ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCENCE

CENTER FOR ENVIRONMENTAL SCIENCE

PHOTOCATALYTIC DEGRADATION OF 2,4-D BASED PESTICIDES FROM SURFACE WATER AND INDUSTRIAL WASTE USING TiO_2-CuO-CLAY SOIL COMPOSITE

MASTER'S THESIS

SISAY DEMISSE GEDA

A THESIS SUBMITTED TO THE CENTER FOR ENVIRONMENTAL SCIENCE IN PARTIAL FULFILLMENT REQUIREMENT FOR THE DEGREE OF MASTERS OF ENVIRONMENTAL SCIENCE

ADDIS ABABA, ETHIOPIA

MAY, 2024

Photocatalytic Degradation of 2, 4-D based Pesticide from surface water and Industrial waste by using TiO_2-CuO-Clay soil composites

Sisay Demisse Geda

A thesis submitted to the Center for Environmental Science in partial fulfillment of the requirement for the degree of master's in Environmental Science

Supervisors

Dr. Tadesse Alemu (Associate Professor)

Dr. Mekonnen Abebayehu (Associate Professor)

May, 2024

Addis Ababa University

Addis Ababa, Ethiopia

Addis Ababa University

College of Natural and Computational Science

Center for Environmental Science

This certifies that the thesis was written by Sisay Demissie Geda, entitled: Photocatalytic Degradation of 2,4-D Based Pesticide from Surface Water and Industrial waste Using TiO_2-CuO-Clay Soil composites and submitted in partial fulfillment of the Masters of Scinece in Environmental Science requirement comply with University regulations and meets the accepted standards for originality and quality.

Signed by Examining committee

Name	**Signature**	**Date**
Dr. Tadesse Alemu (Supervisor)	_____	_____
Dr. Mekonnen Abebayehu (supervisor)	_____	_____
Dr._____ (Internal Examiner)	_____	_____
Dr._____ (External Examiner)	_____	_____

Chair Center for Environmental Science Graduate program

May, 2024

Declaration

I declare that, this paper is my original Work that it has not been presented for a degree in any other University and that kinds of materials used for this thesis have been acknowledged properly.

Sisay Demissie Geda Signature _____Date _____

This thesis is being presented with the approval of:

Tadesse Alemu (PhD) Signature_____ date _____

Mekonnen Abebayehu (PhD) Signature _____date_____

Acknowledgements

First and foremost, I want to express my gratitude and praise to God, the Almight for providing me with so many opportunities, knowledge and benefits that have made it possible for me to finish my thesis.In addition to my own efforts, a great deal of support and direction from numerous person is necessary for this thesis to succeed. This is my chance to express my gratitude to everyone who helps me to fish my thesis successfully.

My supervisor Dr. Tadesse Alemu has my sincere gratitude for all of his support and encouragements. Without his unwavering support and dedication, finishing this thesis would have been all but impossible. I am grateful for his financial support derived from his thematic research. I would also like to thanks my co-advisor Dr.Mokonnen Abebayehu for invaluable guidance and support throughout my thesis work. And also I thanks, the employees and lab technicians of the Department of Environmental science at Addis Ababa University, Eastern Industrial Zone Laboratory (Dukem) for their support and friendliness and Michael Girmay for helping me during sample collections.

Also like to thanks Chemical and Construction Inputs Industry research Development Center for offering of the scholarship, which allowed me to study at the Center for Environmental Science. Finally, but just as importantly, want to sincerely thanks my family for their hope and support. I genuinely thanks all of the continuous support and encouragement I have gotten during my academic endeavors.

Abstract

Photo-catalytic Degradation of 2,4-D Based pesticide From Surface Water and Industrial waste by Using TiO_2-CuO-Clay soil composites

Sisay Demissie

Addis Ababa University, 2024

Pesticides are artificially synthesized organic and inorganic compounds that are used to control weeds and increase agricultural productivity. Nowadays pesticide contaminants are a major source of surface water pollutants. Repeated pesticide usage in the soil causes runoff that raises the concentrations of pesticides in surface water. For instance, Ziway Lake whose size is 7300 ha is contaminated with agricultural runoff every year. To resolve the problem of environmental pollution a lot of methods and technologies have been developed hither to, some of these technologies are either, inefficient or too expensive to be used widely. The main goal of this research is photocatalytic degradations of pesticides from surface water and Industrial waste by TiO_2-CuO-Clay soil composites. The morphology, particle size and the resulting TiO_2-CuO-Clay soil composite were characterized by XRD, SEM and FTIR. The composite catalyst was optimized by varying concentrations. The degradations of pesticides from surface water and pesticide factory effluents were done by UV-vis Lamp with wavelength 280 nm and the sample was retained for 2, 5, 7 and 9 h. The optimum pH value used was 4. After the irradiation of UV-vis light the degradation efficiency of 2,4-D was analyzed by HPLC. The effectiveness of pesticides removal was impacted by dopant proportions. Moreover, it was found that the removal efficiency of pesticides increased with increasing irradiation time and nanoparticle concentrations. Pesticides removal efficiency decreases with increasing pesticides concentration and contact time with respect to light intensity. Degradation efficiency of TiO_2-CuO-Clay soil nanocomposite was 96.18% and 99.84% respectively from surface water and pesticide factory effluent. The study's result shows that, TiO_2-CuO-Clay soil nanocomposite is the effective photocatalyst for pesticides degradations from surface water and industrial waste.

Keywords: Degradation, Pesticides effluent, Photocatalysis, 2, 4-D Based pesticides, surface water, TiO_2-CuO-Clay soil composite

Table of Content

Contents

List of Figures

List of Table

List of Abbreviations and Acronyms

AOPs	Advanced oxidation processes
BOD	Biological oxygen Demand
COD	Chemical oxygen Demand
CRV	Central Rift Valley
DDE	Dichlorodiphenyldichloroethylene
DOC	Dissolved organic carbon
EF	Environmental Functions
HCHs	Hexachlorocyclohexane
HPLC	High-pressure Liquid chromatograph
IC	Ionic Chromatographer
PEG	poly (ethylene glycol)
RS	Raman spectroscopy
SAED	selected area electron diffraction
SEM	Scanning Electron Microscope
SSIF	Small-scale irrigated farms
UV-VIS	Ultra Violet-Visible Spectroscopy
XRD	X-ray Diffraction
2,4-D	2,4-Dichlorophenoxyacetic acid
Ha	hectares

CHAPTER ONE

1. Introduction

1.1. Background

Pesticides are artificially synthesized organic compounds. The escalating agricultural methods aimed at satisfying the increasing global food demand are leading to rising contamination of soil, water, and aquatic ecosystems (Fiorenza *et al.,* 2020; Miguel et al., 2012). Particularly the contamination of surface and groundwater with pesticides has become a significant concern in recent years (Zandsalimi *et al.,* 2020). In reality, a mere fraction of the pesticides used prove to be truly effective in safeguarding agricultural produce(Sousa *et al.,* 2016).

The majority of these chemicals end up being lost to the environment due to processes such as volatilization, hydrolysis, photolysis, or microbial activity (Ghormade *et al.,* 2011). It has significantly contributed to guaranteeing food security over the past five decades assisting in boosting agricultural output reducing disease vectors (Teklu., 2016).

The current significant agricultural change in Africa has increased the amount of anthropogenic pollution in the use of pesticides, which is becoming a significant environmental concern (Pretty *et al.,* 2011). Lakes are a unique type of natural asset that convey a general impression of relative calmness and stability in the range of natural resources, they contain and flow into the rivers (Teklu *et al.,* 2018). However, within a watershed, lakes and rivers are connected by several socioeconomic activities and certain environmental functions (EF) (Lin *et al.,* 2013).

In Ethiopia 5.2 ton of 2,4-D pesticides were used from 2000 to 2016 (Teshome, 2023). The Ziway Lake is fresh water that reserves a variety of purposes including irrigation, fishing, water supply, and recreation (Lin *et al.,* 2013). The catchment's number of irrigated agriculture has grown to 5000 ha since 1973. According to the area's land use recorded by the year 2006, the total area of small-scale runoff pollutes 7300 ha of land and those chemicals are Organochlorines pesticides and

those pesticides are Dieldrin, Heptachlor, Chlordane, Endosulfan II, dBHC (delta-benzene hexachloride), Atrazine, Aldrin and 2,4-D, Dimethoate, Endosulfan-s, etc (Teklu *et al.*, 2018). Pesticide pollution means huge areas of land coverage and there is an environmental malfunction.

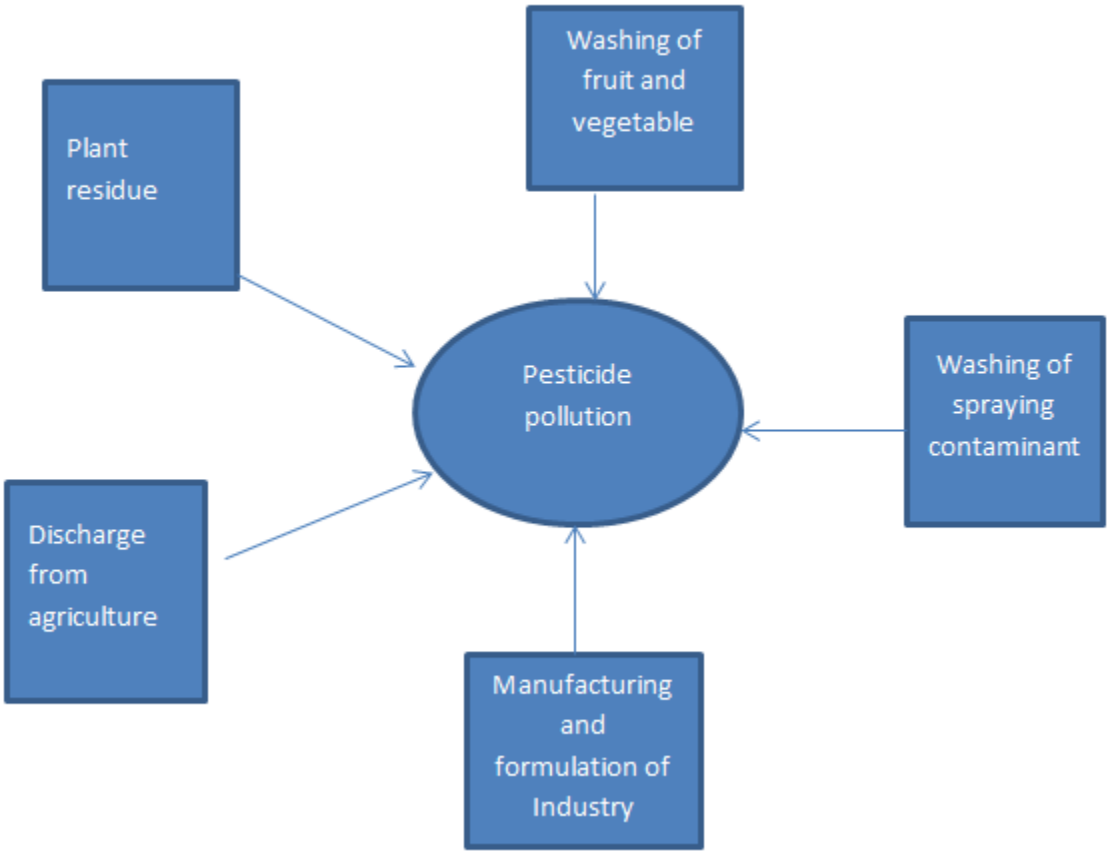


Figure 1 Schematic diagram of Major sources of pesticide pollutions

1.2. Pesticide Treatment methods

The degradations of pesticides from aquatic resources have been studied using a variety of methods including adsorption processes, coagulation and flocculation, biological, and chemical methods. However, because some resistant organic compounds are present in their structure, the conventional methods were ineffective (Toolabi *et al.*, 2019). Due to their great effectiveness in degrading

contaminants from surface water and chemical stability, recovery and stability, advanced oxidation processes (AOPs) have recently attracted and increased global attention (Toolabi *et al.*, 2019).

Photocatalytic degradation is the systematic way of removing pesticides from natural water by using light energy to break down the bond of pesticide molecules. The process of heterogeneous photocatalytic oxidation using semiconductors such as TiO_2 and UV-vis spectroscopy is a promising technique for the destruction of persistent organic pollutants that have been developed (Carbajo *et al.*, 2014). To achieve or speed up a chemical reaction of pesticides with catalysts and with UV-vis light involves the use of radiation and catalysts (Miguel *et al.*, 2012).

The commonly found, inorganic ions and dissolved organic matter in natural water may inhibit the photo-efficiency in a variety of ways, including by competing with one another for adsorption on TiO_2 surface, by altering the pH, dose of catalyst, irradiation time, concentrations of the catalysts or by acting as competitive scavengers of $^{\bullet}OH/H^{+}$ (Carbajo *et al.*, 2014). These radicals then attack the chemicals in the water, which causes further oxidation and breakdown (Toolabi *et al.*, 2019).

A sequence of hydroxylation processes occurring in aqueous solutions under the influence of UV rays and producing hydroxyl radicals (:OH°), which is due to their strong oxidizing power that promotes the breakdown of contaminants utilizing nanocatalysts (Toolabi *et al.*, 2019). Advanced oxidation processes (AOP), UV-Vis spectroscopy radiations and integrated approaches are currently some of the technologies that have been developed to minimize harmful chemicals in wastewater (Matsumoto *et al.*, 2009). Since AOP is a promising technology and efficiently overcomes the problems raised organochloro pesticides.

Photocatalytic degradation is introduced by the action of light and attributed to chemical reactions that arise from photoionization and it is one of the most significant abiotic transformations of pesticides in surface water (El-Saeid *et al.*, 2021). The high energy of solar rays causes characteristic reactions such as bond separation, rotation, rearrangement, and catalytic compounds could be advantageous during the UV radiation source is applied since UV radiation has sufficient

energy for chemical bond breakdown (EL-Saeid *et al.*, 2015). New research is required to make photo-remediation using UV light, an efficient solution for wastewater treatment systems (El-Saeid *et al.*, 2021).

It is possible to develop highly efficient photocatalysts capable of degrading 2, 4-D and other environmental pollutants, contributing to a cleaner and healthier environment. This research provides the important insights into the effect of various molar ratios of TiO_2, CuO, Clay soil and calcination temperature on photocatalytic degradations of 2,4-D from surface water. By carefully optimizing catalyst molar ratios, it is possible to develop highly efficient photocatalysts capable of degrading 2, 4 D and other related environmental pollutants, in contributing to cleaner and healthier surface water and industrial waste

1. 2. 1. Mechanism of photocatlysis

The expected scheme of 2, 4-D degradations on the surface of TiO_2-CuO-Clay soil composite was outline in Figure 2.

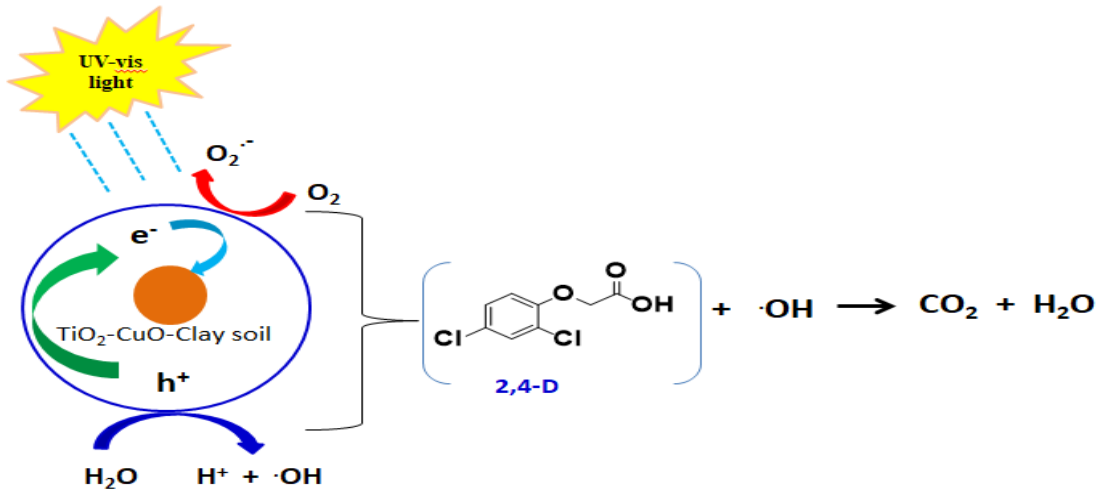


Figure 2 Schematic photocatalytic degradations mechanism of 2, 4-D

2,4-D (2,4-Dichlorophenoxyacetic acid) can be degraded using photocatalyst TiO_2-CuO-Clay soil composite. The following steps shows the mechanism followed during the reactions:

i. **Absorption of light energy**: Titanium dioxide (TiO_2), copper oxide (CuO), and clay soil, absorbs light energy (hν) from a light source. This energy excites an electron (e^-) from the valence band (VB) of both TiO_2 and CuO into the conduction band (CB), leaving behind positively charged holes (h^+) in the VB.

$$TiO_2 + CuO + h\nu \rightarrow TiO_2\ (e^-CB + h^+\ VB) + CuO(e^-CB + h^+VB) \quad (1)$$

ii. **Formation of reactive species**: The photogenerated holes (h+) in the valence band of TiO_2 and CuO can react with water (H_2O) or hydroxide ions (OH^-) adsorbed on the ocomposite surface, producing hydroxyl radicals ($OH^\bullet$). Meanwhile, the photo generated electrons (e−) in the conduction band can react with oxygen molecules (O_2) adsorbed on the nanocomposite surface, generating superoxide radicals ($O_2^{\bullet-}$).

$$TiO_2\text{-}CuO\text{-}Clay\ (h^+\ VB) + H_2O \rightarrow TiO_2\text{-}CuO\text{-}Clay + OH^\bullet + H^+ \quad (2)$$

$$CuO\text{-}Clay\ (h^+VB) + H_2O \rightarrow CuO\text{-}Clay + OH^\bullet + H^+ \quad (3)$$

$$TiO_2\text{-}CuO\text{-}Clay\ (e^-\ CB) + O_2 \rightarrow TiO_2\text{-}CuO\text{-}Clay + O_2^{\bullet-} \quad (4)$$

Degradation of 2,4-D: The hydroxyl radicals ($OH^\bullet$) and superoxide radical anions ($O_2^{\bullet-}$), which are powerful oxidizing agents, can react with 2,4-dichlorophenoxyacetic acid (2,4-D), breaking its molecular bonds and converting it into simpler, less toxic products such as CO_2, H_2O, and other mineral acids. The degradation reactions occur on the clay soil surface.

$$C_8H_6C_{l2}O_3 + OH^\bullet \rightarrow H_2O + CO_2 \quad (5)$$

1.3. Statement of the problem

Surface water contamination in Ethiopia is caused by agricultural development, industrial expansion, and population growth. Pesticide use in agriculture is one of the contaminants that pollute Ziway Lake. Nowadays the usage and industrial production of pesticides are highly increased for rural agricultural use. Studies undertaken in the past have shown that Ziway Lake is extremely contaminated as a result of agricultural runoff into the Lake (Ahmed., 2015).

The risk presented to people and the environment by the use of pesticides may be rising in light of the current intensification of agricultural operations and increased intensity of pesticide usage, combined with the nation's abundance of surface water bodies (Teklu., 2016). Ziway Lake is used

for drinking by the local people and they filter the water using sheets (A single garment) to remove dirty particles, which allow pesticide and contaminant to be ingested. This could increase the risk of cancer and associated diseases due to its bioaccumulation.

The year-round outflow of farm effluents, which may contain residues of pesticides and fertilizers from the production process raises concern about the possibility of pesticides residues formation of Lake eutrophication and makes Wildlife unhealthier (Muhammed., 2016). In vegetable agriculture, the use of pesticide is common to control diseases and pests, but the environment and public health are frequently sacrificed in the process (Rift., 2022).

The existence of pesticides in Ziway Lake was confirmed by many researchers (Jansen *et al*., 2011), (Muhammed., 2016). However, the treatment methods of pesticide-contaminated water from Ziway Lake were not studied. Therefore, the objective of this study was to access the photocatalytic degradations of 2,4-D pesticides using TiO_2-CuO-Clay soil composite.

1.4. Objective

1.4.1. General Objective

The general objective of this study is the photocatalytic degradation of Pesticides from surface water and Industrial waste by using TiO_2-CuO-Clay soil composite.

1.4.2. Specific Objectives

- To purify and characterize Clay soil
- To synthesize and characterize TiO_2-CuO-Clay soil composite for photo-degradation of pesticides
- To optimize the efficiency of the catalyst molar rations and evaluate the degradation efficiency of TiO_2-CuO- Clay soil composites

1.5. Significance of the study

The outcome of this research revealed the degradation of pesticides in Ziway Lake Oromia-Ethiopia. The possible degradation techniques from polluted water describe the effect of catalysts.

Photocatalytic degradation of pesticides from surface water results showed zero Valente pesticides and overcame the Health issues caused by agricultural used pesticides. It provides users with helpful suggestions on how to use less pesticide and substitute synthesized pesticides by natural means. Additionally, this finding will benefit the community by raising awareness of safeguarding people, and motivating academic and research institutes to conduct more research on photocatalytic degradation of pesticide concentrations from industrial effluent and surface water in Ethiopia.

1.6. Scope of the study

This research investigates pollution status and pesticides removal from surface water in some selected areas along Ziway Lake. Several pesticides pollute Ziway Lake, but only 2, 4-D pesticides were taken into account in this study. This study covers water samples from agricultural used pesticides that accumulated in Ziway Lake and Adami Tullu pesticide factory as a industrial waste. The Ziway Lake, at the site of Bulbula River, waters sample was used for analysis. Because of the resource availability and direct inlet of pesticide from agricultural runoff to the Lake. The degradations of organochloro pesticide 2, 4 D, from the Ziway Lake water sample, were the subject of this study.

1.7. Research question

1. What is the use of characterizing TiO_2-CuO-Clay soil composite for photocatalaytic degradation of pesticides?
2. How can pesticides be treated in Ziway Lake?
3. Does TiO_2 -CuO-Clay soil composite efficiently remove pesticides from surface water?

CHAPTER TWO

2. Literature Review

2.1. Status of Pesticide Pollution in Ethiopia

Soil, Water and Aquatic Environments are getting increasingly contaminated due to increased agricultural techniques implemented to fulfill the world's increasing food needs (EL-Saeid *et al.*, 2021; Fiorenza *et al.*, 2020). In light of this, the main problems of the past ten years have been the pesticides-related contamination of surface and ground waters.

These chemical compounds' toxicity as well as their great mobility and persistence in water contribute to their detrimental effects on media (Rezaei Kalantary *et al.*, 2022). One of the African Nation's, Ethiopia impacted by the issues of outdated pesticides stocks is stepping up with food and agriculture organizations to monitor pesticides. Despite inherent hazards, chemical pesticides are widely used in Ethiopia's rapidly changing agricultural sector (Negatu *et al.*, 2016). Ethiopian farmers have been using pesticides to control crop pests since mid-1940's and in 1960s, small holder farmers were introduced to pesticides containing agricultural inputs through agricultural extension networks and agricultural Advising system (Teklu., 2016).

The central rift valley (CRV) of Ethiopian's Zeway Lake study states that burying storing pesticides canisters and dumping empty pesticide canisters on farmland are prevalent among 75% of farm workers on both large-scale outdoor farms (LSOFs) and small irrigated farms (SIFs) were reported (Negatu *et al.*, 2016). There have been noticeable increases in usage of pesticide chemicals, the unauthorized use of Endosulfane and DDT on food crops and the direct importation of pesticides without following Ethiopian official registration procedures (Negatu *et al.*, 2016).

According to the assessment (Teklu, 2016), Ethiopia imports more than 2400 tons of pesticides annually for commercial farmers, accounting for about 80% of its use, with the remaining 20% of

total imports being used in smallholder agriculture. According to (Jansen *et al.*, 2011) assessment of 2009 and 2010 results revealed that the majority of surface water sample taken from north Ziway Lake's agricultural areas and between the towns of Meki and Ziway had pesticide residues concentrations of pesticides occasionally exceeding the European and Dutch drinking water standard of (1.0 µg/Kg to 251 μgKg^{-1}) by 0.1 μgKg^{-1}.

The assessment of Ziway Lake (Habtamu, 2020), reported that the samples of succulent grass and sediment include the low ratio of Dichlorodiphenyl dichloroethylene to Dichlorodiphenyltrichloroethane which suggests that DDT poisoning of the Lake occurred recently. Therefore, it is necessary to pay attention to controlling the circulation of illegal band organochlorine pesticides and clearing the eco-system of outdated pesticides.

2.2. Pesticide treatment methods

For durations of long time, farming and agriculture have routinely used pesticides. However, the indiscriminate use of these chemicals has led to the contamination of soil, water, and air. This has resulted in the need for alternative methods of pesticide degradation. It has been demonstrated that photocatalysis is a reliable and affordable method for cleaning water of both organic and inorganic contaminants (Devipriya *et al.*, 2005).

Photocatalytic degradation is one such method that has been widely studied in recent years. 2, 4-D is a common herbicide used in agricultural farming and known to be toxic to both plants and animals. Using titanium dioxide (TiO_2) as the photocatalyst, numerous investigations have been carried out on the photocatalytic degradations of 2, 4-D. As (Zhang *et al.*, 2017) reports that TiO_2 was used to analyze the degradations of 2,4-D with UV-vis radiation lamp. According to this study, the degradation rate rises as the starting concentrations of TiO_2 and degradation efficiency of 2,4-D increases.

As the reaction time grew, so did the rate of degradations. TiO_2 has been the photocatalyst in anumber of investigations on the photocatalytic degradations of several pesticides. Photocatalytic degradation using TiO_2 is a practical techniques for the degradations of 2,4-D pesticides. The pace at which the degradation occurs rises as the initial concentration of the pesticide and TiO_2, as well as with an increase in reaction time. Further research is needed to explore the use of other photocatalysts and to determine the feasibility of this method for large-scale applications.

2.3. Photocatalytic degradations of pesticides

The study on the Ebro River basin(Miguel *et al*., 2012), Demonistrated that, decreasing water toxicity and dissolved organic carbon (DOC) level is possible with a 30 minute photocatalytic treatment using 1 g/L of TiO_2. This treatment yields an average removal rate of 48% of pesticide tested and the chlorine requirement. Furthermore, the results shown that the addition of hydrogen peroxide at a concentration of 10 mM increased the average degradation of pesticides to 57%.

This suggests that hydrogen peroxide can speed up photocatalytic degradation of pesticides from surface water, including dicofol,parathion methyl,Chlorpyrifos, 3,4-dichloroaniline, and hexachlorocyclohexane (HCHs) and endosulfan-sulphate.

The nanocomposite produced about 96.5% of the photocatalyic activity needed to remove herbicides of DDT from surface water when exposed to UV-vis lamp (Ismael *et al*.,2020). They stated that the TiO_2/GO/$CuFeO_4$ catalyst's has high adsorption performance and photocalaytst carrier separation efficiency were the reasons behind its good photocatalytic performance. *(*El-Saeid *et al.*, 2021) investigated pesticide photocatalytic remedation by photolysis and photocatalysis of TiO_2 (0.001 g/10 mL) on dieldrin and deltamethrin pesticides (2000 µg) were evaluated using UV/TiO_2 about 12 h at wavelength of 254 and 306 nm. The photolysis was more successful at 306 nm than 254 nm. TiO_2 (0.001 g/10 mL) was enhanced the degradation at both measured wavelength suggesting that might act as a catalyst for the breakdown of both pesticdes (El-Saeid *et al.*, 2021).

The five most common pesticides' photocatalytic degradation was investigated by (El-Saeid *et al.*, 2022) at wavelength of 306 nm, both in the presence and absence of 1% TiO_2 or ZnO photocatalysts with UV radiation. The findings demonstrated that all atrazine (OCP), Chlorpyrifos methyl, dimethoate, hepachloro and methomyl umder goes complete photolysis when exposed to UV light for 64- 100 h with TiO_2 photocatalyst demonstrating greater activity than ZnO.

2.4. Advanced Oxidation Process

For several decades, a distinct set of chemical oxidative advances for the remediation of waste water defined as oxidation forms (AOPs) has been analyzed as a crucial area of studies, either from a mechanical or scholarly stand point. These developments in oxidation preparation are typified by the production of highly sensitive and amorphous hydroxyl radicals, which are remarkably active oxidants in aqueous media. Through a process known as mineralization, these reactive and active radicals have the ability to oxidize practically all organic compound to water, carbon dioxide and mineral salts (Choi *et al.,* 2016). According to the principle of Advanced Oxidation Processes (AOPs), photocatalytic degradation can achieve higher efficiency in treating pollutants like 2, 4-D (Dichlorophenoxyacetic Acid) in aquatic environment.

2.5. Principle of AOP

The enhanced oxidation process technology has been applied to remove 2,4-D from surface water, especially for degradations of 2,4-D pesticides industries and its mechanism action is the production of highly oxidizing and reactive free hydroxyl radical, which are employed with growing attention because of their strong oxidation's power (Hinojosa *et al.,* 2019).

Principle of advanced oxidation processes (AOPs) holds the premise that exposure to light can activate titanium dioxide (TiO_2) photocatalysts, enabling a photocatalytic degradation process. This process can break down molecular bond of contaminants, such as 2,4-D (2,4-Dichlorophenoxyacetic acid), into relatively safer by-products. According to a study conducted by (Mondal *et al.,* 2008),

photocatalytic oxidation over hampered TiO_2 resulted in effective degradation of 2,4-D, showcasing the potential of AOPs in treating contaminants in aquatic environments (Mondal *et al.,* 2008).

However, hydroxyl radicals, which are essential and active during the reaction process are involved in the advanced oxidation (Giri; Golder, 2019). The hydroxyl radicals, which are unstable and highly reactive appear to the active species most frequent responsible for the eliminations of pollutants during the advanced oxidation process, even if other species are also involved. These radicals must be continuously produced with the system chemical or photochemical reactions outlined in the literature due to their instability and high reactivity (Huang *et al.,* 2019).

2.6. Factors Affecting Photocatalysis

The degradation efficiency of photodegradation process affected by several operational parameter and its catalytic kinetics (Foster *et al.,* 2011; Wong *et al.,* 2010). The impact and importance of each operational parameter will discuss in this section.

2.6.1. Morphology of the photocatalyst

The photocatalytic activity of photocatalytsts is highly determined by their shape. Different morphological structures can impact the surface area, light absorption, and separation efficiency of electron-hole pairs produced by photolysis . Therefore, the efficacy of photocatalytic degradation processes, like the removal of 2, 4-D a Common Herbicide Present in surface water, can be influenced by the morphology of photocatalyts (Zhang L *et al.,* 2013). When assessing the morphological impacts on the photocatalytic degradation of 2,4-D, some important parameters to take into account are:

i. Surface area: The higher surface areas of photocatalysts often result in higher photocatalytic activity, because there are more active sites available for adsorption and reaction. For instance,

porosity and pore size can affect reactant and product accessibility, which in turn can affect the rate of reaction as a whole.

ii. Light absorption: The morphology of photocatalysts can impact their capacity to take in light, particularly in the visible region, where light penetration is higher. Increasing electron-hole pair production can result from higher light adsorption on the surface of the photocatalysts, which can boost photocatalytic activity.

iii. Electron-hole separation and recombination: Morphological features, such as the presence of different crystal facets or mesoporosity, can influence, the effectiveness of photogenerated electron-hole pair separation. Efficient separation of electron-hole pairs is crucial for the production of reactive species capable of degrading target pollutants like 2, 4-D.

iv. Adsorption: The roughness and microstructure of photocatalyst surfaces can impact the adsorption of target pollutants, thus affecting the overall photocatalytic degradation efficiency. Because there is a direct correlation between organic chemical and the photocatalyt"s surface coverage, surface morphology, such as particle size and structure are the main elements to be taken into account in the photocatalytic degradation processes. The pace of reaction is controlled by the photon that reaches the photocatalyts indicating that the reaction only occurs during the photocatalyst's absorbed phase (Wong *et al.,* 2010).

2.6.2. Temperature

The temperature can significantly impacts on 2,4-D photocatalytic removal of surface water. The main consequences of temperature on this process are mainly related to the kinetics and overall reaction rate, as well as the adsorption and photocatalytic activities of the photocatalyst (Wang, B *et al.,* 2011; Ma, M. L *et al.,* 2013). The optimized parameters during photocatalytic studies from different groups, temperatures higher than 80 ^{0}C encourages charge carrier recombination and organic chemical adsorption on the titanium surface (Foster *et al.,* 2011; Zhang Z., *et al.,* 2014).

When assessing the impact of temperature on the photocataytic degradation of 2,4-D, some important variables to take into account are:

i. **Reaction kinetics:** The Arrhenius equation states that the reaction rate is directly in line with temperature. As the temperature rises, the rate constant and overall reaction rate of the photocatalytic process increase, provided that the photocatalyst remains stable. The equation is commonly given in the form of an exponential function,

$k=Ae(-Ea/RT)$.

Where:

- ✓ K- denotes the rate constant of the reaction
- ✓ A-denotes the pre-exponential factor which in terms of collision theory, the frequency of correctly oriented collision between the reaction species.
- ✓ e - is the base of the natural logarithm (Euler's number)
- ✓ E_a - denotes the activation energy of the chemical reaction (interms of energy per mole)
- ✓ R -denotes the universal gas constant
- ✓ T- denotes the absolute temperature associated with the reaction (in Kelvin)

ii. Activation energy: The activation energy needed for the process to proceed more quickly often decreases with increasing temperature. Lower activation energy can leads to more product formation of reactive species in photocatalytic processes enhancing the total efficiency of 2, 4-D photocataytic degradations.

ii. Photocatalyst stability: At higher temperatures, the risk of photocatalyst degradation or phase transformation can increase. These changes may lead to a reduction in photocatalytic activity or even complete deactivation of the photocatalyst.

One of the variables that influence the pace at which 2, 4-D photocataytic degradation is temperature. The removal of 2, 4-D with a semiconductor photocatalyts causes the reaction

temperature to rise, which increases photocataytic activity, also scavenges the hydroxyl and hole radicals reducing photoactivity (Wong *et al.,* 2010)

Desorption of the products restricts, when the temperature drops because it happens more slowly than surface degradation and reactant desorption. Conversely, the limiting step becomes the 2, 4-D adsorption on TiO_2 surface at higher temperature and the rate constant decreases as a result of the organic and dissolved oxygen's reduced adsorptive capacity at higher temperatures (Wong *et al.,* 2010).

2.6.3. Light intensity

The degree of light adsorption by the semiconductor catalyst at a particular wavelength is determined by its intensity, which also influences photodegradation. The light intensity affects the 2, 4-D degrading efficiency when employing semiconductor photocatalyst (Dasineh Khiavi *et al.,* 2019). The higher intensities lead to higher photocatalytic reaction rates. Nevertheless, the photocatalysis reaction rate during the semiconductor of TiO_2 start is not greatly reliant on light intensity, while a small amount of energy in the form of photons can adequately trigger the surface reaction (Sanzone *et al.,* 2018).

A relatively high light intensity is necessary to sufficiently supply each TiO_2 surface active site with the photon energy needed to achieve a high photocatalytic reaction rate, especially in waste water treatment. In other words, more light intensity means more titanium dioxide nanoparticles can produce electron pair hole (Wang *et al.,* 2016).

Using 0.239 C/C_0, the UV/catalyst doped system efficiently broke down 2,4-D pesticides in surface water in 60 minutes (Amiri *et al.,* 2021). According to this study neither UV system nor the catalys system alone could remove 2,4-D to a significant degree. The improved elimination of 2,4-D in the UV/catalyst–doped system may be explained by an energy increases in the electrons in the semiconductor power layer caused by light emitted photons colliding with UV light.

Consequently, a conductive tape transmission that is higher in energy than the film capacity may cause positive cavities and negatively charged electrons to separate, which may start a reaction. (Samadi MT *et al.,* 2010).

2.6.4. Initial solution of pH

The size of the aggregate band gap energies of the conductance and valance bands, the surface charge on the solid catalyst particles and the adsorption characteristics of the organic molecules are all impacted by the pH solution (Wong *et al.,* 2010). There is no consensus in the literature about the impact of pH on the rate of photocataytic degradation, despite that the expansion of this impacts. In order to add the curiosity of this study, an experiment is conducted to determine the pH of optimal arrangement and the effect of the initial arrangement of pH on the reduction of organic molecules.

pH levels significantly influences photocatalytic degradation processes, since it establishes the catalyst's surface charge and adsorption characteristics which in turn affects the reaction kinetics (Malato *et al.,* 2002) found that the photocatalytic degradation of 2,4-D was most efficient at pH 4, suggesting that it is crucial to maintain a slightly acidic environment for enhanced degradation of this compound.

The optimal pH for photocatalytic degradation varies depending on the specific catalyst used. For example, tiopronin-sensitized TiO_2 maintain optimal degradation at pH 4, while phenol and aniline degradation are most effective at pH 3.3 (Ha7zin *et al.,* 2000). This highlights the importance of tailoring pH levels to specific catalysts and chemical reactions.

In addition, the pH level can also affect the stability of pollutants in water, potentially altering the rate of photocatalytic degradation. For instance, when 2, 4-D hydrolyzed, a number of chemical species are formed that depending on the pH are more prone to degradation. An investigation by

(Bradwal and Shrivastava 2007) indicates that the greater vulnerability of the hydrolyzed products to photocatalytic degradation is reflected in the higher hydrolysis of 2, 4-D with decreasing pH.

Therefore, for molecules like 2, 4-D, the pH level is critical to photocatalytic removal. Maintaining an optimal pH level not only influences the catalyst's surface charge and adsorption behaviour but also affect pollutant stability, consequently impacting the degradation rate.

2.6.5. Photocatalyst dose

Numerous organic pollutants, like phenol and phenol derivatives, can be degraded more efficiently by preventing the development and building of non-photocatalytically degradable intermediates as well as catalyst surface saturation. This has been illustrated that the most elevated high efficiencies are obtained at certain concentration edges (Aboutaleb *et al.*, 2019).

The lower degradation efficiencies are the consequence of distinct processes, such as catalyst poisoning, predominating at higher dose rates. Dose of photocatalyst in a wastewater suspension includes a noteworthy impact on the response rate and total 2, 4-D degradation capability. This condition may be related to a reduction in the UV radiation that penetrates the fixed layer of nanoparticles on the glass plate (Ghaneian M *et al.*, 2016; Amiri et al., 2021).

2.6.6. Inorganic ions

Numerous inorganic cations and anions found in waste water such as magnesium, iron ,Zinc, copper, bicarbonate, phosphate, nitrate, sulfate, and chloride can influence the rate at which organic contaminants are degraded by photocatalysis, because they can absorb on the catalyst surface (Kant, 2012).

In contrast to calcium, magnesium, and zinc, which have minimal effect on the photodegradation of organic materials due to their maximal observation, water cation like copper, iron and phosphate can decrease the photocatalytic effectiveness at specific concentration. The stage of oxidation making it

impossible for them to affect the process of deterioration (Foster *et al.,* 2011l1; Wong *et al.,* 2010). However, any inorganic anions including sulfate, carbonates, chlorides,and nitrates can also reduce the surface activity of photocatalyst.

Salts have the potential to decrease colloidal stability, which raises the mass transfer and decreases the impurity of photocatalyst surface contact (Foster *et al.,* 2011). Certain anions,like phosphate,sulfate,carbonates, and chloride scavenge the hydroxyl radical and the hole which reduces phohotoactivity (Wong *et al.,* 2010).

2.6.7. Effect of contact time

The durations of contact time between a target pollutant and a photocatalys, such as 2,4-D, significantly impacts the efficiency of photocatalytic degradation. As contact time increases, the likelihood of collisions between photogenerated carriers and the pollutant molecules also increases, enhancing the degradation process. The Langmuir-Hinshelwood (L-H) model can be used to explain the link between contact time and photocatalytic degradation efficiency. This model takes into account the adsorption of reactants onto the catalyst surface and the ensuing surface reaction (Hoffmann *et al.,* 1995).

A higher concentrations of reactive species on the catalyst surface as a result of enhanced adsorption at longer contact durations speed up photocatalytic degradation of pesticides (Ogunlaja, *et al.,* 2014). They found that the degradation efficiency increased significantly with increasing contact time up to 3 hours, beyond which there was no significant improvement. This suggests that there is an optimal contact time for achieving maximum degradation efficiency.

Similarly (Amini *et al.,* 2018) explored the use of different TiO_2 nanostructures in the photocatalytic degradation of metronidazole. They discovered that increasing the contact time from 1 to 4 h significantly increased the degradation efficiency. However, further increasing the contact time to hours resulted in no significant improvement. Irradiation time is one of the most important variables

in the elimination of contaminants. The contact time affects 2, 4-D removal process. The process efficiently increased as the contact time increased at interval of 10,20, 30, 45,60, and 90 min.

It is noteworthy that after 120 min, the removal efficiency did not change, because may be reach the maximum point of degradation. This phenomenon could be brought on by the pesticde's metabolites being oxidized as a result of pesticides irregular reduction in concentration and increased generation of free radicals with longer contact time. Furthermore, duration may vary based on the pesticides' stability and chemical makeup (Amiri *et al.*, 2021).

2.7. Photocatalytic degradations of pesticides

The study on the Ebro River basin(Miguel *et al*., 2012), Demonistrated that, decreasing water toxicity and dissolved organic carbon (DOC) level is possible with a 30 minute photocatalytic treatment using 1 g/L of TiO_2. This treatment yields an average removal rate of 48% of pesticide tested and the chlorine requirement. Furthermore, the results shown that the addition of hydrogen peroxide at a concentration of 10 mM increased the average degradation of pesticides to 57%.

This suggests that hydrogen peroxide can speed up photocatalytic degradation of pesticides from surface water, including dicofol,parathion methyl,Chlorpyrifos, 3,4-dichloroaniline, and hexachlorocyclohexane (HCHs) and endosulfan-sulphate.

The nanocomposite produced about 96.5% of the photocatalyic activity needed to remove herbicides of DDT from surface water when exposed to UV-vis lamp (Ismael *et al*.,2020). They stated that the TiO_2/GO/$CuFeO_4$ catalyst's has high adsorption performance and photocalaytst carrier separation efficiency were the reasons behind its good photocatalytic performance. *(*El-Saeid *et al.*, 2021) investigated pesticide photocatalytic remedation by photolysis and photocatalysis of TiO_2 (0.001 g/10 mL) on dieldrin and deltamethrin pesticides (2000 µg) were evaluated using UV/TiO_2 about 12 h at wavelength of 254 and 306 nm. The photolysis was more successful at 306 nm than

254 nm. TiO_2 (0.001 g/10 mL) was enhanced the degradation at both measured wavelength suggesting that might act as a catalyst for the breakdown of both pesticdes (El-Saeid *et al.*, 2021).

The five most common pesticides' photocatalytic degradation was investigated by (El-Saeid *et al.*, 2022) at wavelength of 306 nm, both in the presence and absence of 1% TiO_2 or ZnO photocatalysts with UV radiation. The findings demonstrated that all atrazine (OCP), Chlorpyrifos methyl, dimethoate, hepachloro and methomyl umder goes complete photolysis when exposed to UV light for 64- 100 h with TiO_2 photocatalyst demonstrating greater activity than ZnO.

2.8. Environmental and health impacts of pesticides

Pesticides uses affect crop quality and food safety in a several ways. It increases yield by keeping pests and illnesses, but it also damages most agricultural soils and natural ecosystems (Palma *et al.*, 2014). Pesticide poses a threat to both humans and the environment because of their extensive global use, which contaminates water, soil, and the atmosphere. Additionally, the degradation products produced by pesticides also spread throughout the ecosystem.

When surface water is utilized for human consumption, the increased susceptibility of water to pesticides in areas of intensive agriculture is a serious concern. To boost agricultural production, a variety of pesticides, frequently employed incultivating citrus, vegetable, and other crops region. These pesticides include those with organochloride, organophosphorus, carbamate, and pyrethroid molecules. Due to the usage of such synthetic compounds, food and fibre output has increased, and agricultural profits have increased(Tchounwou *et al*., 2002). However, their use has also been linked to several issues, such as health risks to people, the mortality of farm animals, and changes to the local ecosystem. These substances are frequently employed as herbicides, insecticides, and fungicides. In the food chain, they typically bio-accumulate, bio-concentrate, and bio-magnify.

Pesticides have been widely used in the environment, and as a result, they have poisoned water sources. According to reports from many environmental protection organizations across the world,

these compounds have disruptive qualities, and human exposure to or ingestion of them can have harmful effects on their health (Rezaei Kalantary *et al*., 2022). The prevalence of pesticides related illnesses and poisoning is greater in rular agricultural areas with inadequate work place safety regulations, little enforcement of laws about pesticides, poorly labelled pesticide containers, low literacy rates, inadequate facilities for washing protective clothing, and users who are unaware of the dangers of pesticides.

Pesticides effects on human health are a major concern. Long-term and short-term helath problems including cancer,neurological disorder, and respiratory problems can be brought by pesticide exposure. A person who work in agricultural areas are more likely to be exposed. Base on a combination of exposure assumption and result from pesticide analyses, health risk assessment were completed. The assumptions were made in light of US environmenta protection Agency recommendation: assumed body weight for children and adults are 10 Kg and 70 Kg respectively and there is 10% bioavailability rate and 100% maximal absorption rate. The Egyptian Institute of Food Technology's recommendations were used to determine water and food consumption rates (Tchounwou *et al.*, 2002). Children and pregnant women are more susceptible to the harmful effects pesticides since their bodies are still developing and may be more susceptible to those effects (Wigle *et al*., 2005; Blair *et al.*, 2014).

A survey on the safe application and mixing of pesticides revealed that 98.9% farmers did not wear glove, and 98.4% did not wear goggles or eye glasses. Additionally, 35% farmers never applied insecticides while wearing long pant and shoes. About 84% people felt uncomfortable when pesticides were being applied (Tchounwou *et al.*, 2002).

Pesticide exposure has been linked in numerous studies to harmful health outcomes, such as cancer, neurological abnormalities, and reproductive issues. For instance, a study indicated that agricultural workers who were exposed to pesticides had a higher risk of acquiring Parkinson's disease.the

journal of occupational and environmental medicine was published this study. Another investigation indicates, women who used pesticides at home had a greater risk of breast cancer (Joubert., 2019). In the State of Ceara, a lot of pesticides are utilized, although few studies have examined the possibility of water resource contamination (Sousa *et al.,* 2016).

2.9. Environmental and health impacts of pesticides in Ethiopia

Ethiopia is "water tower of Africa" since it has more than 96 rivers, over 12 significant swamps or wetlands, 4 crater lakes. The Rift Valley Basin contains the vast majority of the lakes. The total surface area of the man-made and natural lakes in Ethiopia is around 7500 Km^2, and most of the country's lakes are fish-rich. Since these smaller water bodies are more vulnerable to pesticide contamination than larger water bodies, the risk evaluated is focused on them.

The nation's surface water bodies and the current intensification of agricultural activities and pesticide consumption may be contributing to a rise in the risk that pesticide use poses to people and the environment.There is an increasing need to implement a science- based pesticides registration procedure that weeds out pesticides that are hazardous to people and the environment.

Pesticide risk reduction program- Ethiopia (PRRP-Ethiopia) is a collaborative endeavor on pesticide registration and post-registrations that aims to develop a dependable tool (Teklu *et al.,* 2015). The risk of evaluation was concentrated on these smaller water bodies since they are more susceptible to pesticide contamination than larger water bodies. (Muhammed, 2016). Its goal is to create a trustworthy instrument.

According to survey conducted on small-scale farmers' use and management of pesticides , 60% of participants were not aware that pesticide runoff and drift could potentially contaminate adjacent surface water.The majority of farmers (91%) mixed and washed chemical container near rivers or canals, and 71% did not spray pesticides at a safe distance from them.

In the last five years, 82% increased pesticide applications and 67% of them cited insect resistance as the primary cause. (Teklu *et al.,* 2016). According to a related study, farmers used hazardous storage facilities during applications in unsafe manner.Farmers also sprayed pesticides contrary to standard recommendations. The same study discovered that 88% of farmers had increased their usage of pesticides over the previous five years,(Mengistie *et al*., 2016). According to a study on water samples from Jimma and Addis Ababa, 2,4 –D means concentration respectively, ranged from 0.11 to 138 g/l and 1.59 to 13.90 g/l. The same analysis found that some of the pesticide residual levels were excides the Europeans drinking water guidelines (Negatu *et al*., 2016 ; Teklu *et al.*, 2015; Van den Brink *et al.,* 2016).

3. Materials and Methods

3.1. Description of the study area

Ziway Lake is Found in the central Rift valley (CRV) of East show zone Oromia and covers an area of 7148 km^2, failing between gradients of $7^0$22’36’’N and $8^0$18’21’’ N latitude and $37^0$53’40’’E and $39^0$28’9’’E longitude. Ziway Lake is 168.2 km far away from Addis Ababa in the south from the capital city of Ethiopia as shown on Figure 1. It is the water that comes from the Meki River, Bulbula River, Ketar River and agricultural farm runoff.

The Land use record shows that, the area of irrigated agricultural runoff in the Lake catchment has increased. Along its catchments, the Lake is subject to pollution from non-point sources of pollutants. It includes under the pressure of pesticides and nutrient pollution due to agricultural activities and urbanization.

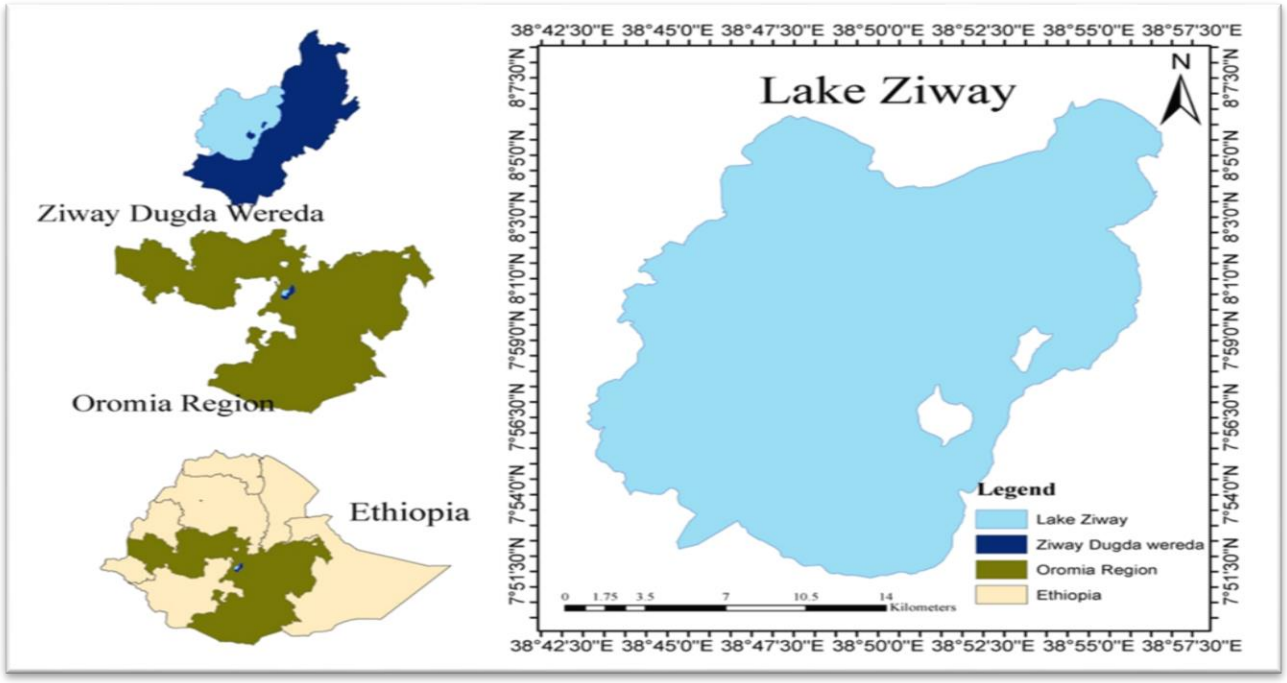


Figure 3 Ziway Lake surface water Study Area

3.2. Chemicals

Laboratory graded commercial including Titanium dioxide (TiO_2 98% BDH Chemical Ltd Poole, England), hydrogenperoxide (H_2O_2 (98% BDH Chemical Ltd Poole England), sodium hydroxide pellets NaOH 98% Himedia Laboratory Pt; India), hydrochloric acid (HCl RFCL limited new Delhi-India), Sulfuric, acid (H_2SO_4 98.0%, Lobal chemical-India), Acetonitrile, methanol (all HPLC grade. and Dichlorophenoxyacetic acid (2,4-D, 99% Tianjin chemical reagent-China) were used for this investigation (Carbajo *et al.*, 2014) and additionally copper oxide (CuO), Copper (II) acetate, Clay soil and 2,4-D pesticides were used without any further treatment.

3.3. Instruments

Polyethene bottles , Drying Oven (mode GX65B), SHO-2D Wise shaker, SX-2.5-10 muffle furnace, EFA-6UDRVW-8 Hood, JENWAY 3510 pH meter, 65FT-IR (PerkinElmer), High-pressure liquid chromatography (HPLC), Scanning electron microscopy (SEM), X-ray diffraction (XRD), UV reactor and FT-IR were used during this thesis work.

3.4. Sample collection

Surface water collection system was based on the spatial changes in the water stream and irrigation system, the ability to collect a representative sample of the particular water, water samples were collected from Zeway Lake in the site of Bulbula River because of agricultural runoff and Industrial waste from Adami tulu pesticide factory. Clay soil was collected from Addis Ababa –Asko Area.

Figure 4 Collections of Surface water, pesticide factory effluent and Clay soil collections.

3.5. Experimental Setup

3.5.1. Purification of Clay soil

The collected Clay soil was dried it for 30 min (Dry oven GX-65B), ground (Nima Japan NM-8300) and passed through 0.5 mm sieve (ISO 3310-1) (Tarekegn *et al.,* 2022). The grinded clay soil was dispersed in hydrogen peroxide solution for 20 min at 30^0 to remove organic carbon. Oxidations of soil organic matte occurred during H_2O_2 reactions with clay soil and the pH content had significant impact on the breakdown of organic matter. Therefore, the degree of oxidation was low at high pH and under acidic conditions up to 90% of organic matter was removed (R.E.Redmann., 1978). Subsequently, the suspensions were evaporated and allowed to cool. Slurry was then rinsed with acidified distilled water (pH 4), while being continuously shaken at 300 rpm (Wise shaker, SHO-2D) for 30 min to eliminate any remaining inorganic carbon. Finally, it was settled for 3 h. After carefully removing the floating materials and supernatant from settled nano-clay, the remaining was transferred to 500 mL beaker and dried at 105^0C overnight. And it was grinded for 5 h in ball mill.

Figure 5 Preparation steps of Clay soil images

3.5.2. Synthesis of TiO_2-CuO-Clay soil composite

Following the processing of clay soil, TiO_2-CuO-Clay soil composite was synthesized. Afterwards, two procedures were taken to synthesize photocatalyst TiO_2-CuO-Clay soil composite oxide systems. First, 5% Copper (II) acetate aqueous solution was prepared. The two different concentrations of composites were prepared by using different grams of TiO_2, CuO and Clays soil of 2 g of TiO_2, 3 g of CuO and 7 g of clay soil and for the second composite 4 g of TiO_2, 3 g of CuO and 5 g of Clay soil were respectively dissolved 25 mL 5% aquous solutions of copper (II) acetate. Additionally, 2 g of poly (ethylene glycol) (PEG) was added to it. PEG was used as a modifier to strengthen the bond between the prepared composite.

The ratio of TiO_2: CuO:Clay soil composites of different concentrations were 2:3:7 and 4:3:5. According to report by (Miguel et al., 2012; Asmael *et al.,* 2020) , the degradation efficiency of catalysts increases from 57% to 96.5% with increasing concentrations of TiO_2 from 1 g/L to 5 g/L. as the concentrations of TiO_2 increase the degradations efficiency of catalysts increases from 1 g/L of TiO_2 (57%) to 5 g/L TiO_2 (96.5%). The resulting solution was put on magnetic stirrer and 1 M of sodium hydroxide solution was added to adjust the pH of TiO_2-CuO-Clays soil oxide to 12.

Lastly, the mixture was treated with by microwave for 10 min at 105^0C with power of 300 W(SP-D80, CEM). The synthesized oxide system was washed three times with deionized water, filtered, dried at 70^0C for 7 h. The treatment was done according to (Kubiak e*t al*., 2020 ; Tarekegn *et al.*, 2022) report.

Figure 6 Synthesize of TiO_2 -CuO-Clay soil composite

Table 1 Composition rations of TiO_2-CuO-Clay soil composites

1st Composite of TiO_2-CuO-Clay soil composites			
Catalysts	TiO_2	CuO	Clay soil
Quantity in grams	2	3	7
In per cent	16.7%	25%	58.33%
2nd Composite TiO_2-CuO-Clay soil composites			
Catalysts	TiO_2	CuO	Clay soil
Quantity in (g)	4	3	5
In percent	33.33%	25%	41.7%

The UV-vis measurements was conducted by using Shimadzu UV-vis spectrophotometer and the band gap energy was calculated using kubelka-Munk equation(E_g=1240Ev/ λ) from reflectance spectra (Muzakki *et al.,* 2016). Based on the experimental result of 2,4-D degradations, TiO_2-CuO-Clay soil nanocomposite had the best photocatalytic for UV-vis photocatalytic degradation of 2,4-D, when TiO_2, CuO and Clay soil was synthesized with a molar ration of 4:3:5 and calcined at the temperature of 720^{o}C for 6 h. Furthermore, the TiO_2-CuO-Caly soil photocatalytic performance, SEM,XRD,FTIR,XRD, band gap energy and functional group were demonistrated vial equation 1.

E_g=1240Ev/ λ …….equation 1.

E- the band gap energy which is the difference between the valance band and the conduction band of solid material

λ - Is wavelength

1240 – Constant number

The percentage degradations of 2, 4-D was calculated by:

$$R\ (\%) = \left(\frac{C_o - C_t}{C_o}\right) * 100\%$$

Where A_o and A_t were the initial and final concentrations at a particular time respectively. The photocatalytic activity of TiO_2-CuO-Clay soil composite were compared with different ratios of photocatalysis under UV irradiatio.

3.6. Photocatalytic degradations of 2,4-D Experiment

The prepared TiO_2-CuO-Clay soil composite 2 g was measured and mixed with 1 L of polluted water for UV treatment. The UV lamp light was shined on the prepared sample to breakdown the molecules of pesticides and then, the sample was filtered. Finally the sample was analyzed by HPLC to know the concentrations of the 2,4-D after photocatalytic treatment as.

Figure 7 Sample preparations for HPLC analaysis

CHAPTER FOUR

4. RESULTS AND DISCUSSION

To achieve the aim of this research work, the experiments were carried out according to the methodologies stated in the previous chapter. The findings of the experiment were presented in this chapter characterizations of the synthesized composites, kinetics, degradation efficiency of TiO-CuO-Clay soil composite and optimization conditions of catalyst molar ratios and also includes the discussions of other related research that have been reported.

4.5. Purification and characterizations of TiO_2-CuO-Clay soil composite

4.1.1. Effect of Calcination Temperature on photocatalytic degradations of 2, 4-D

The UV-Vis photocatalysis of TO_2-CuO-Clay soil composite was calcined at 720^oC for 6 h. The calcination temperature leads to the change of catalyst's crystalline structure, particle size and surface morphology. A high calcination temperature could lead to improved crystallinity and better photocatalytic activity, an unnecessarily high temperature might result in particle agglomeration and reduced performance. Therefore, the optimal combinations of molar ratios and calcination temperature needs to be carefully selected to achieve the desired photocatalytic degradation performance.

4.5.2. XRD analysis

Using the X-ray diffraction methods, the crystalline structure of TiO_2-CuO-Clays soil composite was examined. Figure 8 indicates XRD analysis result and the substance exhibited crystalline properties of TiO_2-CuO-Clay soil composite with molar ratio of 4:3:5 in A at $2\theta = 15^o$, 25°, 38°, 42°, 49°, 50°,55° and 55° With corresponding peaks of (445), (450), (510), (750), (860) and (1290).

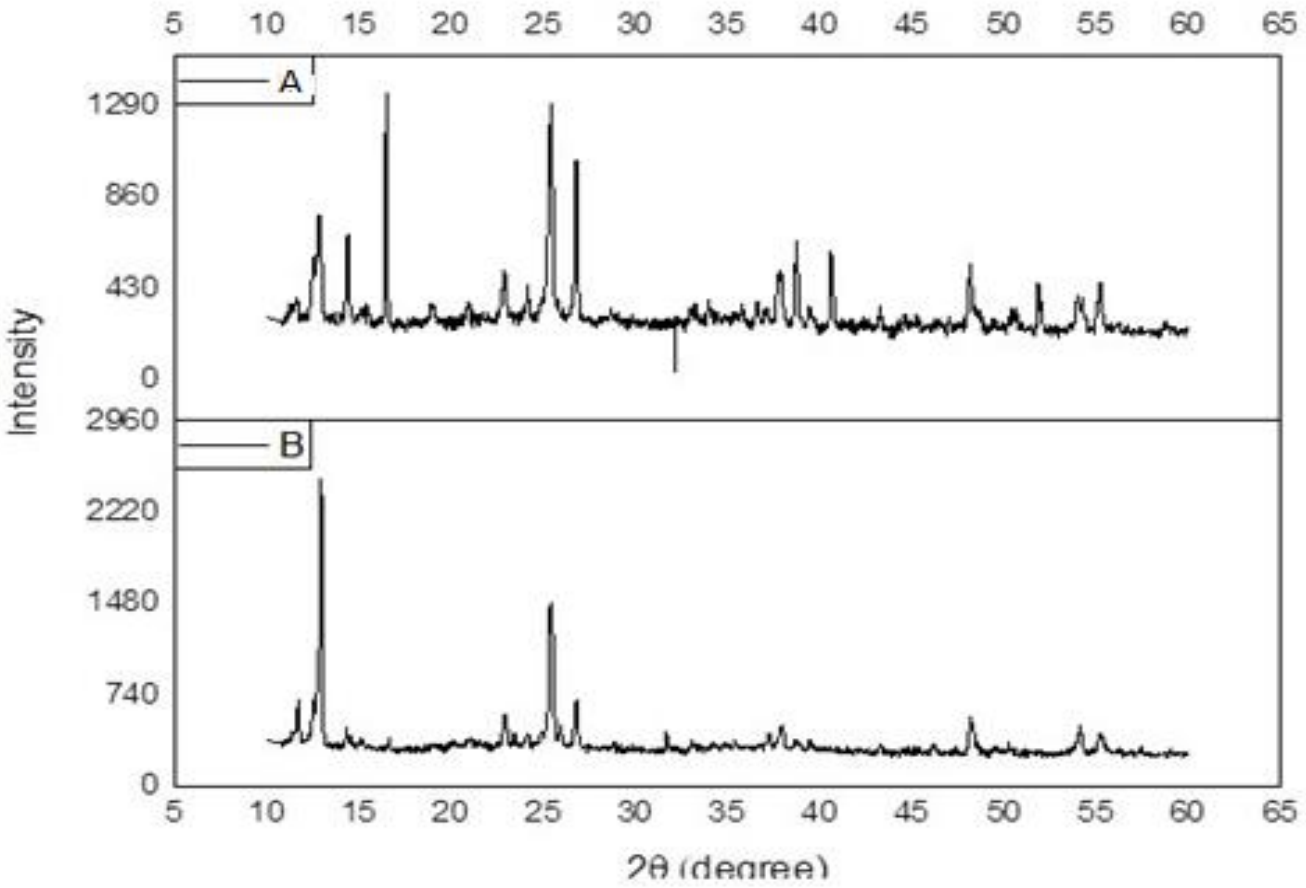


Figure 8 X-ray Diffraction of TiO_2 -CuO-Clay soil composite catalyst

But the crystalline properties of TiO_2-CuO-Clay soil composite molar ratio of 2:3:7 in B at $2\theta=13^oC$,26^oC,48^oC, 54^oC and 56^oC with corresponding peaks (600),(700),(1480) and (2520).

The materials' current crystalline orientation was revealed by the increasing intensity seen on peaks (Kuiak *et al.*, 2020). The XRD result shows that the composite samples confirm the presence of TiO_2-CuO-Clay soil crystallites. The prominent peak pattern seen for the composite materials was

mainly caused by the amorphous. The TiO_2-CuO-Clay soil composites' purity and crystallinity are demonstrated by the sharp peak of XRD, which is notable for its high intensity and use in determining crystal size.The average crystalline size was calculated by Scherer equation ($D=K\lambda/B\cos\theta$) and the TiO_2-CuO-Clay soil composite diffraction peak with highest intensity has 8.29 nm. The crystalline size reported by (Nithyadevi *et al.,* 2015) was in range from 8 to 37 nm which related with the crystalline size of TiO_2-CuO-Clay soil composite.

4.1.2. **SEM analysis**

SEM imaging techniques were employed to determine the catalysts' particle morphology. The SEM used to examine the morphology of the produced composite was a field emission High-vac. SED PC-std. 15kV x 200 (44mm). The SEM image of the TiO_2-CuO-Clay soil composites as they were created was shown in Figure 9. The represented by A is the particle molar ratio 2:3:7 and in B is 4:3:5 catalyst molar ratio.The TiO_2-CuO-Clay soil composite powder was scanned using a scanning electron microscope (SEM), and the grain sizes in A and B were 20 µm and 10 µm, respectively. Additionally, the images reveal details about the electrocatalyst's surface structures, and Figure 9. (a) Displays the SAED of TiO_2-CuO-Clay soil composites as they have been created. Both images demonstrated the particles' strong crystallization (Dong *et al.,* 2017).

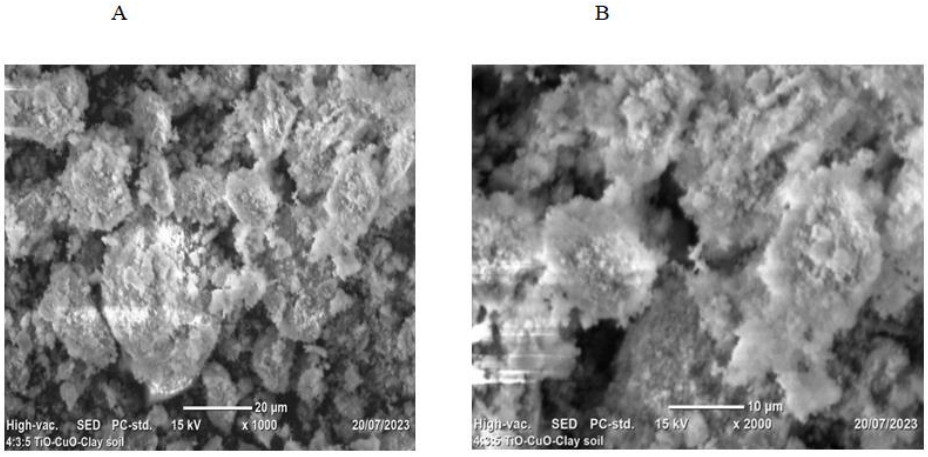


Figure 9 SEM image of the synthesized TiO_2 -CuO-Clay soil Nano composite.

4.1.3. ***FT-IR analysis***

The measurements using Fourier Transform Infrared (FT-IR) were performed to confirm the effectiveness of the molecular imprinting process and the FT-IR spectrum ranges 4000-400 cm^{-1} was

used for characterizations of the crystal phases of synthesized oxide as indicated on Figure 10. Both have comparable traits and patterns, with the exception of green line (2:3:7) shorter than the blue line (4:3:5) but less pronounced at the green line (2:3:7) 3200-3600 cm^{-1}. The stretching vibration of the O-H (metal hydroxyl or the hydroxyl of water molecules of crystallization) is responsible for the broad band at 3200-3600 cm^{-1} in both catalyst molar ratios of 2:3:7 and 4:3:5.

The bending vibrations of O-M-O (O-Ti-O or O-Cu-O) are attributed to the bands between 600 and 800 cm^{-1} blue and green lines which represent 4:3:5 and 2:3:7 catalyst molar ratios respectvely, while M-O (Ti-O or Cu-O) vibrations are typified by the bands between 400 and 600 cm^{-1} for the catalyst molar ration 2:3:7 which represented by green line. This results related with the articles reported by (Etape *et al.*, 2017; Zafar *et al*., 2020).

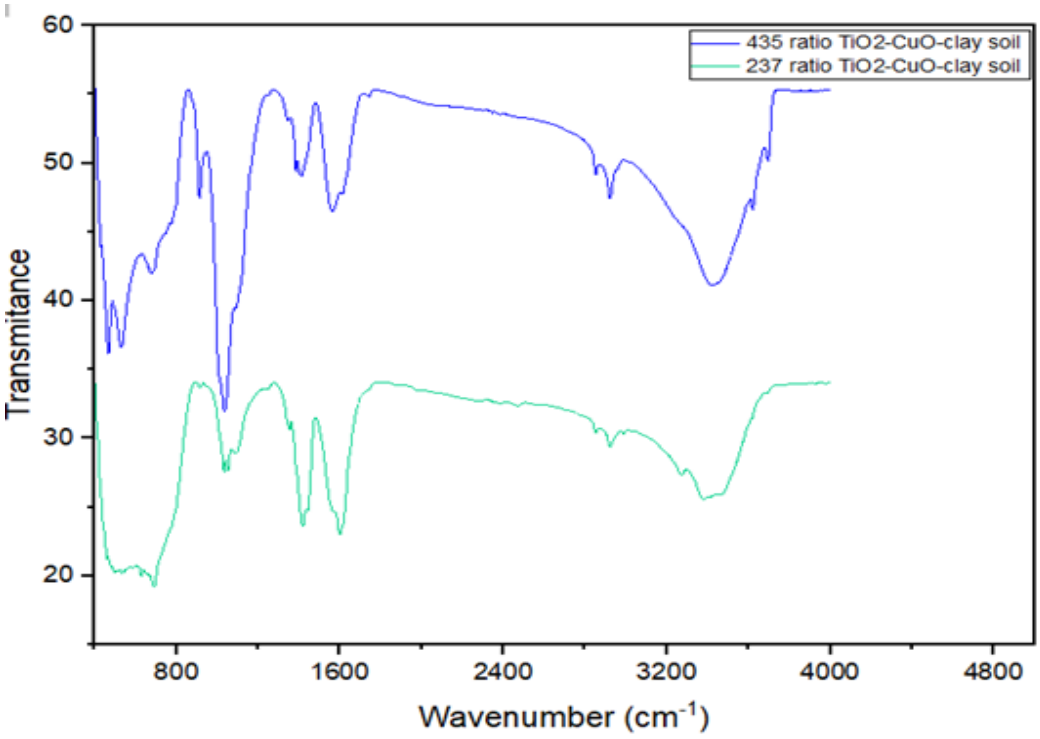


Figure 10 FT-IR characterizations of TO_2-CuO-Clay soil composite

4.2. **UV-Vis analysis**

As shown on Figure 9. the UV-vis absorption peak of TiO_2-CuO-Clay soil composite with core-shell particles situated approximately at 350 nm. Other studies indicate that the center of the UV-vis

absorption peak core-shell particles is around 375 nm. According to (Zandsalimi *et al., 2020*), a study indicates that the absorbance of Crystalline nanoparticle is considerably lower than the nanoparticles' surface of Plasmon resonance. The significant effect absorption in the UV-vis spectrum shifted from 450 to 350 nm reported in related literature (Yang *et al.,* 2014). This is probably because the surface of the CuO and Clay soil particles are densely coated with TiO_2, which has a strong absorption in the UV-visible region.

The absorption spectra of UV-vis for TO_2-CuO-Clay soil composite (2:3:7 and 4:3:5 ratios) are between 150 nm and 450 nm. The higher light absorbance of TO_2-CuO-Clay soil composite was observed at a maximum wavelength of 350 nm. The TiO_2-CuO-Clay soil has the potential to be excited by longer wavelength radiations in the visible range and can be used effectively for UV-Vis photocatalysis.

Table 2 UV-vis Absorbance and wavelengthlength TiO_2-CuO- Clay soil composites.

Ratio of TiO_2-CuO-Clay soil	Absorbance	Transmittance	Wavelength (nm)
2:3:7	0.09 $\pm$ 0.012	64 $\pm$ 0.23	150
	0.094 $\pm$ 0.30	63 $\pm$ 0.11	250
	0.095 $\pm$ 0.20	62.5 $\pm$ 0. 30	350
	0.097 $\pm$ 0.31	62.10 $\pm$ 0.25	450
4:3:5	0.190 $\pm$ 0.40	89 $\pm$ 0.85	150
	0.191 $\pm$ 0.31	90 $\pm$ 0.20	250
	0.194 $\pm$ 0.51	90 $\pm$ 0.56	350
	0.197 $\pm$ 0.31	82 $\pm$ 0.35	450

According to the band gap energy equation, the sample's band gap energy was estimated at 3.54 eV which is higher than the band gap energy of TiO_2 (3.2.eV). Higher band gap energy justfies the solar

photocatalytic activity of TiO_2-CuO-Clay soil composites as shown in Figure 11 in terms of photocatalytic degradations of 2,4-D from polluted water.

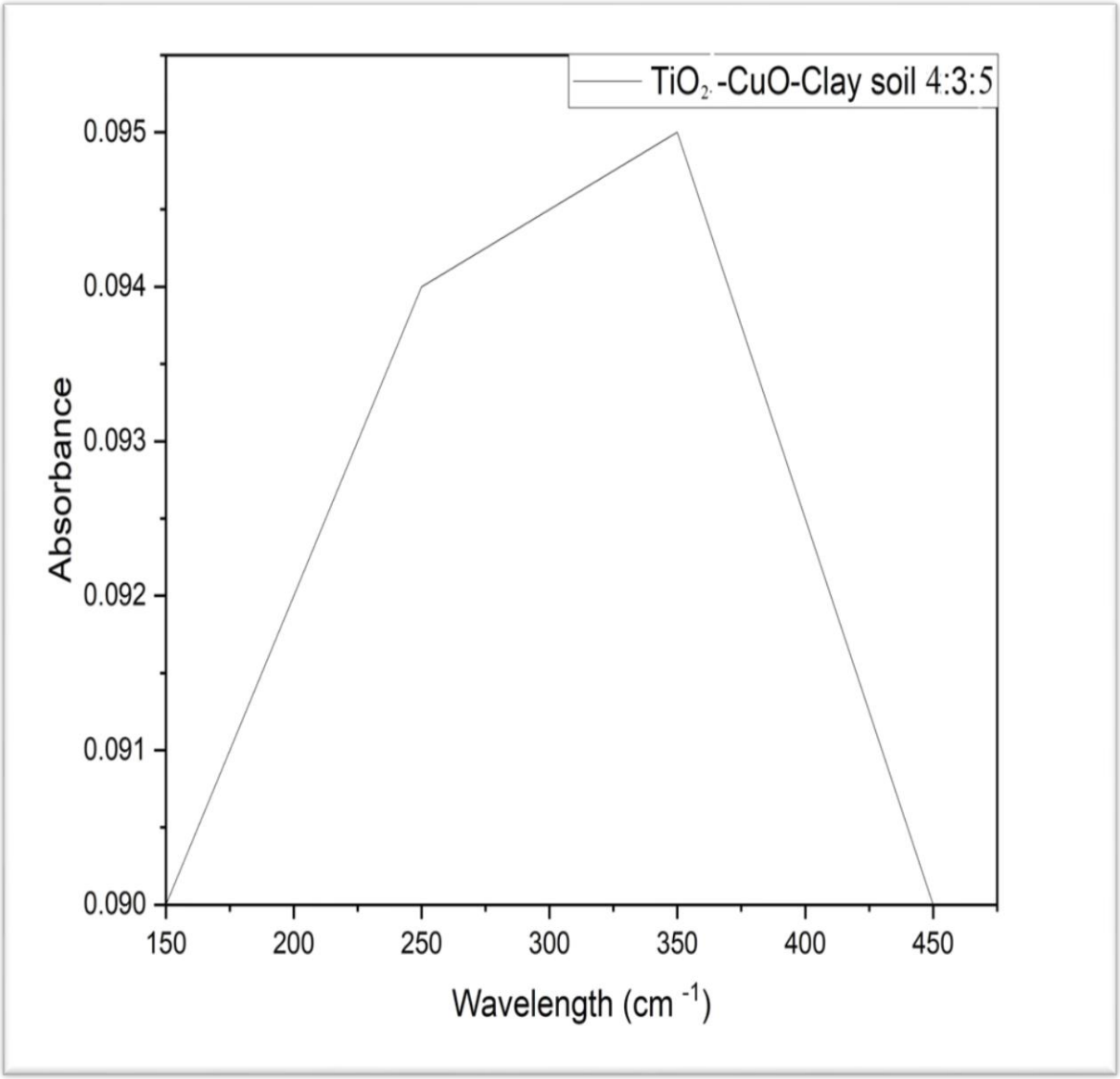


Figure 11 UV-vis spectra for TiO_2-CuO-Clay soil composites

4.2.1. Effect of contact time

In order to examine how irradiation time affects the effectiveness of photocatalytic degradation of pesticide, the procedure of sample with an ideal pH solution and nanoparticle concentration, doped nanoparticle and ultraviolet light was exposed at optimal light intensity (Zandsalimi *et al.*, 2020).

At pH 4, the concentration of impurities was 35.10 µg/L and 157.63 µg/L for surface water and industrial waste respectively and the efficiency of the process improved when exposure time increased to 2, 5, 7 and 9 h. It was noted that the removal efficiency increased constantly by 9 h. These phenomena may be caused by pesticides concentrations that are periodically reduced and the increase of free radical generation when the exposure time increases and this leads the pesticide metabolites to be oxidized. In addition, the stability and chemical makeup of pesticides can affect how long it takes.

The effect of the catalyst injected on variations of time, the degradations of 2, 4-D under UV-vis spectroscopy Lamp and the highest degradations were seen at 9 h of irradiations times. Table 3 A and B show that the per cent degradations of 2,4-D increase as irradiation time increases from 94.40 to 95.38% and 96.94 to 98.72% respectively for surface water and industrial wastes from pesticide factories with constant catalyst dose. The same is true for B (4:3:5 ratio) the degradations of 2, 4-D increase from 95.18 to 96.20% and 97.9 to 99.84% respectively with irradiation time.

Table 3 the change of concentrations of 2, 4-D by Catalyst dose ratio A (2:3:7) B (4:3:5).

(A) Effect of irradiation time for 2:3:7 ratio

Irradiation time (h)	Degradations of 2, 4-D from Surface water (%)	Degradations of 2, 4-D Industrial waste (%)
2	94.4	96.94
5	94.58	97.16
7	94.87	98.49
9	95.38	98.72
(B) Effect of irradiation time for 4:3:5 ratio		
2	95.18	97.90
5	95.27	99.10
7	95.49	99.58
9	96.20	99.84

4.2.2. Effect of molar ratio

The result shown in Table 3, the percentage degradations of 2,4-D by TiO_2-CuO-Clay soil composite was effectively degraded by 4:3:5 catalyst molar ratios were 96.20%) and 99.84%) respectively form surface water and Industrial waste respectively. The degradation efficiency of TiO_2-CuO-Clay soil composite was increased by increasing catalyst molar ratios with the increasing irradiation times and catalytic molar ratio.

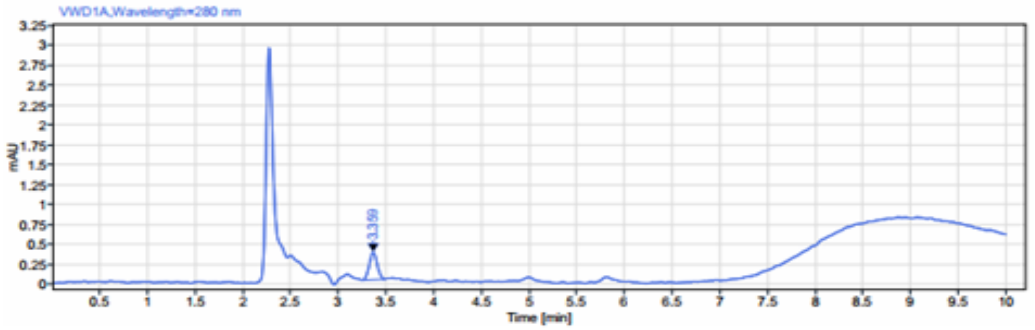
The molar ratio of 4:3:5 synthesis mixture and constant calcination temperature 720^0C were optimum conditions for 2, 4-D photocatalytic activities of degradations under UV-vis spectroscopy light irradiations. For this case, the 4:3:5 molar ratio of TiO_2-CuO-Clay soil composite at a calcination temperature of 720^0C was further used for photocatalytic degradations of pesticides from the surface and industrial waste. As reported in Literature, the rate of pesticides degradation

increased in proportion to the mass of the catalyst and the optimal amount, expressed as a gram of catalyst per liter of solution was equivalent to 2.5 g/L as reported (Herrmann & Guillard., 2000).

4.2.3. Effect of surface and Industrial waste Concentration

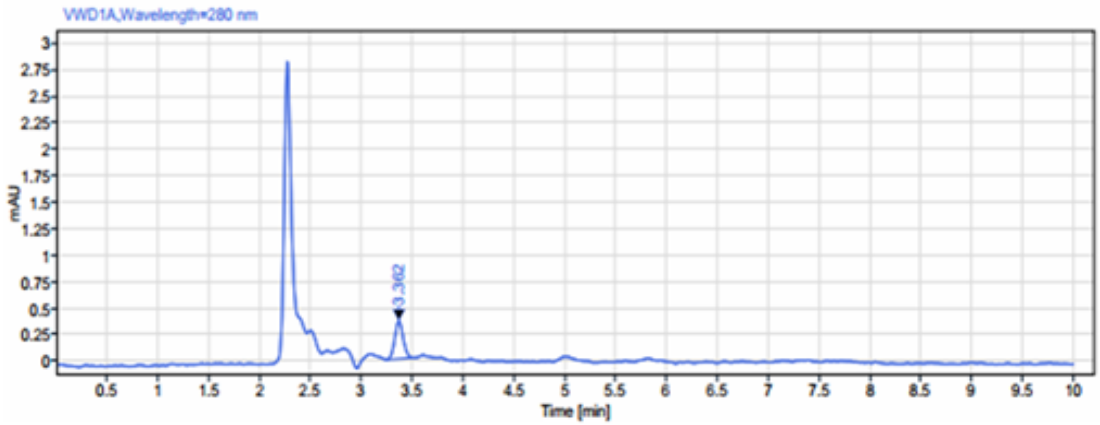
The effect of 2, 4-D concentration with constant catalyst dose of 2 g, was the major factor with the irradiation time for degradations of pesticides from contaminated water. The degradations of 2,4-D concentrations after 9 h of irradiation time was dramatically recorded and decreased from 35.10 µg/L to 1.62 µg/L and 1.34 µg/L as shown on Figure 12 from surface water with catalytic dose 2 g with the ratio of (2:3:7) and (4:3:5) TiO_2-CuO-Clay soil composites respectively.

(A)



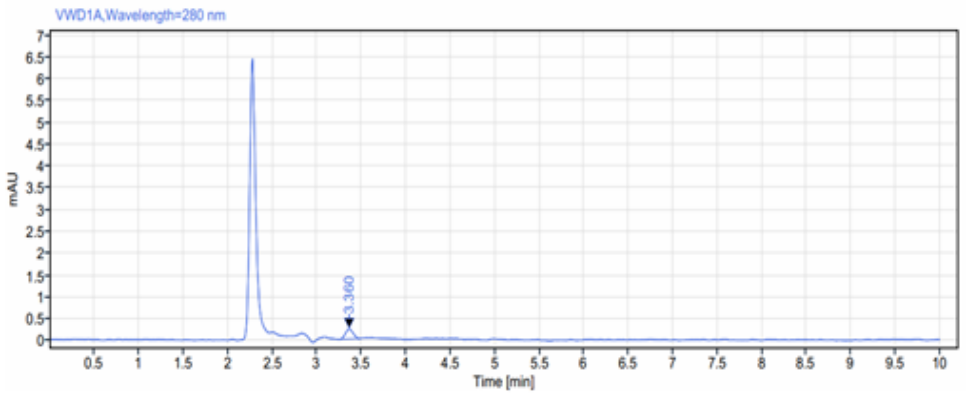
Concentrations of Surface water (35.10 µg/L)

(B)



Analysis result with 2:3:7 ratio (1.62 µg /L) after (9 h)

(C)

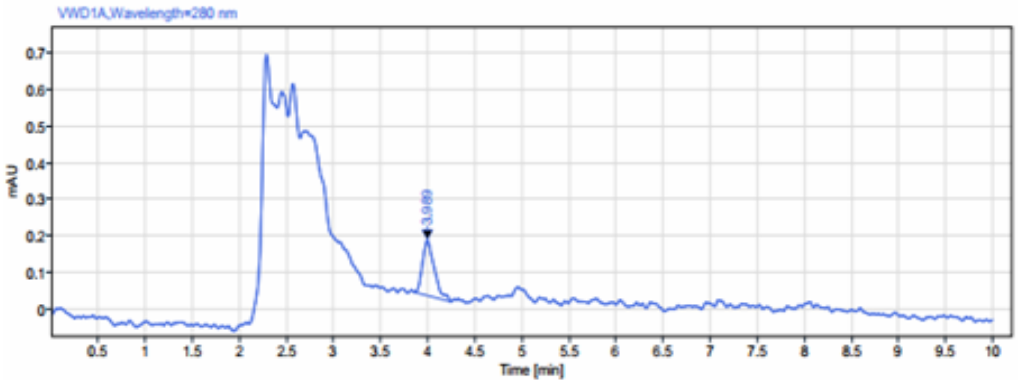


Analysis result with 4:3:5 ratio (1.34 µg/L) after (9 h)

Figure 12 (A, B, C) concentrations of 2, 4-D degradations of surface water

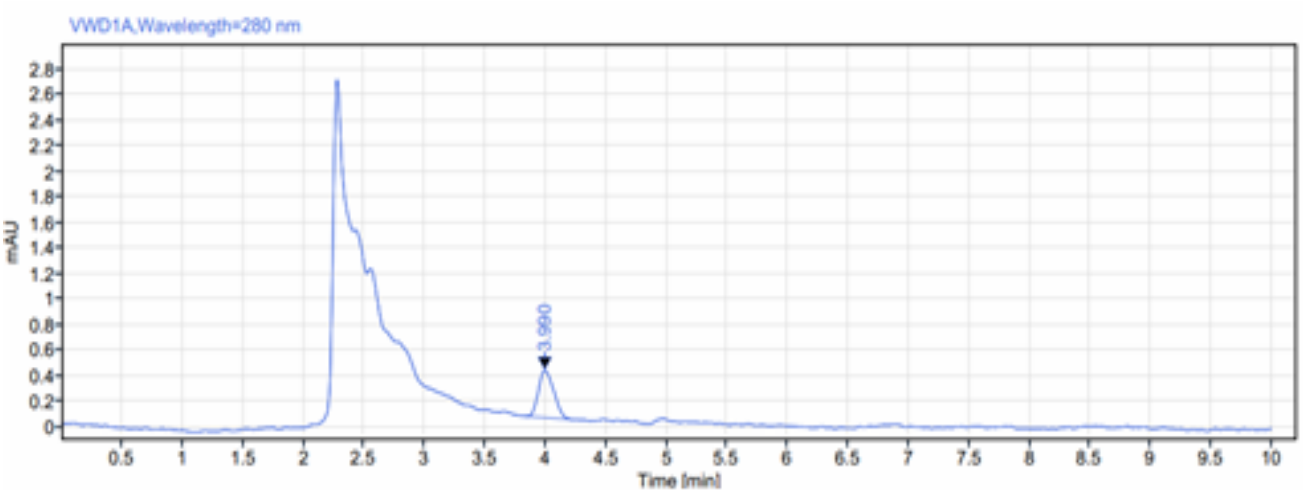
The same was true for Industrial wastes taken from the pesticide factory and the concentrations of 2,4-D decreased from 157.63 µg/L to 2.01 and 0.24 µg/L as indicated in Figure 12 with catalytic molar ratios of 2:3:7 and 4:3:5 respectively. It is noticeable that, the decrease in the initial concentrations of 2,4-D leads to a significant improvement in the efficiency removal of pesticides. So in contrast with the initial concentrations of 2, 4-D, the concentration was decreased from 35.10 to 1.34 µg/L and 157.68 to 0.24 µg/L from Surface water and industrial waste respectively.

A



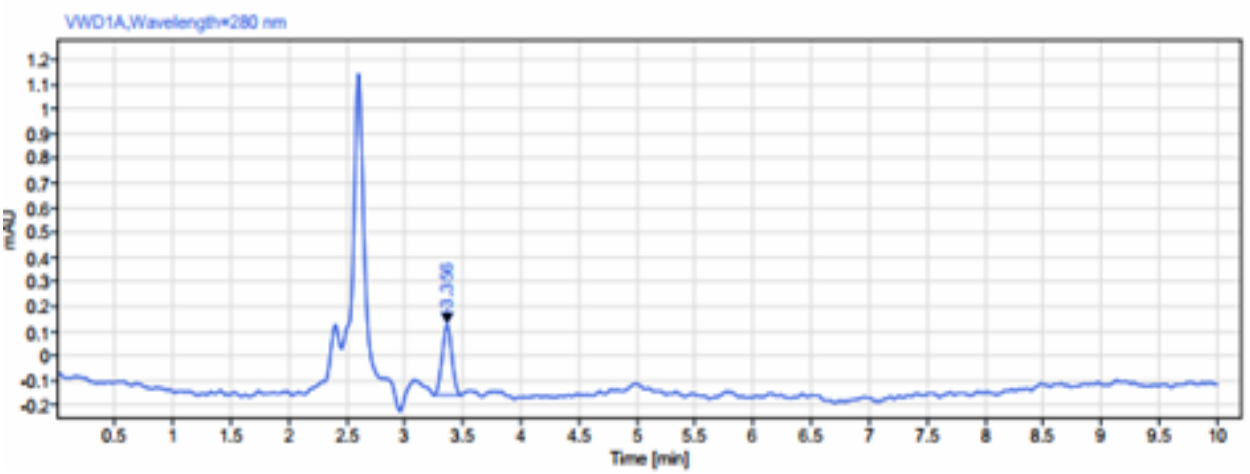
Concentrations of Industrial waste (157.63 µg/L)

B



Analysis result with catalyst 2:3:7 (2.01 µg/L) after (9 h)

C



Anaysis result with 4:3:5 (0.24 µg/L) after (9 h)

Figure 13 Pollutant concentrations of 2,4-D during photocatalytic degradation of Industrial waste

4.3. Kinetics of TiO2-CuO-Clay soil photocatalytic degradations of 2,4-D pesticide

In this research work, the kinetics of 2,4-D removal by TiO_2-CuO-Clay soil composite was conducted using first order kinetic models.

Table 4. First order kinetic model for degradation of 2,4-D by TiO_2-CuO-Clay soil

Time (hr.)	C_o (µg/L)	C_f (µg/L)	$Ln(C_o/C_f)$
2	157.63	4.82	3.4
5	157.63	4.47	3.6
7	157.63	2.37	4.2
9	157.63	2.01	4.4

The photocatalytic degradation of 2, 4-D was carried out with initial 2,4-D concentration of 35.10 µg/L and 157.68 µg/L respectively for surface and industrial waste and the catalyst loading was 2.0 g. The result of kinetic parameters are shown in Table 4 and Figure 12 demonstrates that, the degradation rate of 2,4-D confirmed with Pseudo-first–oerder kinetic model. This result was matched with pseudo-first-order kinetic for 2,4-D degradation reported by (Amiri *et al.*, 2021). The kinetic studies of the absorption and degradation phenomena involved in the photocatalytic degradation of 2,4-D were studied using batch reactor and UV irradiation.

Many researchers (Khanna & Shetty., 2014; Mohammadi-Aghdam *at al.,* 2014 ; Jawad *et al.,* 2016 ; Boutra *et al.,* 2021) have employed the modified Langmuir-Hinshelwood (L-H) kinetic expression to successfully investigate the heterogeneous photocataytic reaction kinetics. To correctly characterize the solid-liquid reaction, the data from solar Photocatalvsis experiments carried out under ideal reaction conditions have been justified in terms of a modified L-H kinetic model.

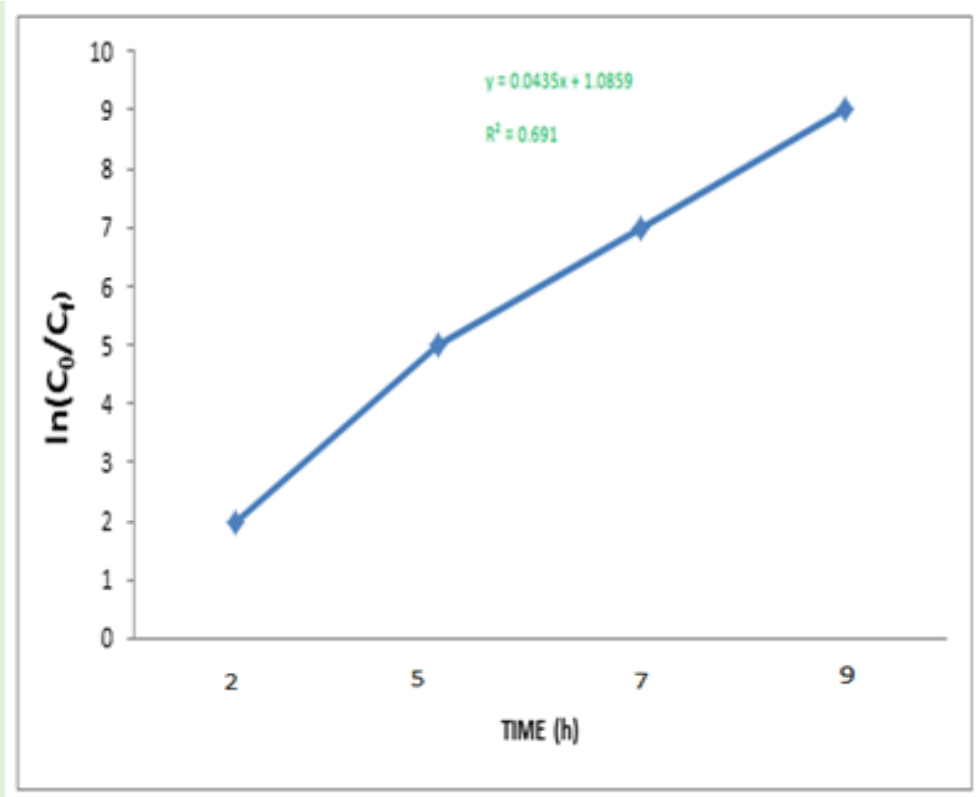


Figure 14 kinetics of 2, 4-D degradation by TiO_2-CuO-Clay soil composite

4.4. Comparison of Photocatalytic activities ratio

Photocatalytic activity of material was typically measured by monitoring the rate of 2,4-D degradation, that exposed to UV-Vis light in the presence of the photocatalyst. The comparison of photocatalytic activities of different molar ratios of the same catalysts was expressed in terms of their reaction rates and degradation efficiencies.

During UV, the photocatalytic degradation efficiency of TiO_2-CuO-Clay soil composite, the degradation of 2, 4-D with an initial concentrations of 35.10 µg/L and 157.68 µg/L from surface water and industrial waste with catalyst loading of 2 g were compared respectively. As shown in Figure 14, when TiO_2-CuO-Clay soil (2:3:7) compared with TiO_2-CuO-Clay soil (4:3:5) ratios of composites, TiO_2-CuO-Clay soil with catalyst molar ratio (4:3:5) was the most effective photocatalysts for degrading 2, 4- D.

The Overall degradation of 2,4-D in the presence of TiO_2-CuO-Clay soil catalyst took place at 9 h and its efficiency was 99.84% from industrial waste. We can conclude that TiO_2-CuO-Clay soil photocatalyst has high degradation efficiency with 4:3:5 catalytic ratio than 2:3:7 of TiO_2-CuO-Clay soil composites. According to (Tammy *et al.,* 2018) report, the degradation effect of photocatalysts on their degradation efficiency of TiO_2 and ZnO for the degradation of 2, 4-D was around 85% and this indicates that it has less removal efficiency than 99.84% of TiO_2-CuO-Clay soil composites.

4.5. Degradation efficiency of TiO_2-CuO-Clay soil composite in surface water and industrial waste

To confirm that the photocatalytic process and the removed 2, 4-D from surface water and industrial waste, the experiment were conducted under the operational conditions of UV-vis light, HPLC analysis and TiO_2-CuO-Clay soil composites catalysis. During this test, a 150 W xenon arc lamp with wavelength of 280 nm was shined on the sample used as a UV-vis spectroscopy radiation source. The injection volume, capillary column Agilent, and pressure of 9.3825 psi and 80 ^{0}C were 1.0 mL and 30m x 250 mm x 0.25 mm respectively.

The TiO_2-CuO-Clay soil composite doped was efficiently degraded the concentrations of 2, 4-D pesticides to 1.34 µg/L and 0.24 µg/L from surface water and industrial waste in 9 h irradiation time respectively. The reason for enhanced photocatalytic degradation of 2, 4-D in UV/TiO_2-CuO-Clays soil system may be due to the collisions of light-emitting photons with UV-vis and electrons in the semiconductor power layer increasing the electron energy. This may be due to the energy transfer of the conduction band being greater than the membrane capacity, which can lead to the generation of positive holes and negatively charged electrons, which are released and can under goes reaction (Fiorenza *et al.,* 2020; Zandsalimi *et al.,* 2020).

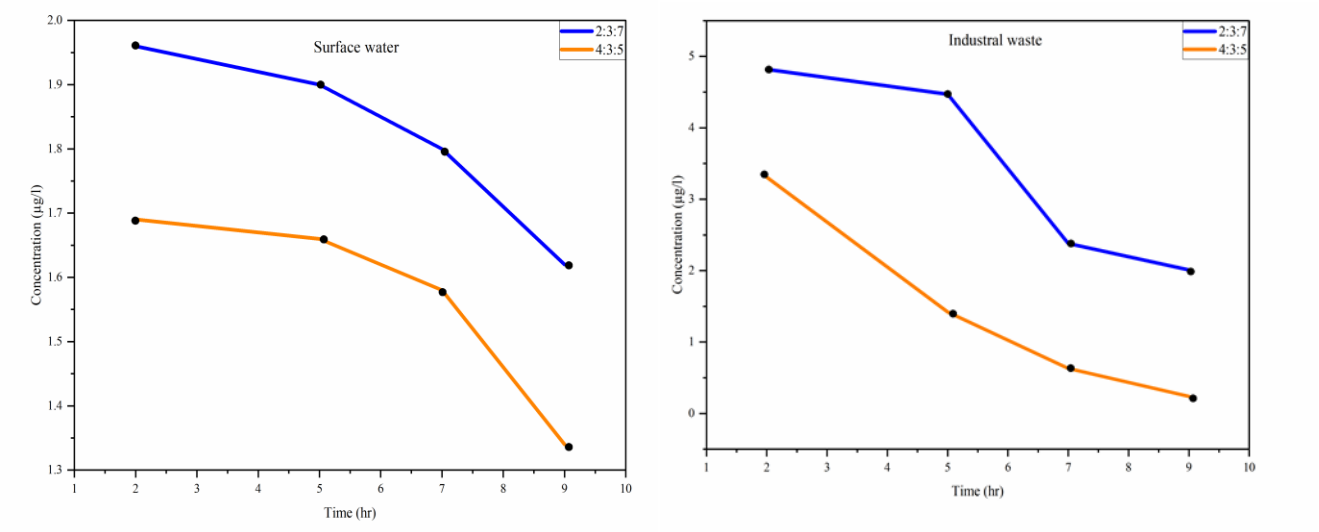


Figure 15 Photo catalytic degradation efficiency of TiO2-CuO- Clay soil composite

The degradation of pesticides from surface water was effective with the photocatalysis of TiO_2-CuO-Clay soil composites. The catalysts used were efficiently removed 2, 4-D from surface water and industrial wastes of pesticide factory effluent. The concentration of pesticide under investigation is listed in Figure 15 with the concentrations of tested samples with different irradiation times and the final concentration following photocatalytic treatments.

During UV-vis light, the photocatalytic degradation efficiency of 2,4-D pesticides from surface water and real factory effluents, and the degradation efficiency of TiO_2-CuO-Clay soil composite photocatalysts were compared. As stated earlier, the concentrations of 2,4-D were of 35.10 µg/L and 157.63 µg/L from surface water and pesticide factory effluent with a catalyst loading dose of 2 g, were respectively degraded. The catalytic molar ratios of 2:3:7 and 4:3:5 TiO_2-CuO-Clay soil composites, the ratio of (4:3:5) TiO_2-CuO-Clay soil composite was more effective Catalysts for degrading 2, 4-D. The overall degradations of 2,4-D in the presence of TiO_2-CuO-Clay soil catalyst took place 9 h and its efficiency was 96.18 and 99.84% from surface water and industrial waste in respectively with wavelength of 280 nm. Therefore it is possible to say that, Photocatalytic

degradations of 2, 4-D from surface water and real pesticide effluent by TiO_2-CuO-Clay soil composite and UV-vis spectroscopy is efficient.

CHAPTER FIVE

5. Conclusion and Recommendation

5.1.Conclusion

The degradation of pesticides from surface water and Industrial wastewater has been extensively researched on a laboratory scale by researchers using different photocatalysis. This study was used TiO_2-CuO-Clays soil composite and UV irradiation to investigate the photocatalytic degradation of 2, 4-D. It has been shown that TiO_2-CuO-Clay soil is a promising option for photocatalytic degradation of 2, 4-D by exposed to UV. Photocatalytic degradation of the TiO_2-CuO-Clay soil composites shows that the catalytic molar ratio of 4:3:5 performance was an efficient in aqueous environment. TiO_2-CuO-Clays soil composite was successfully degrade 2,4-D from surface water and Industrial waste. This investigation shows that the parameters, namely catalyst molar ratio, pollutant concentration and irradiation time had a significant impact on photocatalytic degradations of 2,4-D from surface water and pesticide factory effluents.

5.2. Recommendation

- The effect of oxidizing agents, pH, COD, BOD and light intensity on this characteristics has not yet been evaluated.
- It is important to look into the factors impact on the breakdown of pesticides molecules.
- More research required to determine economically and practical viability of TiO_2-CuO-Clay soil composites.
- Academic and research institutes' could be focus on potocatalytic degradations of pesticides from surface water by varying catalyst molar ratio.

References

Ahmed, F., M. A. Aziz, M. J. Alam, M. A. Hakim, M. A. S. Khan, dan M. A. R. (2015). Impact on Aquatic Environment for Water Pollution in the Vahirab River. *The International Journal Of Engineering And Science*, *4*(8), 56–62.

Amiri, F., Dehghani, M., Amiri, Z., Yousefinejad, S., & Azhdarpoor, A. (2021). Photocatalytic degradation of 2,4-dichlorophenoxyacetic acid from aqueous solutions by Ag3PO4/TiO2 nanoparticles under visible light: Kinetic and thermodynamic studies. *Water Science and Technology*, *83*(12), 3110–3122. https://doi.org/10.2166/wst.2021.193

Carbajo, J., García-Muñoz, P., Tolosana-Moranchel, A., Faraldos, M., & Bahamonde, A. (2014). Effect of water composition on the photocatalytic removal of pesticides with different TiO2 catalysts. *Environmental Science and Pollution Research*, 12233–12240. https://doi.org/10.1007/s11356-014-3111-5

Devipriya, S., & Yesodharan, S. (2005). Photocatalytic degradation of pesticide contaminants in water. *Solar Energy Materials and Solar Cells*, *86*(3), 309–348. https://doi.org/10.1016/j.solmat.2004.07.013

Dong, C.-D., Chen, C.-W., Kao, C.-M., & Hung, C.-M. (2017). Synthesis, characterization, and application of CuO-modified TiO 2 electrode exemplified for ammonia electro-oxidation. *Process Safety and Environmental Protection*, *112*, 243–253. https://doi.org/10.1016/j.psep.2017.05.016

EL-Saeid, M. H., Al-Turki, A. M., Nadeem, M. E. A., Hassanin, A. S., & Al-Wabel, M. I. (2015). Photolysis degradation of polyaromatic hydrocarbons (PAHs) on surface sandy soil.

Environmental Science and Pollution Research, *22*(13), 9603–9616. https://doi.org/10.1007/s11356-015-4082-x

EL-Saeid, M. H., Alotaibi, M. O., Alshabanat, M., Alharbi, K., Altowyan, A. S., & Al-Anazy, M. (2021). Photo-Catalytic Remediation of Pesticides in Wastewater Using UV/TiO2. *Water*, *13*(21), 3080. https://doi.org/10.3390/w13213080

El-Saeid, M. H., Baqais, A., & Alshabanat, M. (2022). Study of the Photocatalytic Degradation of Highly Abundant Pesticides in Agricultural Soils. *Molecules*, *27*(3). https://doi.org/10.3390/molecules27030634

Etape, E. P., Ngolui, L. J., Foba-tendo, J., Yufanyi, D. M., & Namondo, B. V. (2017). *Mixed Oxide by a Modified Oxalate Route*. *2017*.

Fiorenza, R., Di Mauro, A., Cantarella, M., Iaria, C., Scalisi, E. M., Brundo, M. V., Gulino, A., Spitaleri, L., Nicotra, G., Dattilo, S., Carroccio, S. C., Privitera, V., & Impellizzeri, G. (2020). Preferential removal of pesticides from water by molecular imprinting on TiO2 photocatalysts. *Chemical Engineering Journal*, *379*, 122309. https://doi.org/10.1016/j.cej.2019.122309

Habtamu, wodajo. (2020). Detection of Organochlorine Pesticide Residues in Lake Ziway and Health Risk Assessment. *Advances in Environmental Studies*, *4*(2), 345–349. https://doi.org/10.36959/742/230

Herrmann, J. M., & Guillard, C. (2000). Photocatalytic degradation of pesticides in agricultural used waters. *Comptes Rendus de l'Academie Des Sciences - Series IIc: Chemistry*, *3*(6), 417–422. https://doi.org/10.1016/S1387-1609(00)01137-3

Ismael, A. M., El-Shazly, A. N., Gaber, S. E., Rashad, M. M., Kamel, A. H., & Hassan, S. S. M. (2020). Novel TiO2/GO/CuFe2O4nanocomposite: a magnetic, reusable and visible-light-driven

photocatalyst for efficient photocatalytic removal of chlorinated pesticides from wastewater. *RSC Advances*, *10*(57), 34806–34814. https://doi.org/10.1039/d0ra02874f

Jansen, H. C., & Harmsen, J. (2011). Pesticide Monitoring in the Central Rift Valley 2009 - 2010: Ecosystems for Water in Ethiopia. *Alterra Wageningen UR*, 44.

Kubiak, A., Bielan, Z., Kubacka, M., Gabała, E., Zgoła-Grześkowiak, A., Janczarek, M., Zalas, M., Zielińska-Jurek, A., Siwińska-Ciesielczyk, K., & Jesionowski, T. (2020). Microwave-assisted synthesis of a TiO2-CuO heterojunction with enhanced photocatalytic activity against tetracycline. *Applied Surface Science*, *520*(January), 146344. https://doi.org/10.1016/j.apsusc.2020.146344

Lin, H., Thornton, J. A., & Slawski, T. M. (2013). Participatory and evolutionary integrated lake basin management. *Lakes and Reservoirs: Research and Management*, *18*(1), 81–87. https://doi.org/10.1111/lre.12015

Matsumoto, E., Kawanaka, Y., Yun, S. J., & Oyaizu, H. (2009). Bioremediation of the organochlorine pesticides, dieldrin and endrin, and their occurrence in the environment. *Applied Microbiology and Biotechnology*, *84*(2), 205–216. https://doi.org/10.1007/s00253-009-2094-5

Miguel, N., Ormad, M. P., Mosteo, R., & Ovelleiro, J. L. (2012). Photocatalytic degradation of pesticides in natural water: Effect of hydrogen peroxide. *International Journal of Photoenergy*, *2012*. https://doi.org/10.1155/2012/371714

Muhammed, R. (2016). *Monitoring potential impacts of flower farm effluent into Lake Ziway, using physico-chemical parameters and biotic index. master's thesis Addis Ababa University*. 48.

Muzakki, A., Shabrany, H., & Saleh, R. (2016). Synthesis of ZnO/CuO and TiO2/CuO nanocomposites for light and ultrasound assisted degradation of a textile dye in aqueous

solution. *AIP Conference Proceedings*, *1725*(2016). https://doi.org/10.1063/1.4945505

Negatu, B., Kromhout, H., Mekonnen, Y., & Vermeulen, R. (2016). Use of chemical pesticides in Ethiopia: A cross-sectional comparative study Onknowledge, attitude and practice of farmers and farm workers in three farming systems. *Annals of Occupational Hygiene*, *60*(5), 551–566. https://doi.org/10.1093/annhyg/mew004

Palma, P., Köck-Schulmeyer, M., Alvarenga, P., Ledo, L., Barbosa, I. R., López de Alda, M., & Barceló, D. (2014). Risk assessment of pesticides detected in surface water of the Alqueva reservoir (Guadiana basin, southern of Portugal). *Science of the Total Environment*, *488–489*(1), 208–219. https://doi.org/10.1016/j.scitotenv.2014.04.088

Pretty, J., Toulmin, C., & Williams, S. (2011). Sustainable intensification in African agriculture. *International Journal of Agricultural Sustainability*, *9*(1), 5–24. https://doi.org/10.3763/ijas.2010.0583

R.E.Redmann. (1978). Canadian journal. *Canadian Journal of Soil Science*, *58*(May), 119–124.

Rezaei Kalantary, R., Barzegar, G., & Jorfi, S. (2022). Monitoring of pesticides in surface water, pesticides removal efficiency in drinking water treatment plant and potential health risk to consumers using Monte Carlo simulation in Behbahan City, Iran. *Chemosphere*, *286*(P1), 131667. https://doi.org/10.1016/j.chemosphere.2021.131667

Rift, C. (2022). *Review of Pesticide Use in Vegetable Farms and Its Consequences in Ethiopia's Central Rift Valley*.

Sousa, A. S., Duaví, W. C., Cavalcante, R. M., Milhome, M. A. L., & Do Nascimento, R. F. (2016). Estimated Levels of Environmental Contamination and Health Risk Assessment for Herbicides and Insecticides in Surface Water of Ceará, Brazil. *Bulletin of Environmental Contamination*

and Toxicology, *96*(1), 90–95. https://doi.org/10.1007/s00128-015-1686-2

Tarekegn, M. M., Balakrishnan, R. M., Hiruy, A. M., Dekebo, A. H., & Maanyam, H. S. (2022). Nano-Clay and Iron Impregnated Clay Nanocomposite for Cu2+ and Pb2+ Ions Removal from Aqueous Solutions. *Air, Soil and Water Research*, *15*(May 2023). https://doi.org/10.1177/11786221221094037

Tchounwou, P. B., Ashour, B. A., Moreland-Young, C., Ragheb, D. A., Romeh, A. A., Goma, E. A., El-Sheikh, S., Lidell, F. P., Ibitayo, O., & Assad, J. C. (2002). Health risk assessment of pesticide usage in Menia El-Kamh province ofSharkia Governorate in Egypt. *International Journal of Molecular Sciences*, *3*(10), 1082–1094. https://doi.org/10.3390/i3101082

Teklu, B. M. (2016). *Environmental risk assessment of pesticides in Ethiopia: a case of surface water systems*.

Teklu, B. M., Adriaanse, P. I., Ter Horst, M. M. S., Deneer, J. W., & Van den Brink, P. J. (2015). Surface water risk assessment of pesticides in Ethiopia. *Science of the Total Environment*, *508*, 566–574. https://doi.org/10.1016/j.scitotenv.2014.11.049

Teklu, B. M., Adriaanse, P. I., & Van den Brink, P. J. (2016). Monitoring and risk assessment of pesticides in irrigation systems in Debra Zeit, Ethiopia. *Chemosphere*, *161*, 280–291. https://doi.org/10.1016/j.chemosphere.2016.07.031

Teklu, B. M., Hailu, A., Wiegant, D. A., Scholten, B. S., & Van den Brink, P. J. (2018). Impacts of nutrients and pesticides from small- and large-scale agriculture on the water quality of Lake Ziway, Ethiopia. *Environmental Science and Pollution Research*, *25*(14), 13207–13216. https://doi.org/10.1007/s11356-016-6714-1

Teshome, A. (n.d.). *Pesticide Lifecycle in Ethiopia : challenges , opportunities and leverage points*.

1.

Toolabi, A., Malakootian, M., Ghaneian, M. T., Esrafili, A., Ehrampoush, M. H., AskarShahi, M., Tabatabaei, M., & Khatami, M. (2019). Optimizing the photocatalytic process of removing diazinon pesticide from aqueous solutions and effluent toxicity assessment via a response surface methodology approach. *Rendiconti Lincei*, *30*(1), 155–165. https://doi.org/10.1007/s12210-018-0751-2

Zafar, H., Aziz, T., Khan, B., Mannan, A., Rehman, R. U., & Zia, M. (2020). CuO and ZnO Nanoparticle Application in Synthetic Soil Modulates Morphology, Nutritional Contents, and Metal Analysis of Brassica nigra. *ACS Omega*, *5*(23), 13566–13577. https://doi.org/10.1021/acsomega.0c00030

Zandsalimi, Y., Maleki, A., Shahmoradi, B., Dehestani, S., Rezaee, R., & McKay, G. (2020). Photocatalytic removal of 2,4-Dichlorophenoxyacetic acid from aqueous solution using tungsten oxide doped zinc oxide nanoparticles immobilized on glass beads. *Environmental Technology (United Kingdom)*, 1–36. https://doi.org/10.1080/09593330.2020.1797901

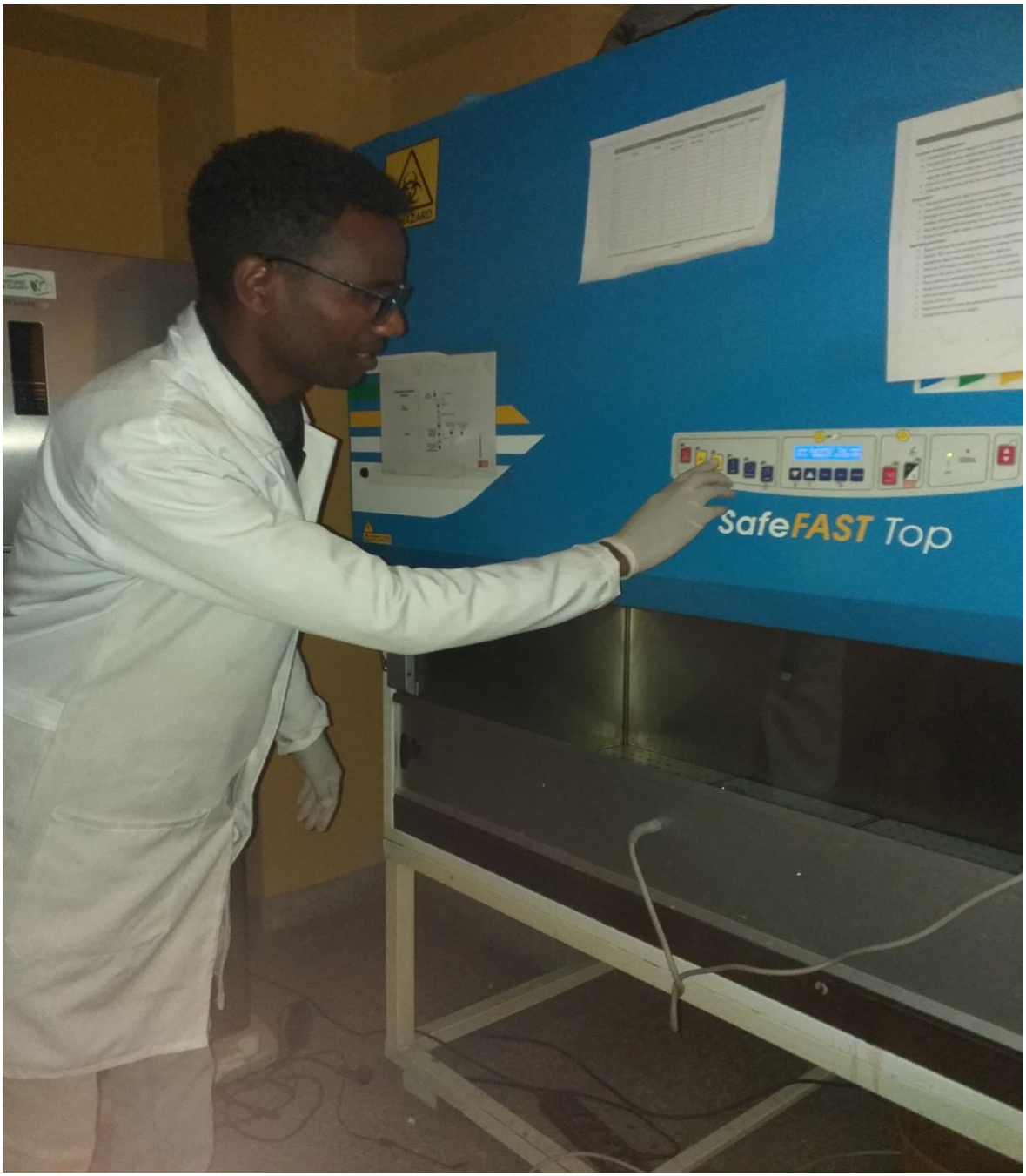
Appendix

Balancing of TiO2-CuO-Clay soil nanocomposite

Treating of the contaminated water with different ratios of TiO_2-CuO-Clay soil nanocomposite

UV-vis treatment of contaminated water

Adjusting of UV-vis lamp



UV-vis light shunning on the sample

Fitration of the sample treated by UV-vis for HPLC analysis