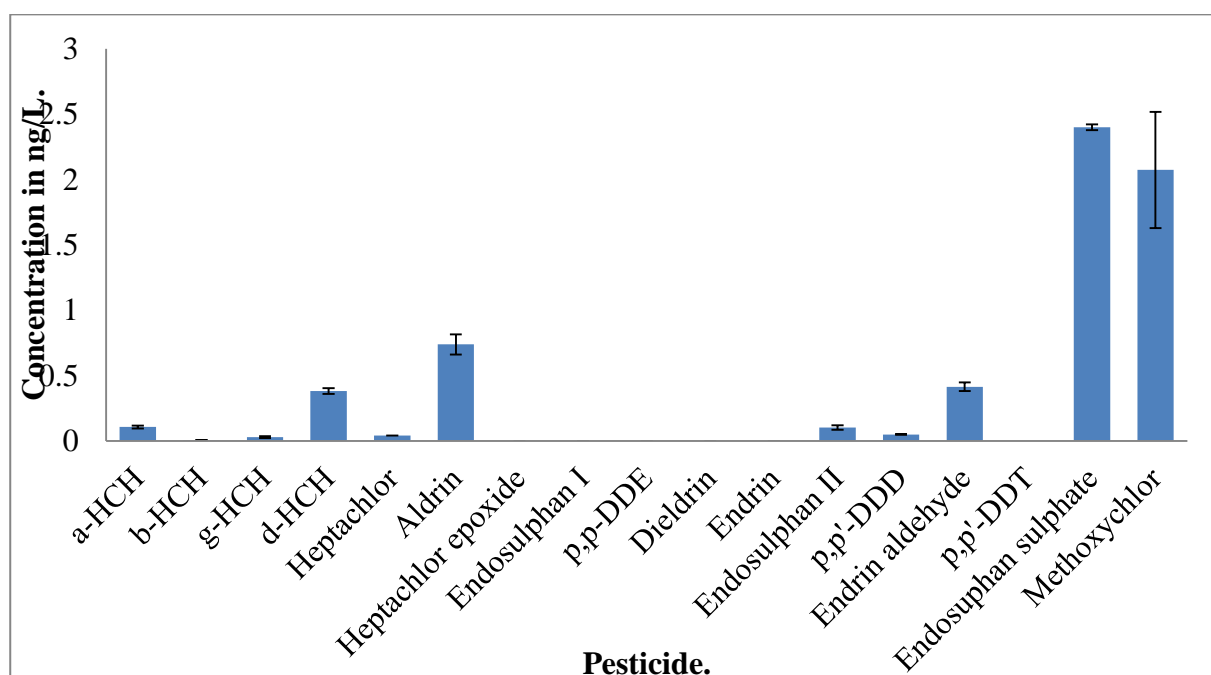


Figure 4.11: Organochlorine pesticide residue levels in Lake Victoria water samples.

When the water sample was filtered using TiO₂ modified clay filter pH was reduced to 7.44 ± 0.009, turbidity 0.379 ± 0.031 NTU, TDS 116.876 ± 600 mg/L and TSS 0.052 ± 0.002 mg/L. No *E. coli* colonies were detected (Table 4.10). Copper and lead were also not detected in the filtered

water sample (Table 4.10). All the OCP residues were not detected in the water which had been filtered by TiO₂ modified clay filters. The reaction mechanism in each of the analyzed parameters follow similar pathway to the ones analyzed in the spiked laboratory and Nairobi River water samples. The results of the analysis done on the filtered water samples from the laboratory, Nairobi River and Lake Victoria showed that modified clay filters are improved version of natural clay filters and are very effective in removing organochlorine pesticides from water.

4.9 DISCUSSION

Results from the experiment done on the degradation of methyl orange using suspended TiO₂ showed steady decrease in absorbance levels. These together with the discoloration of the methyl orange solution were clear indication of methyl orange degradation by the photocatalyst. The experimental of physico-chemical parameters showed that. All the four filters did not effectively reduce dissolved solids from the water samples, as shown in Table 4.6. The results also indicate that clay filters whether natural or modified cannot be used to effectively remove dissolved solids from water.

Results of the analysis done on the water samples which had been filtered by each of the filters showed a reduction of the total suspended solids from 276 mg/L to below 2 mg / l. Water filtered by natural Kenyatta University clay filter contained TSS of 1.665 ± 0.577 mg/l while the modified one left the filtered water having 1.493 ± 0.598 mg/l total suspended solids. Water filtered by natural Got Ramogi clay filter contained 1.527 ± 0.33 mg/L TSS while modified Got Ramogi clay filter filtered water which contained 1.00 ± 0.328 mg /L. Results given above clearly show an improved efficiency in water filtration and purification by the filter modification with TiO₂ . Results of the analysis done on the filtered Lake Victoria water sample show marginal reduction of pH and TDS, while TSS and turbidity were reduced to 0.052 ± 0.002 mg/L and 0.379 ± 0.031 NTU respectively. These figures compare favorably with WHO guidelines (Appendix A) which placed the recommended levels of PH, TDS, TSS and turbidity at 6.5-8.0, 1000 mg/l, nil, 5NTU respectively. The analysis results above show the effectiveness of TiO₂ modified clay in purifying water.

Tests done on water samples, which were filtered by natural clay filters showed 100% removal of the *E. coli* (Table 4.6). The same result was also realized when similar test was conducted on water samples which had been filtered by modified clay filters. Earlier tests in this study on *E. coli* using suspended TiO₂ showed that *E. coli* was completely destroyed in three hours (Figure 4.10). Tests done on the water sample collected from Lake Victoria when filtered by TiO₂ modified clay

indicated that there were no *E. coli* colonies detected (Table 4.6). This result is also in line with the WHO guidelines of nil *E. coli* colonies in both domestic and drinking water.

Tables 4.7 and 4.8 show how natural and modified clay filters were able to reduce heavy metal concentration in water. Natural clay filters from Kenyatta University were able to reduce copper and lead concentrations of between 1 ppm and 20 ppm to below detection level after filtration, while 50 ppm, 100 ppm, 500 ppm and 1000 ppm were reduced by 99.95% for copper and lead (Table 4.7). The modified Kenyatta University clay filters reduced 500 ppm and 1000 ppm copper in the filtered water sample by 99.95% and the same concentration of lead by 99.94%, while concentration of 100 ppm down to 5 ppm could not be detected in the filtered water by the AAS machine.

Interestingly, natural clay filters made using natural Got Ramogi clay reduced both copper and lead in the water samples which had up to 100 ppm initial concentration to a level which could not be detected by AAS. The same clay filters reduced 500 ppm and 1000 ppm copper and lead concentrations in the water samples by 99.95%. The analysis results proved that modified clay filters are capable of removing heavy metals from water. This confirms that modification of clay filters greatly improve their efficiency. The modified clay filter which was used to filter water sample from Lake Victoria reduced copper and lead concentrations to below detection level. WHO placed the minimum concentration of copper and lead in drinking water for household use to 2 mg/L and 0.01 mg/L respectively (Appendix A). This is an indication that modified clay filter can effectively be used to remove lead and copper from water collected from the lake for domestic use.

When water samples were spiked with a mixture of 16 organo-chlorine pesticides (OCP) then filtered using TiO₂ modified filters from Got Ramogi the results indicated that only 390 ng/L of δ-HCH were detected while the rest of the pesticides were reduced to below detection level of the GC/MS machine. The analysis results obtained proved that TiO₂ coated clay filters can be used to reduce the concentration of the organo-chlorine pesticides from water. Analysis done to determine the level of OCPs in the filtered Lake Victoria water showed that all the pesticides, which were earlier on detected, had been effectively removed by the modified clay filter. These results of the analysis done on pesticides showed that TiO₂ modified clay filters reduced the levels to below the ones recommended by WHO shown in appendix A. These results strongly affirm the effectiveness of the TiO₂ modified clay filter in removing OCP pesticides from water.

Results from the experimental analysis of the water quality parameters show that there is synergy between natural clay and the modified clay filters. Coating clay filter with titanium dioxide improves its performance in filtering water.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The chemical analysis done on clay soils revealed that Got Ramogi clay had the lowest SiO₂/Al₂O₃ ratio of 2.7 compared to that from Kenyatta University clay of 3.8. Analysis done on both filters clearly showed superiority of Got Ramogi clay over Kenyatta University clay in removing pollutants from water, making it the most suitable soil to be used in filter making.

Results of the experiment done to degrade methyl orange showed that TiO₂ can be used to remove methyl orange from any of water, whether domestic or waste water.

Results of the experiment done on both natural and TiO₂ modified clay filters showed that modified clay filter was more efficient in removing pollutants from water than natural clay filter.

According to the data obtained from the analysis results, filters were able to reduce pH in the water sample to levels which are within the WHO guidelines which is in the range of 6.5-8.0. Turbidity of the water samples were reduced from 24.667±0.0577 NTU to below the 5 NTU set by the WHO and KEBS (Appendix A). Modified filters also reduced total suspended solids from 276 mg/L ± 14.730 mg/l to 1.000 ± 0.328 mg/l even though the level is slightly above the WHO guidelines that require no suspended solids in drinking water.

Both natural and modified clay filters effectively removed *E. coli* from the water samples. However, whereas natural clay filters simply removed *E. coli* from the water then retaining them in the filters, TiO₂ modified clay filters remove them from water then destroy them through photo degradation process.

Analysis done on heavy metals proved that TiO₂ modified clay filters could effectively remove up to 1000 ppm of lead and copper from water. Since most domestic water contains much lower concentrations, clay filter filtration may provide cheap and efficient means of removing heavy metals from water.

Modified clay filters managed to degrade all the organochlorine pesticides that were spiked in the laboratory water sample except for delta-HCH which still had 390±108.5 ng/L. No pesticide

residues were detected in the filtered Lake Victoria water sample. The result show that modified clay filters can be used to remove organochlorine pesticides from domestic water.

Results from the analysis done on all parameters show that modifying clay filter with Titanium (iv) Oxide improves its efficiency in removing pollutants from water and in the process water quality is also improved. Therefore there is a synergy between natural and TiO_2 modified clay filters.

The study done on water sample from Lake Victoria using TiO_2 modified clay filters showed that the filters can be used as cheap means of purifying house hold water.

5.2 Recommendations

More research on water purification need to be done using composite of titanium (iv) oxide modified clay to assess whether doping can improve the efficiency and degradation time of the photocatalyst in purifying water. Here dopants such as chromium, iron and nitrogen should be adopted for the study.

There is need to use both natural and titanium (iv) oxide modified clay filters from Got Ramogi on water samples from pans, ponds and rivers in Bondo district to determine whether they could be used as point of use purifier for all household waters.

Research should be done to determine whether TiO_2 modified filters could be used to remove viruses, fungi and polychlorinated benzene (PCB) from water.

There is need to explore possibility of adoption of TiO_2 modified clay filters with respect to a suitable design for large scale application.

There is need to study impact of TiO_2 particles by including their analysis in filtered water as a control.

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APPENDIX

Appendix A: WHO 1996 GUIDELINES FOR DRINKING WATER QUALITY

Parameters	Guidelines
Selected soil properties	Values
Suspended matter	Nil
pH	6.5-8.0
TDS	1000 mg/L
Turbidity	5 NTU
Level of heavy metals	mg/l
Arsenic	0.01
Boron	0.5
Cadmium	0.003
Chromium	0.05
Copper	2
Lead	0.01
Manganese	0.5
Mercury	0.001
Molybdenum	0.07
Nickel	0.02
Selenium	0.01
Uranium	0.002
E. Coli	CFU/100 ml
<i>E. coli</i> or thermoresistant coliform bacteria.	Must not be detectable in any 100 ml sample.
Organochlorine pesticides	ng/L
Aldrin/Dieldrin	0.08
Chlordane	0.2
DDT	2
Heptachlor and Heptachlor epoxide	0.03
Hexachlorobenzene	1
Lindane	2
Methoxychlor	20

Appendix B: Calibration graphs of heavy metals.

1. Calibration graph for copper.

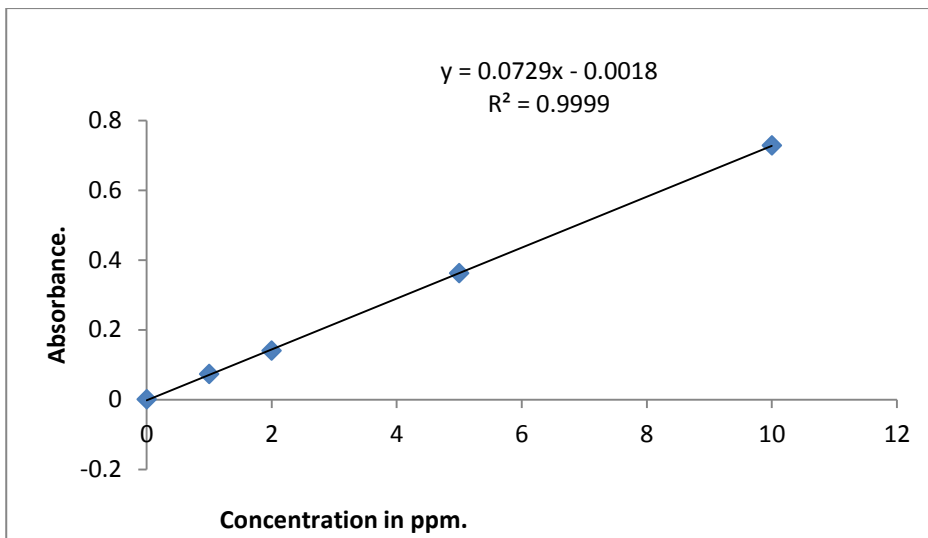


Figure B1: Calibration graph for copper ions in water.

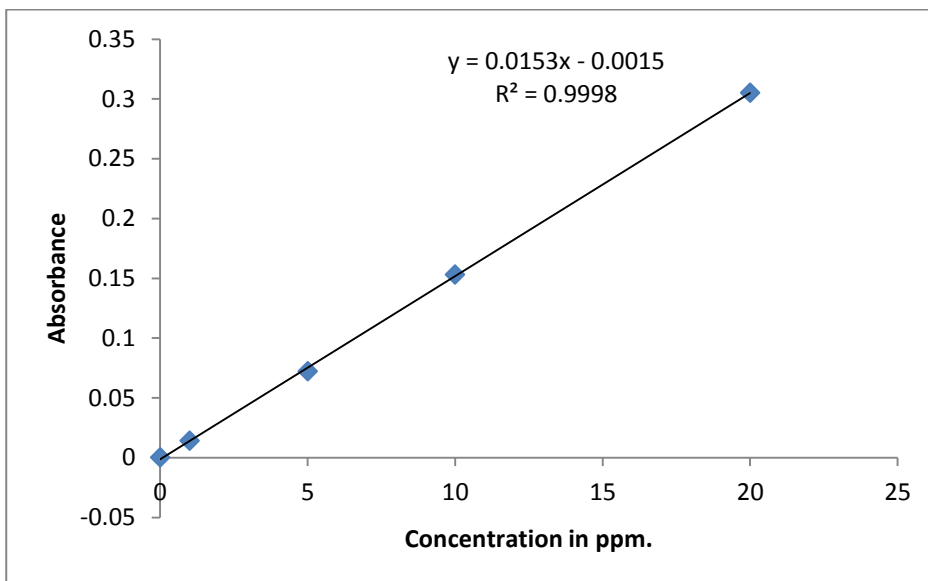


Figure B2: Calibration graph for lead ions in water.

APPENDIX C: OCP chromatographs.

Title : ECD TEST RUN
 Run File : c:\star\data\3800.44150.run
 Method File : c:\star\pops\pops nitrogen method 29sept 2013.mth
 Sample ID : Manual Sample

Injection Date: 10/3/2013 4:11 PM Calculation Date: 10/18/2013 7:42 PM

Operator : x Detector Type: 3800 (10 Volts)
 Workstation: Bus Address : 44
 Instrument : Varian Star #1 Sample Rate : 10.00 Hz
 Channel : Front = ECD Run Time : 36.963 min

** Star Chromatography Workstation Version 5.3 ** 00379-7520-4C1-0191 **

Run Mode : Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent

Peak No.	Peak Name	Result (ng/ml)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.1111	10.544	0.000	28073	BB	0.0	
2	alpha HCH	8.9892	10.681	-0.020	2270413	BB	2.9	
3		0.0421	10.800	0.000	10621	BB	0.0	
4		0.0869	10.860	0.000	21949	BB	0.0	
5		0.6538	10.916	0.000	165138	BB	0.0	
6		0.2521	10.995	0.000	63675	BB	0.0	
7		0.0911	11.054	0.000	23010	BB	0.0	
8	gama HCH	10.6941	11.188	-0.028	2701019	BB	2.9	
9		0.0626	11.513	0.000	15809	BB	1.4	
10		0.4361	11.601	0.000	110139	VB	0.0	
11	beta HCH	14.5698	11.986	0.134	3679908	BB	2.1	
12		0.0395	12.192	0.000	9970	BB	3.7	
13		0.0057	12.321	0.000	1441	BB	0.0	
14	delta HCH	6.3450	12.379	-0.002	1602571	BB	1.9	
15		0.3823	12.490	0.000	96550	VB	0.0	
16		0.1734	13.129	0.000	43796	BB	0.0	
17	Heptachlor	8.3305	13.249	-0.004	2104041	BB	2.3	
18		0.0238	13.354	0.000	6017	VB	0.0	
19	isodrin	0.0204	14.153	-0.008	5161	BB	0.0	
20	Aldrin	6.5830	14.358	-0.003	1662675	BB	2.6	
21	Heptachlor e	5.3796	15.725	-0.005	1358717	BB	3.2	
22		0.0047	15.849	0.000	1178	BB	0.0	
23	Endosulphan	5.4702	16.218	-0.020	1381612	BB	3.8	
24		1.1057	16.550	0.000	279268	BB	3.4	
25	pp-DDE	6.5362	16.881	-0.002	1650841	BB	3.7	
26	Dieldrin	4.1260	18.029	-0.003	1042118	BB	4.3	
27	Endrin	3.4990	18.513	-0.034	883749	VV	5.2	
28	Endosulphan	4.2366	18.713	-0.006	1070038	VB	3.8	
29		0.0040	18.874	0.000	1013	VB	0.0	
30		0.0052	19.087	0.000	1309	BB	0.0	
31		0.0060	19.099	0.000	1517	BB	0.0	
32		0.0043	19.237	0.000	1087	BB	0.0	
33	pp-DDD	1.9188	19.378	-0.007	484620	BB	4.8	
34		0.0049	19.844	0.000	1249	BB	0.0	
35		0.0050	19.896	0.000	1255	BB	0.0	
36	Endrin aldeh	2.5628	20.053	-0.011	647284	BB	3.8	
37	pp-DDT	2.9054	20.323	-0.007	733808	BB	3.9	
38		0.0045	20.489	0.000	1136	BB	0.0	
39		0.0049	20.746	0.000	1232	BB	0.0	
40	Methoxychlor	0.7576	22.089	-0.012	191342	BB	7.1	
41		0.3039	22.259	0.000	76744	BB	0.0	
42		0.0062	26.301	0.000	1558	VV	0.0	
43		0.0045	26.342	0.000	1149	VV	0.0	
44		0.0054	26.385	0.000	1363	PV	0.0	
45		0.0051	26.414	0.000	1288	VV	0.0	
46		0.0093	26.465	0.000	2350	VV	0.0	
47		0.0093	26.559	0.000	2353	VV	0.0	
48		0.0057	26.630	0.000	1433	VB	0.0	
49		0.0040	26.691	0.000	1012	BV	0.7	

Print Date: Fri Oct 18 19:37:19 2013

Page 1 of 2 91

Title : ECD TEST RUN
Run File : c:\star\data\3800.44160.run
Method File : c:\star\pops\pops nitrogen method 29sept 2013.mth
Sample ID : Manual Sample

Injection Date: 10/4/2013 11:50 AM Calculation Date: 10/18/2013 7:37 PM

Operator : x Detector Type: 3800 (10 Volts)
Workstation: Bus Address : 44
Instrument : Varian Star #1 Sample Rate : 10.00 Hz
Channel : Front = ECD Run Time : 24.975 min

** Star Chromatography Workstation Version 5.3 ** 00379-7520-4C1-0191 **

Run Mode : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent

Peak No.	Peak Name	Result (ng/ml)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		8.2159	10.589	0.000	208183	VB	0.0	
2	alpha HCH	0.6092	10.773	0.072	15436	VB	0.0	
3		8.7795	10.905	0.000	222465	BB	0.0	
4		16.5816	10.974	0.000	420164	VB	0.0	
5		3.8691	11.612	0.000	98040	BB	1.2	
6	beta HCH	28.4805	11.954	0.102	721673	BB	2.0	
7		10.1251	12.240	0.000	256562	BB	5.2	
8	delta HCH	0.1628	12.399	0.018	4124	BB	0.0	
9		0.5741	12.493	0.000	14547	BB	0.0	
10		0.0968	12.512	0.000	2454	BB	0.0	
11		0.0602	12.538	0.000	1526	BB	0.0	
12		0.3886	13.065	0.000	9846	BB	0.0	
13		0.0474	13.242	0.000	1201	BB	0.0	
14	Heptachlor	0.0508	13.259	0.006	1288	BB	0.0	
15		0.0975	13.343	0.000	2471	BB	0.0	
16		0.0554	13.428	0.000	1403	BB	0.0	
17		0.1777	13.957	0.000	4502	BB	13.1	
18	isodrin	0.0625	14.111	-0.050	1583	BB	0.0	
19	Aldrin	0.0611	14.335	-0.026	1549	BB	2.0	
20		0.2156	14.422	0.000	5463	BB	1.9	
21		0.1523	14.582	0.000	3860	BB	0.0	
22		0.0428	14.602	0.000	1085	BB	0.0	
23		0.0550	15.543	0.000	1394	VE	0.0	
24	Heptachlor e	1.2344	15.656	-0.074	31279	VE	0.0	
25		1.0229	15.844	0.000	25920	BB	0.0	
26		0.0429	15.861	0.000	1086	BB	0.0	
27		0.0584	15.955	0.000	1481	BB	0.0	
28	Endosulphan	1.0983	16.180	-0.058	27831	BB	0.0	
29		0.0436	16.315	0.000	1105	BB	0.0	
30		0.0440	16.528	0.000	1114	BB	0.0	
31		0.0455	16.567	0.000	1152	BB	0.0	
32		0.0519	16.861	0.000	1315	BB	0.0	
33	pp-DDE	0.0469	16.886	0.003	1189	BB	0.0	
34		0.0588	17.094	0.000	1489	BB	0.0	
35		0.0483	17.889	0.000	1225	BB	0.0	
36	Dieldrin	0.0396	17.910	-0.122	1004	BB	0.0	
37		0.0405	18.155	0.000	1027	BB	0.0	
38		0.0510	18.184	0.000	1293	BB	0.0	
39		0.0961	18.320	0.000	2436	VV	0.0	
40		0.0780	18.326	0.000	1976	VV	0.0	
41		0.1562	18.342	0.000	3959	VV	0.0	
42		0.1802	18.355	0.000	4566	VV	0.0	
43		0.4965	18.379	0.000	12580	VV	0.0	
44		0.3528	18.406	0.000	8940	VV	0.0	
45		0.1566	18.416	0.000	3968	VV	0.0	
46		0.8459	18.440	0.000	21434	VV	0.0	
47		0.5499	18.461	0.000	13934	VV	0.0	
48		0.7261	18.477	0.000	18400	VV	0.0	
49		1.0171	18.491	0.000	25772	VV	0.0	

63

Title : ECD TEST RUN
 Run File : c:\star\data\3800.44149.run
 Method File : c:\star\pops\pops nitrogen method 29sept 2013.mth
 Sample ID : Manual Sample

Injection Date: 10/3/2013 11:42 AM Calculation Date: 10/18/2013 7:35 PM

Operator : x Detector Type: 3800 (10 Volts)
 Workstation: Bus Address : 44
 Instrument : Varian Star #1 Sample Rate : 10.00 Hz
 Channel : Front = ECD Run Time : 36.963 min

** Star Chromatography Workstation Version 5.3 ** 00379-7520-4C1-0191 **

Run Mode : Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent

Peak No.	Peak Name	Result (ng/ml)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		5.3860	10.595	0.000	207603	VB	0.0	
2	alpha HCH	0.2017	10.781	0.080	7776	VB	0.0	
3		2.8449	10.917	0.000	109658	BB	0.0	
4		3.8337	10.975	0.000	147772	BB	0.0	
5		2.9059	11.609	0.000	112008	BB	0.0	
6	beta HCH	13.5009	11.962	0.110	520394	BB	1.5	
7		4.2858	12.252	0.000	165197	BB	5.3	
8	delta HCH	4.0548	12.496	0.115	156293	BB	0.0	
9		0.4496	13.075	0.000	17330	BB	0.0	
10	Heptachlor	0.1481	13.355	0.102	5707	BB	8.0	
11	isodrin	0.0953	14.106	-0.055	3671	BB	0.0	
12		0.3397	14.242	0.000	13095	VB	0.0	
13	Aldrin	0.2440	14.448	0.087	9407	VB	0.0	
14	Heptachlor e	1.2098	15.667	-0.063	46633	BB	3.2	
15		0.5116	15.872	0.000	19719	BB	0.0	
16		0.3677	15.988	0.000	14174	BB	4.7	
17		0.0444	16.071	0.000	1711	BB	0.0	
18	Endosulphan	0.5391	16.205	-0.033	20780	BB	3.3	
19		0.2114	16.358	0.000	8147	VB	0.0	
20		0.1037	16.659	0.000	3995	BB	0.0	
21		0.0905	16.725	0.000	3487	VB	0.0	
22	pp-DDE	0.2344	16.860	-0.023	9034	VB	0.0	
23		0.7210	17.017	0.000	27793	VB	0.0	
24	Dieldrin	0.0847	18.152	0.120	3264	BB	0.0	
25		0.0325	18.212	0.000	1252	BB	0.0	
26		0.2101	18.298	0.000	8100	BV	0.0	
27		0.2777	18.346	0.000	10706	VV	0.0	
28	Endrin	2.2101	18.555	0.008	85188	VV	0.0	
29		0.3484	18.603	0.000	13428	VV	0.0	
30		1.8462	18.625	0.000	71161	VP	0.0	
31		1.4308	18.958	0.000	55151	FB	0.0	
32		0.0534	19.309	0.000	2058	BB	0.0	
33	pp-DDD	0.0483	19.452	0.067	1862	BB	0.0	
34		0.1301	19.541	0.000	5014	BB	0.0	
35		0.0877	19.835	0.000	3381	BB	0.0	
36	Endrin aldeh	0.0794	20.012	-0.052	3060	BB	5.8	
37		0.1139	20.219	0.000	4390	BB	0.0	
38	pp-DDT	0.1313	20.419	0.089	5061	BB	20.8	
39		0.0336	20.482	0.000	1296	BB	0.0	
40		0.0388	21.871	0.000	1494	BB	0.0	
41		0.0341	22.043	0.000	1316	BB	0.0	
42	Methoxychlor	0.0514	22.083	-0.018	1980	BB	0.0	
43		0.0447	22.196	0.000	1722	BB	0.0	
44		0.0569	22.347	0.000	2195	BB	0.0	
45		0.0498	24.979	0.000	1921	BB	0.0	
46		0.0410	25.087	0.000	1581	BP	0.0	
47		0.0308	25.148	0.000	1189	FB	0.0	
48		0.0401	26.359	0.000	1545	VV	0.0	
49		0.0376	26.385	0.000	1451	VV	0.0	

APPENDIX D: GC/MS calibration graphs.

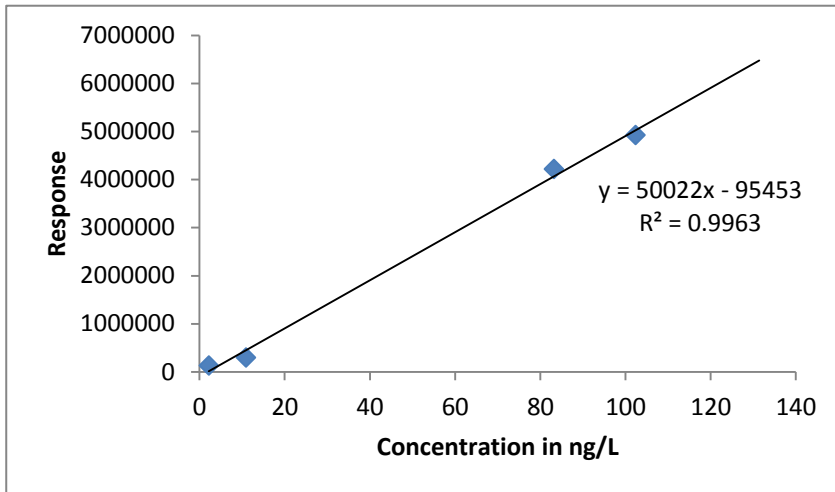


Figure D 1: α -HCH calibration graph.

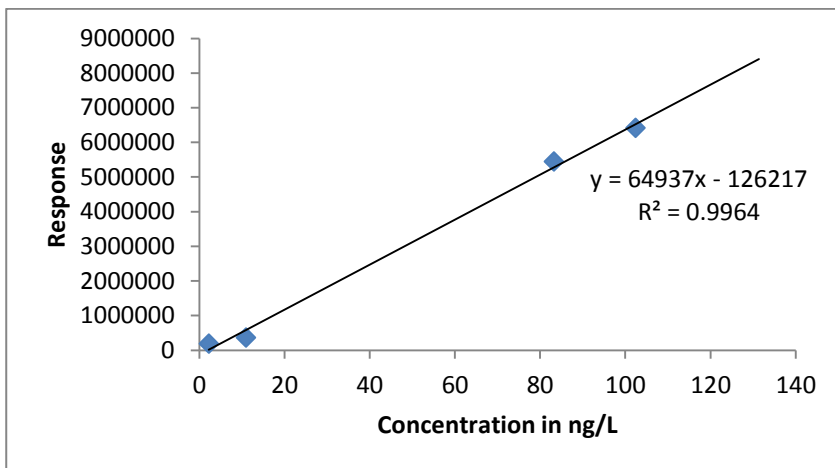


Figure D 2: γ -HCH calibration graph.

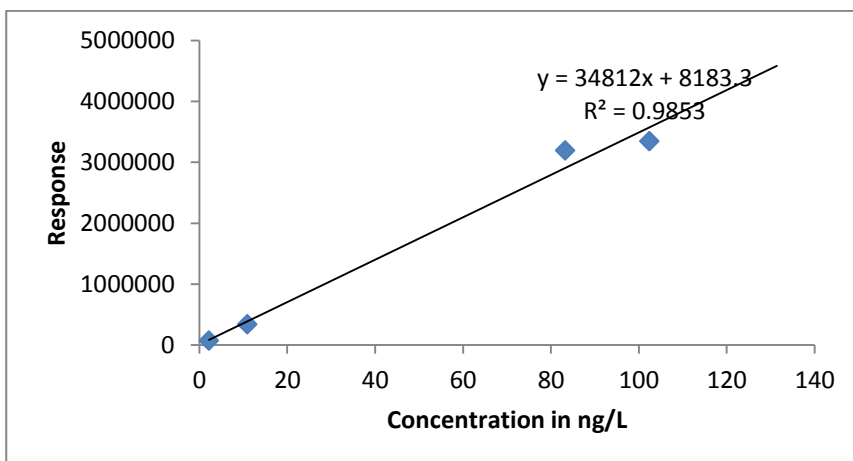


Figure D 3: β -HCH calibration graph.

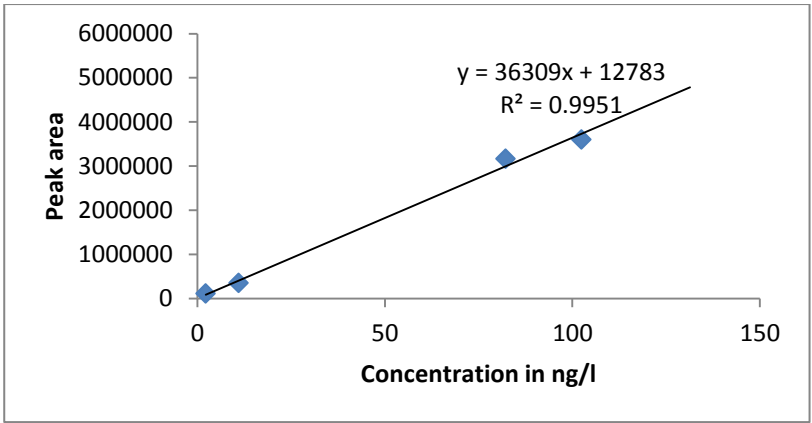


Figure D 4: δ -HCH calibration graph.

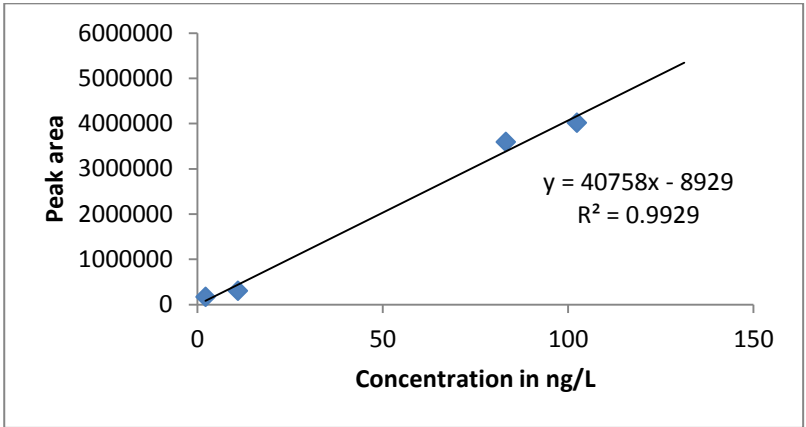


Figure D 5: Heptachlor calibration graph.

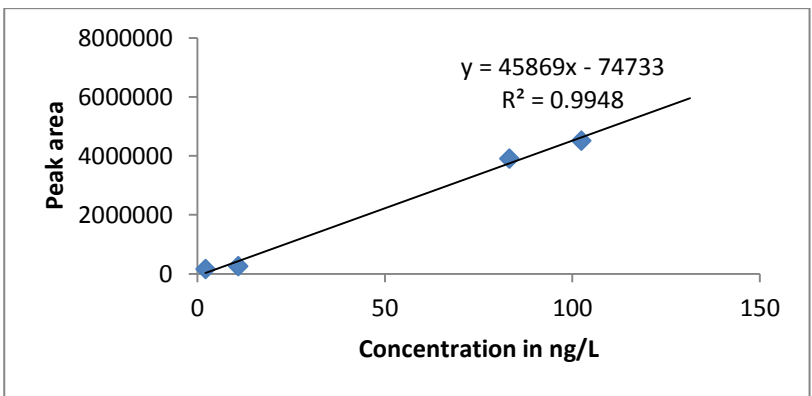


Figure D 6: Aldrin calibration graph.

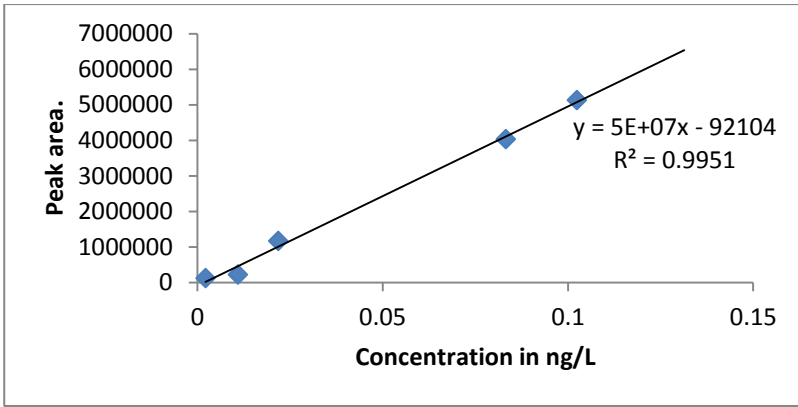


Figure D 7: Heptachlor epoxide calibration graph.

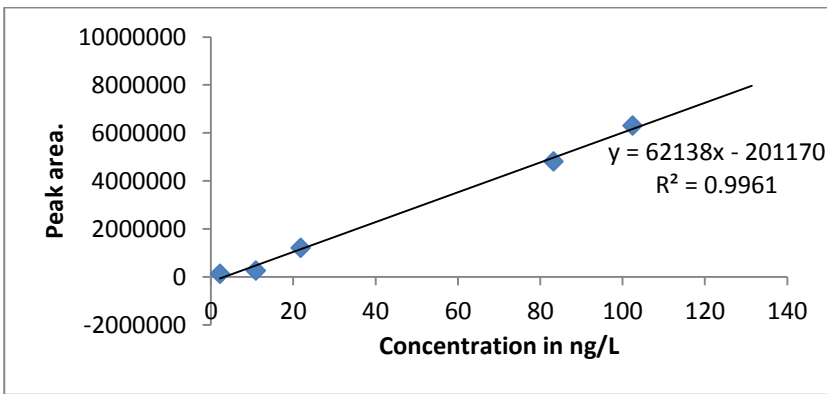


Figure D 8: Endosulphan 1 calibration graph.

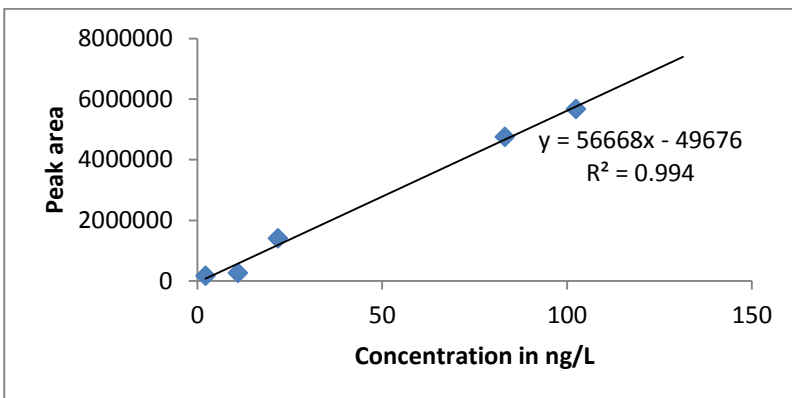


Figure D 9: pp- DDE calibration graph.

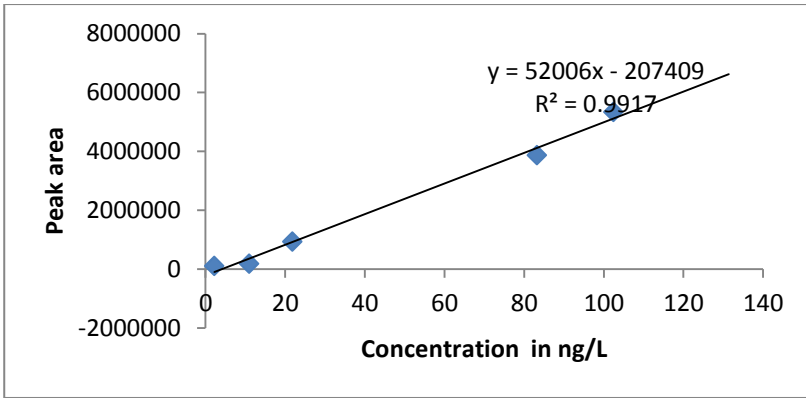


Figure D 10: Dieldrin calibration graph.

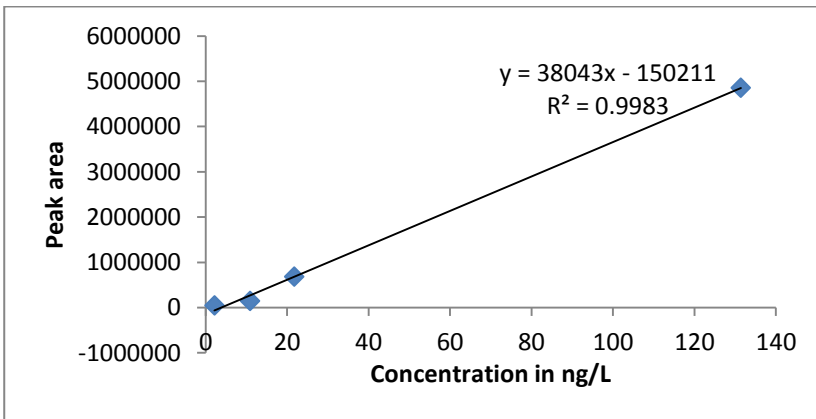


Figure D 11: Endrin calibration graph.

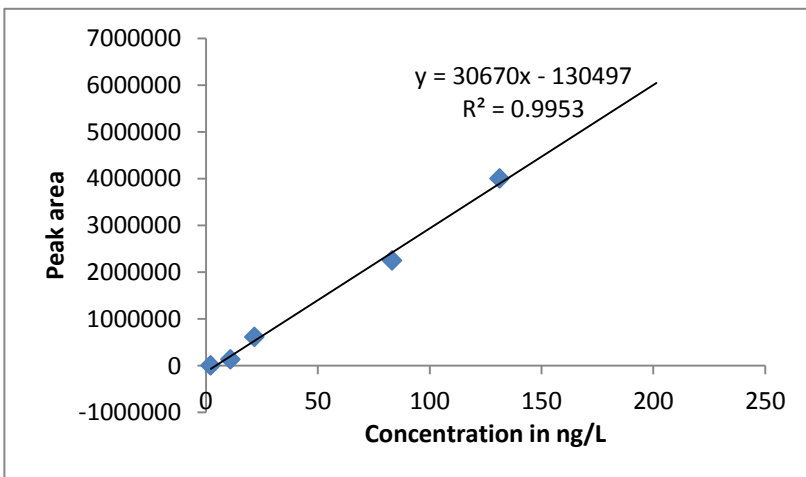


Figure D 12: PP – DDD calibration graph.

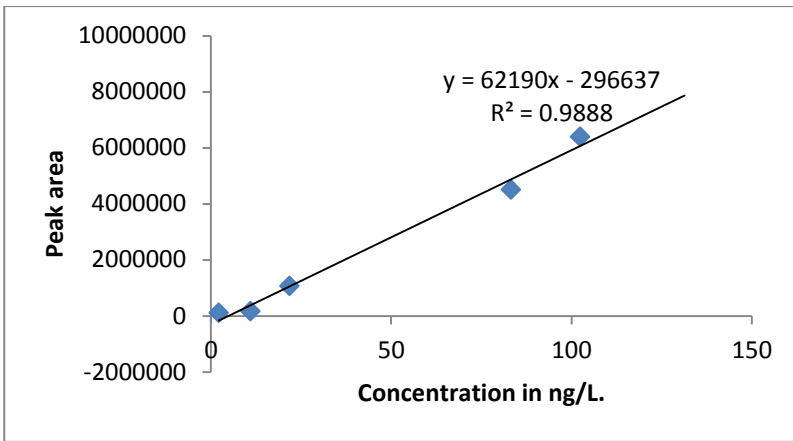


Figure D 13 Endosulphan 2 calibration graph.

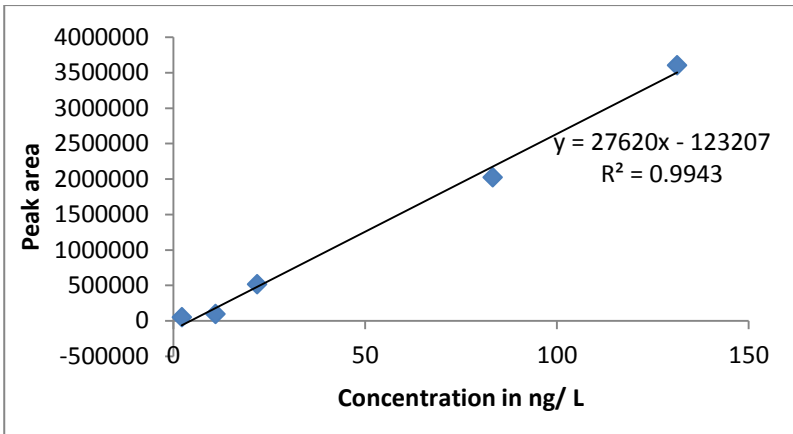


Figure D 14: Endrin aldehyde calibration graph.

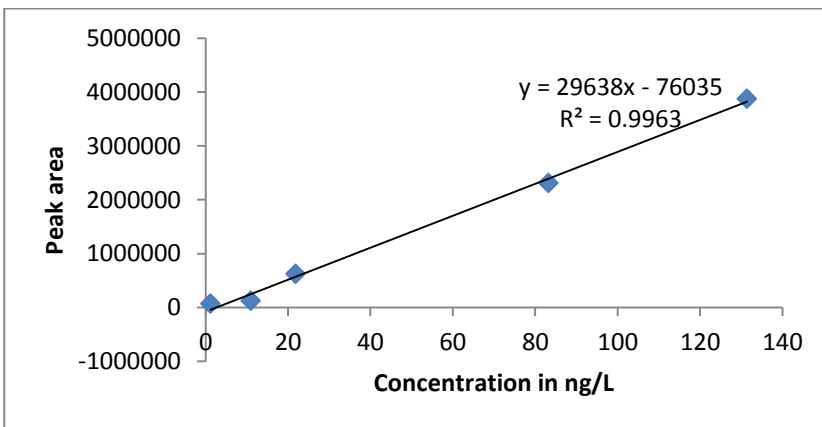


Figure D 15: PP - DDT calibration graph.

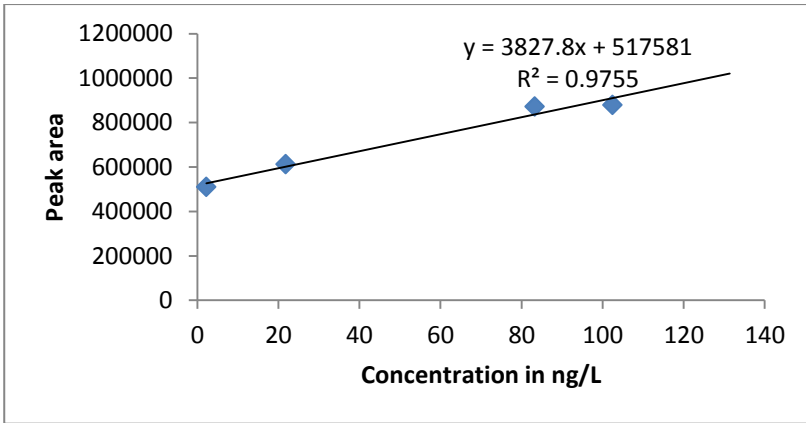


Figure D 16: Endosulphan sulphate calibration graph.

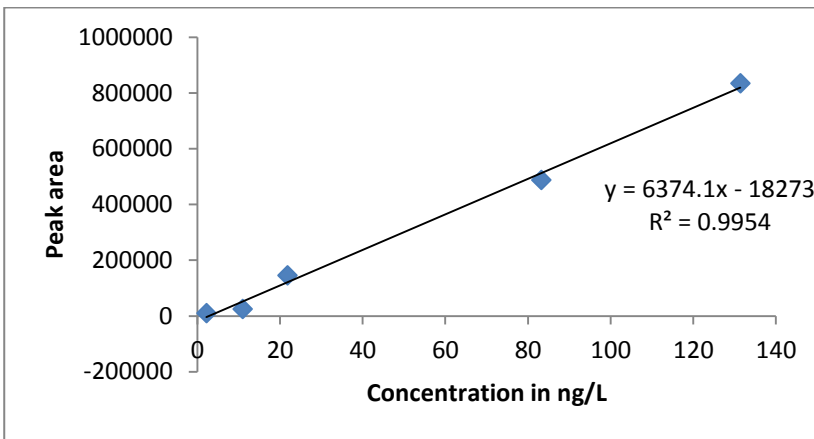


Figure D 17: Methoxychlor calibration graph.

Appendix E: GC/MS SPECTRA

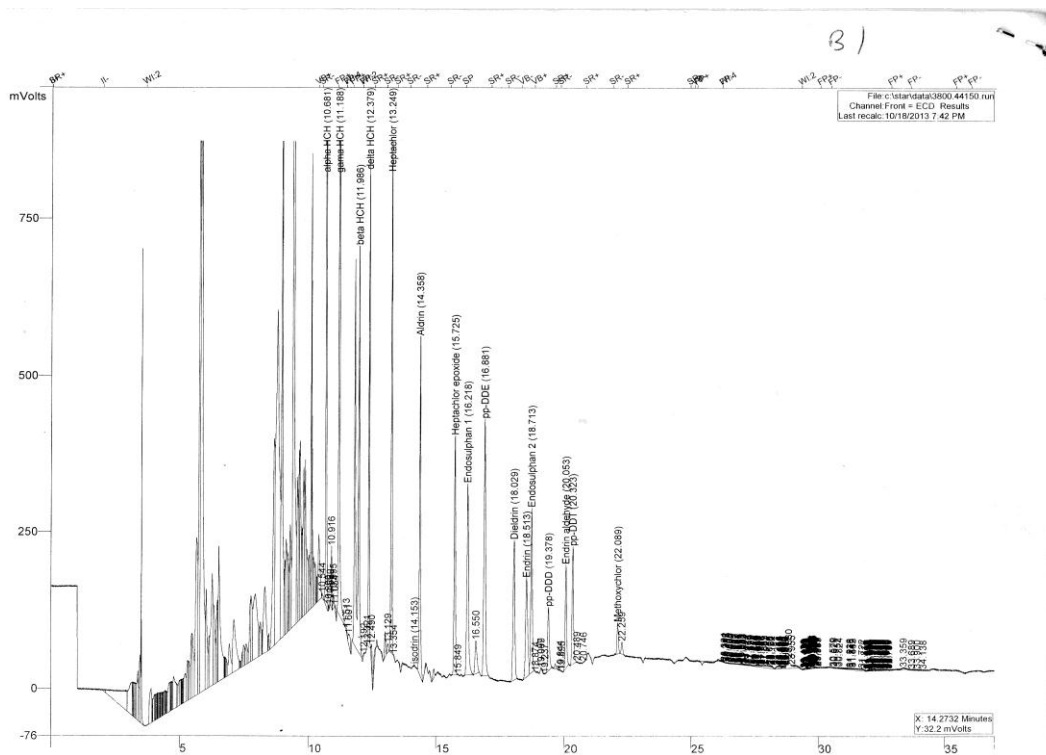


Figure E1: Spectrum of the unfiltered water sample.

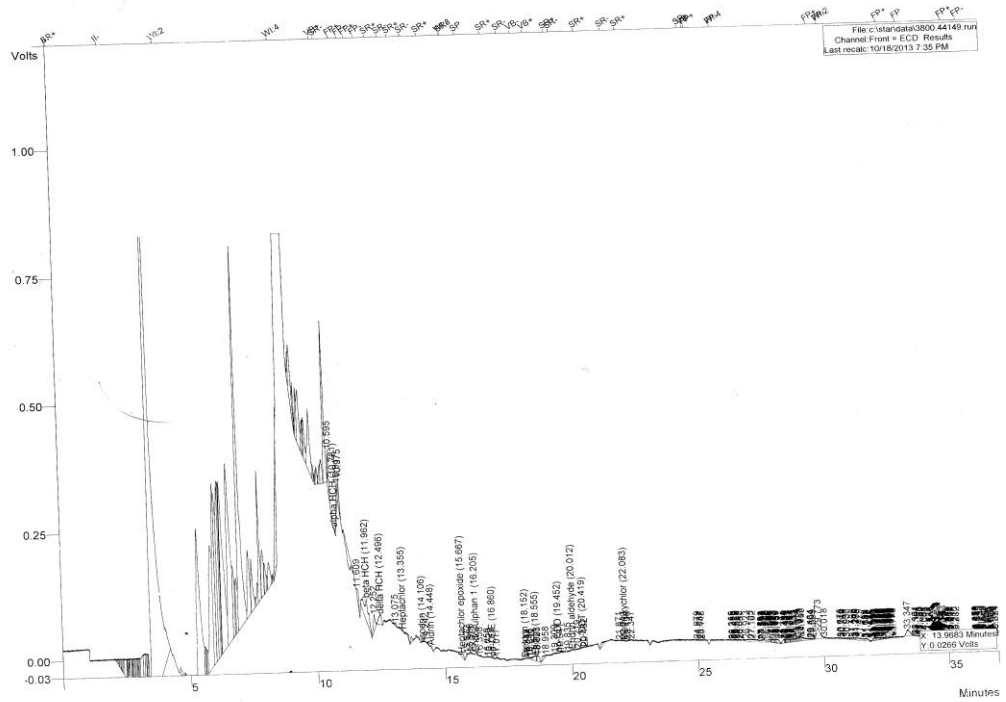


Figure E2: Spectrum of OCP in the filtered sample.