ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAIT) SCHOOL OF CHEMICAL AND BIO ENGINEERING

M.Sc. Program in Environmental Engineering

Treatment of Textile Wastewater Using Titanium Dioxide Photocatalysis to Remove COD and Color

A thesis submitted to Addis Ababa Institute of Technology, School of Chemical and Bio engineering in partial fulfillment of the requirements for the Degree of Master of Science in Environmental Engineering

By: Abeba Kebede

Advisor: Dr. Ing. Berhanu Assefa (Ass. Prof.)

Addis Ababa, Ethiopia

June 2019

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSITUTE OF TECHNOLOG SCHOOL OF

CHEMICAL AND BIOENGINEERING

Treatment of Textile Wastewater Using Titanium Dioxide Photocatalysis to Remove COD and Color

---

Submitted By: Abeba Kebede

A Thesis Submitted to the School of Graduate Studies of Addis Ababa University in Partial Fulfilment of the Degree of Master of Science in Environmental Engineering

Approved by Board of Examiners

Name	Signature	Date
____________________	____________________	____________________
Chair Person		
____________________	____________________	____________________
Internal Examiner		
____________________	____________________	____________________
External Examiner		

Declaration

I declare that, this Thesis work entitled by “Treatment of textile wastewater by using titanium dioxide photocatalysis to remove COD and Color “ for the fulfillment of the degree of masters of science in Environmental engineering at Addis Ababa university institute of technology, which submitted by me is my original work which has not been submitted in any form for another degree in this university or other institute, and that all resources of material used in this thesis work have been duly acknowledged.

Name: Abeba Kebede

Signature

Date of Submission

This thesis has been submitted for examination with my approval as University Advisor.

Name: Berhanu Assefa (Dr. Ing.)

Signature:

Date:

ACKNOWLEDGEMENT

I would like to extend my sincere thanks to all of you which gives me a kind support and help. Foremost, I want to offer this endeavor to GOD almighty for the wisdom he best owed upon me, the strength, peace of my mind and good health in order to finish this research. I am highly indebted to (Dr. Ing.) Berhanu Assefa my advisor for his guidance, encouragement and patience throughout this thesis work.

Special thanks goes to Mr. Ali from Ayka Addis textile factory for his willingness and help in collecting the sample and information about the factory and all the laboratory Staff of Addis Ababa University Institute of Technology, school of chemical and Bio-Engineering and center of environmental science environmental laboratory for their help and collaboration.

I would like to express my gratitude towards my family, for their encouragement and help to accomplish this thesis. My beloved and supportive sister and brother Bogale, Tizita, Aster and Mintamir always by my side when I need them most.

ABSTRACT

Textile industry is faced with serious environmental problems associated with its immense wastewater discharge, high BOD, COD, TS, extreme alkalinity and heavily colored effluent. It is discharged without enough treatment above the discharge limit set by EPA which affects the aquatic environment as well as human beings. Therefore, the objective of this study was to reduce COD and color from the textile wastewater by using TiO_2 *photocatalysis experiment to an acceptable discharge limit. In this study, effect of* TiO_2 *dosage (400-550 mg/l), pH (7-9), and irradiation time (3-5 hr.) were investigated in batch experiment. The influent results revealed that the COD, BOD, TS, TSS, TDS and turbidity of textile wastewater were in concentration of 1150 mg/L, 210.77 mg/L, 2500 mg/L, 850 mg/L, 1650 mg/L and 190 NTU respectively. After* TiO_2 *photocatalytic treatment the effluent resulted at the optimum condition (475 mg/L of* TiO_2 *dosage, pH 9, and irradiation time of 5 hour) for the removal of COD and color showed that 110 mg/L of COD removal which is 90.4% in percent and 88% color removal respectively. When we see the removal of other pollutant load such as BOD, TSS, TDS and turbidity the concentration reduced to 210.77 mg/L, 25 mg/L, 74 mg/L and 22 NTU respectively which shows photocatalytic treatment of textile wastewater is the best treatment choice not only to remove COD and color but also the other pollutant load. Consequently, the experimental result showed that* TiO_2 *photocatalysis is an efficient, cost effective and environmental friendly treatment technology for textile wastewater.*

Key words: Textile wastewater, COD, Color, TiO_2 Photocatalysis

Table of Contents

LIST OF TABLES

LIST OF FIGURE

LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Process
UV	Ultraviolet light
BOD	Biological oxygen demand
BOD5	Five Days Biological Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
SS	Suspended Solids
TS	Total Solid
TSS	Total Suspended Solid
TDS	Total dissolved Solid
NTU	Nephelometric Turbidity Unit
ANOVA	Analysis of variance
RSM	Response surface methodology
BBD	Box Behinken Design
EPA	Environmental protection authority

CHAPTER ONE

1 INTRODUCTION

1.1 Background

Industrialization is considered as the key factor to development of countries in economic terms. However, improper disposal of industrial wastes is the root of environmental damages. The recognition that environmental pollution is a worldwide threat to public health has given rise to new initiatives for environmental restoration for both economic and ecological reasons. With the increased demand for textile products, there is increase in the textile industry and its wastewater proportionally, making it one of the main sources of severe pollution problems worldwide (Punzi, 2015).

In particular, the release of colored effluents into the environment is undesirable, not only because of their color but also because of the breakdown products. The release of colored wastewater in the ecosystem is a remarkable source of esthetic pollution, eutrophication, and perturbations in aquatic life (Allegre, 2003).

Textile effluent usually contains chemicals, including dye, that are toxic, carcinogenic, mutagenic, or teratogenic to various aquatic organisms and fish species (Allegre, 2003). The textile dyeing and finishing industries use wide variety of dyestuffs due to the rapid changes in the customer's demands.

More than 100,000 commercially available dyes are known, and the world annual production of the dyestuffs accounts to more than 7×10^5 tones. It has been estimated that more than 10–15 % of the total dyestuff used in dye manufacturing and textile industry is released into the environment during their synthesis and dying process (Lech k, 2006). Concern arises, as many dyes are made from known carcinogens such as benzidine and other aromatic compounds.

It is therefore of paramount significance to convert textile dyeing wastewater into harmless water before discharging it into drainage system through an efficient and cost-effective technique, which will lead a huge potential market to textile enterprises (Lech k, 2006).

Currently, three principal steps in treating wastewater are available, which are preliminary, secondary and tertiary steps. The purpose of the preliminary step is to remove coarse solids and other large substances that can be easily done by coarse screening and grit removal, to eliminate damage to process units. After that additional primary treatment is applied to remove settable organic and inorganic compounds/solids from sludge by sedimentation of solids and skimming of material that floats. In this step up to 50% of biochemical oxygen demand (BOD), 50% to 70% of total suspended solids and approximately 60% of oil and grease can be removed (Sharmila P, 2013).

In secondary treatment, the target is to remove residual inorganic and organic compounds from primary treatment. There exist various methods of secondary treatment including physical, chemical, mechanical, biological and combined techniques. It can be stated that secondary treatment is the most important part of wastewater treatment. Tertiary treatment is used to remove nitrogen, phosphorous, additional solids, dissolved solids, heavy metals and refractory organics. It is also called advanced treatment process and usually used with or instead of secondary treatment. However, a challenging problem which arises in this is that conventional wastewater treatments are not able to completely remove toxic compounds. Besides, they also perform the long-time operation and require a high cost for implementation (Punzi, 2015).

a number of works have shown that this problem can be overcome by using Advanced Oxidation Process (AOPs) (AL-Kdasi, 2004). The general principle of AOPs treatment is a generation of the very high oxidative [•OH] radicals that has potential to mineralize the organic substances in aqueous media (Carey, 1992).

TiO_2 /UV is one of the heterogeneous advanced oxidation methods which is called photocatalysis From the existing semiconductor photocatalyst materials that have been applied in advanced oxidation treatment, titanium dioxide (TiO_2) has attracted more research attention owing to its reliable long-term stability, high chemical inertness, corrosive resistance, cost effectiveness and low impact on the environment (Segneanu A E, 2013).

The aim of this thesis is to investigate the performance of photocatalytic AOPs technique, with TiO_2, to remove Color and COD from textile wastewater.

As one of the goal, this research focused on finding optimal conditions such as optimum pH, optimum irradiation time and optimum titanium dioxide concentration for photocatalytic treatment of textile wastewater. The treated textile wastewater using photocatalysis can be recycled in the same factory or reused for other applications such as in other industry or agriculture that require less quality of water this is considered to be very excellent means for saving huge amount of water.

1.2 Statement of problem

Textile wastewater contains a large variety of dyes and chemicals that makes it environmentally hazardous not only as liquid waste but also in its chemical composition (Zhezhova S., 2014). Dyeing and finishing processes are mainly responsible as a source for large amount of wastewater. This processes are done by the input of a wide range of chemicals and dyestuffs or pigments which generally are organic and inorganic compound in nature (Punzi, 2015).At present, several methods have been developed to treat textile wastewater mostly aerobic treatment can be used as a treatment option but it is not efficient treatment option in removal of recalcitrant dyes and non-biodegradable organics because textile wastewater have high salinity, high color, high COD and non-biodegradable organics (Zhezhova S., 2014).

Recently in Ethiopia textile factories are growing industry including the oldest factory in almost all of the industry park which built across the country textile factory takes the largest number So, this growing industry can have a high potential to pollute the aquatic environment if the waste is not treated well. Several reports in Ethiopia shown that the values of water quality parameter such as COD, BOD, pH ,TS, TDS and Color of textile wastewater discharge has considerably higher than the safe limits set by Ethiopian environmental protection authority (EPA) (Diriba Dadi, 2014). The main reason to conduct this research is to develop inexpensive and efficient treatment technology that can be used to treat textile wastewater to remove Color and COD. Therefore, TiO_2 Photocatalysis can have a great potential to treat textile wastewater and reduce the environmental pollution.

1.3 Objectives

1.3.1 General objective

- ✓ The general objectives of this research is to study treatment of textile wastewater by using TiO_2 Photocatalysis to remove COD and Color.

1.3.2 Specific objective

- ✓ To characterize textile factory wastewater such as COD, BOD_5, TS, TSS, TDS Color, pH and turbidity**.**
- ✓ To determine the effect of process parameter such as pH, irradiation time and TiO_2 dosage on treatment performance of photocatalysis.
- ✓ To evaluate the performance of prepared photocatalyst in the removal of real textile wastewater Color and COD.

1.4 Significance of the study

The main significance of this study is to treat textile wastewater with Titanium dioxide photocatalysis to remove color and COD which is a recently developed and promising techniques due to its high efficiency and low operational cost.

Textile industry is in great need to reduce its negative impact on the environment so improved treatment methods like photocatalysis is one of the ways to pursue this objective to become green. In addition, this study can have a great significance for:

- ✓ Reducing water pollution (aquatic pollution) which discharged without enough treatment.
- ✓ It can avoid any conflict that may arise due to discharge limits from the government and the society.
- ✓ The treated wastewater can be recycled on the factory or it can be used for other industry which needs low quality water.

1.5 Scope of the study

This study deals with treating textile wastewater which mainly aims to remove COD and color in order to reduce water pollution which can be discharged without efficient treatment and then to use treated wastewater by recycling on the industry or giving it for industry which needs low quality water.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Processing of Cotton Based Textiles

Cotton based textiles are processed through three main stages, comprising spinning, knitting/weaving and wet processing. In general, we can classify the overall processes of cotton based textiles in to two classes; these are dry process and wet process. The dry process includes; spinning, weaving/knitting and the wet process which is the main source for textile wastewater includes; sizing, de-sizing, scoring, bleaching, mercerizing, dyeing and printing (Bhatkhande.S Pangarkar, 2001). Wet process is done on manufactured fabrics. The processes of this stream is involved or carried out in aqueous stage and thus it is called wet process which usually covers pre-treatment, dyeing, printing and finishing (PRG, 1998).

All of these stages are required aqueous medium which is created by water. A massive amount of water is required in these processes per day. It is estimated that, on average, almost 100 liters of water is used to process only 1 kilogram of textile goods. Water can be of various quality and attributes not all water can be used in this wet processing steps it must have some certain properties, quality, color and attributes for being used accurately (Segneanu A E, 2013).

The main problems which is concerned in using water in wet processing step is water hardness caused by the presence of soluble salts of metals including calcium and magnesium which causes problems such as scale formation on boiler, reactions with soap and detergents and reaction with dyes (Lech k, 2006).

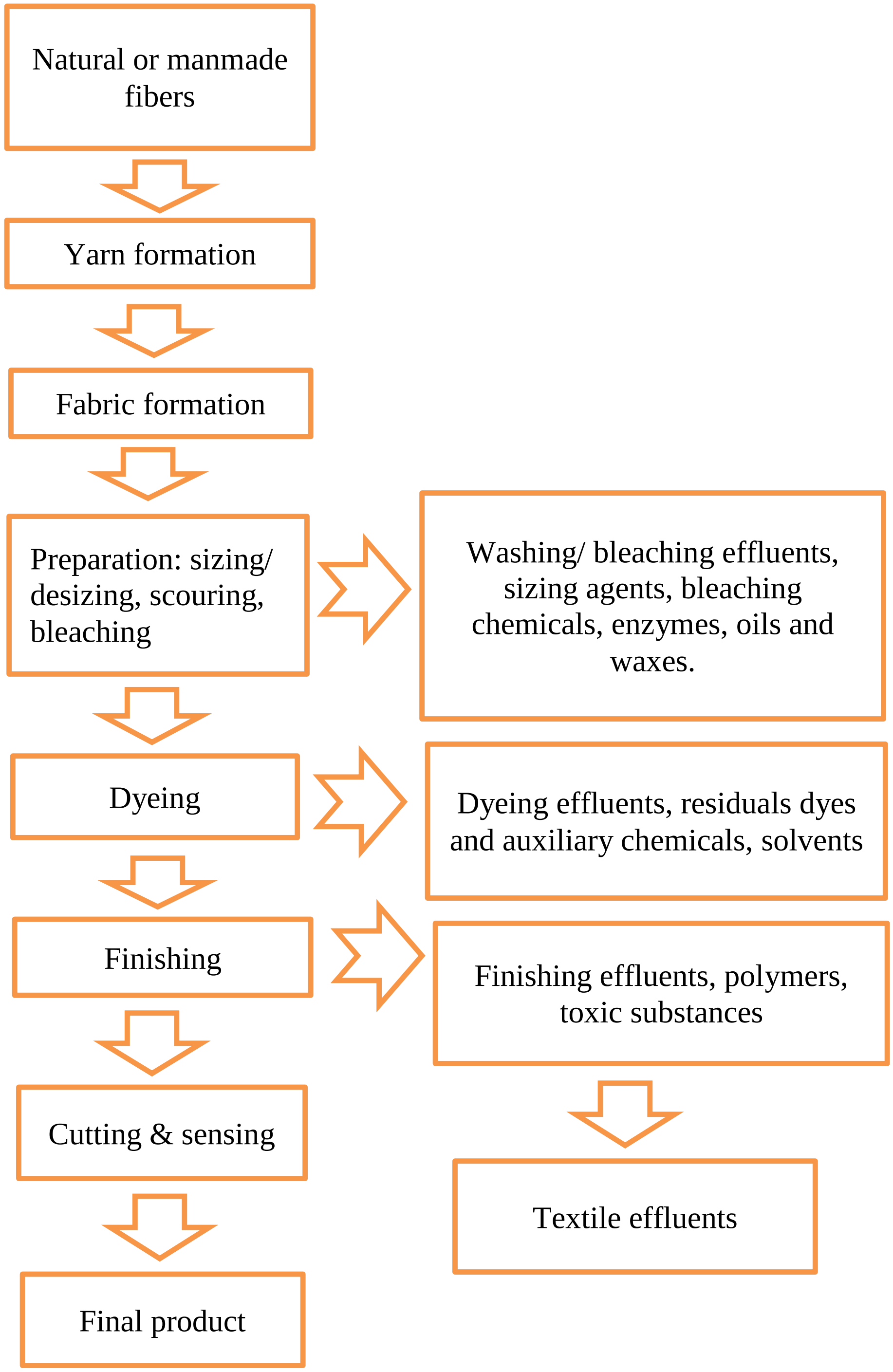


Figure 2.1 Main steps of textile process and the wastewater generated during the wet processing.

2.2 Sources and Characteristics of wastewater in textile industry

Textile wastewater contains a large variety of dyes and chemicals that makes it environmentally hazardous not only as liquid waste but also in its chemical composition (Lech k, 2006).

Dyeing and finishing processes are mainly responsible as a source for large amount of wastewater. These processes are done by the input of a wide range of chemicals and dyestuffs or pigments, which generally are organic or inorganic compounds in nature (Alkhateeb, 2005).

Normal textile dyeing and finishing operations dyestuff usage can vary from day to day and sometimes even several times a day because of the batch wise nature of the processes. Frequent changes of dyestuff employed in the dyeing and finishing processes cause considerable variation in the wastewater characteristics particularly the pH, color and COD (Bizani E., 2006).

Most of the pollutants in textile wastewater from textile industry are high suspended solids, chemical oxygen demand (COD), color, acid, salt, heavy metals, biological oxygen demand (BOD), high temperature, high pH and other soluble substance.

Table 2. 1 source of wastewater, effluent composition and characteristics from textile industry

Source of wastewater (from operational steps)	**Effluent composition**	**Characteristics**
Sizing	Carboxymethyl cellulose (CMC), polyvinyl alchol (PVA)	High in BOD, COD
Desizing	Mineral acid, fats, wax, pectin, CMC, PVA	High in BOD, COD, SS, dissolved solids
Scouring	Caustic soda, soda ash, detergent	High pH
Bleaching	Sodium hypochlorite, hydrogen peroxide, acids, surfactants, sodium phosphate, short cotton fibers	High alkalinity, high SS
Mercerizing	Caustic soda solution, cotton wax	High pH, low BOD, high dissolved solids

Dyeing	Dyestuffs, reducing agent, oxidizing agent, urea, acetic acid, detergent, wetting agent	Strongly colored, high BOD, dissolved solid, low SS, heavy metals
Printing	Paste, urea, starch, gum, oil, binders, acids, thickeners, reducing agents, alkali	Highly colored, high BOD, oily appearance, slightly alkaline

2.3 Environmental impact of textile industry wastewater

With escalating demand for textile products, textile mills and their wastewater have been increasing proportionally causing a major problem of pollution in the world. Many chemicals used in the textile industry cause environmental and health problems (WHO, 2008).

Among the many chemicals in textile wastewater dyes are considered as major pollutant which is toxic and causes undesirable aesthetic impact on receiving waters.

The color of reactive dyes is due to the presence of -N=N- azo bonds and chromophoric groups.

The dyes are first absorbed on the cellulose and then fiber. After fixation of the dyes on the fiber About 10 – 15 % of initial loading is present in the dye bath effluent. Reactive dyes in both Ordinary and hydrolyzed form is not easily biodegradable and thus even after treatment color may be present in the effluent (Punzi, 2015).

Textile effluent is a critical environmental concern since it drastically decreases oxygen concentration due to the presence of hydrosulfides and blocks the passage of light through water body which is detrimental to the water ecosystem. About 40% of globally used colorant contains organically bound chlorine which is a known carcinogenic which causes cancer to human being.

The chemicals from the textile wastewater effluent evaporate into the air we breathe or absorbed through our skin and they show up as allergic reaction and may cause harm to children even before birth (Karachi, 2002).

Heavy metals present in textile industry effluent are not biodegradable hence, they accumulate in human primary organs in the body and over time begin to fester leading various diseases.

Thus, untreated or incompletely treated textile effluent can be harmful to both aquatic and terrestrial life by adversely affecting the natural ecosystem and causing long-term health effects (Karachi, 2002).

2.4 Treatment of Textile Wastewater

There are many ways for treating textile wastewater. The treatment methods differ from plant to plant depending on the size, type of waste and degree of treatment needed (Zhezhova S., 2014).

Table 2.2: Advantages and Disadvantages of Current Methods of Dye Removal from textile wastewater.

Physical/Chemical Methods	**Advantages**	**Disadvantages**
Fentons reagent	Effective decolouration of soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state, no alteration of volume	Short half-life (20 min)
Sodium hypochlorite	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Cucurbturil	Good sorption capacity for various dyes	Expensive
Electrochemical Destruction	Break-down products are non-hazardous	High electricity consumption
Activated carbon	Good removal of a wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removal all dye types	Concentrated sludge production
Ion exchange	No adsorbent loss due to Regeneration	Not effective for all dyes

Irradiation	Effective oxidation at laboratory scale	Requires high concentrations of dissolved oxygen
Electrokinetic coagulation	Economically feasible	High sludge production

2.4.1 Advanced Oxidation Processes (AOPs)

The AOPs method was firstly introduced in 1980 and designed to treat potable water but now a days because of its high efficiency it can be used in treating industrial and municipal wastewater. AOPs involve two stages of oxidation, the first is a generation of the strong oxidizing agent, and the second is the reaction of oxidant with organic contaminants in water (Housitel, 1992).

The common oxidizing agent for AOPs is hydroxyl radicals (•OH). These radicals, when AOPs Applied for wastewater treatment, acts as powerful oxidizing agents, and have enough potential to efficiently destruct pollutants and make wastewater less toxic, even eliminate their toxicity (AL-Kdasi, 2004).

Table 2.3, is presented the oxidants used in different wastewater techniques with the corresponding potential, and among all of them hydroxyl radicals (•OH) has the highest potential. It is essential to understand, that efficiency of treatment depends on the selected type of AOPs, physical and chemical properties of pollutants and operating parameters of the process.

Table 2.3 Standard potential of some relevant oxidants (at 25^{o}c)

Reactive species	**Potential (V)**
Hydroxyl radicals (•OH)	2.86
Oxygen (O_2)	2.42
Ozone molecule (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.78
Chlorine (Cl_2)	1.36
Chlorine dioxide (ClO_2)	1.27
Oxygen molecule (O_2)	1.23

AOPs can be divided into two main categories, depending on reagents used: homogeneous and heterogeneous.

2.4.1.1 Homogeneous AOPs

The principle work of homogeneous AOPs depends on the presence of UV or visible light and oxidants, which generates •OH radicals. Mostly, Ozone (O_3), oxygen (O_2) and hydrogen peroxide (H_2O_2) is used as source of these radicals (Punzi, 2015).

2.4.1.2 Heterogeneous AOPs

Heterogeneous AOPs requires the presence of semiconductors as a photocatalyst, which has already proved their efficiency in removing the organic compounds from wastewater.

Moreover, this process is driven by different sources of light, like UV, solar or visible light.

The main characteristics of the catalyst are its photocatalytic activity, resistance to photo-corrosion, biological immunity and cost (Punzi, 2015).

Photocatalytic activity is dependent on the structural properties, band gap, surface area, particle size distribution, porosity and surface hydroxyl density (Alkhateeb, 2005).

Types of advanced oxidation processes (AOPs) are listed below;

- ✓ TiO_2/UV (photocatalysis)
- ✓ Ozone/TiO_2 / H_2O_2
- ✓ Ozone/ TiO_2 /Electron-beam irradiation
- ✓ H_2O_2/UV/Fe2+ (photo-assisted Fenton)
- ✓ H_2O_2/Fe2+ (Fenton)
- ✓ Ozone/ H_2O_2
- ✓ Ozone /UV/ H_2O_2
- ✓ Ozone and electron beam irradiation
- ✓ Ozone/ultrasonic
- ✓ H_2O_2/UV

In this work TiO_2/UV is selected due to its advantages over other treatment techniques. Photocatalytic degradation process is found to be sustainable treatment technology with “zero” waste after process. Also, for degradation of textile wastewater specially, to remove color and COD the photocatalytic technique is found to be favorable, as no oxidant is required during the reaction and no need for further separation than with other AOPs techniques.

2.4.2 TiO_2 Photocatalysis

2.4.2.1 TiO_2 Catalyst

Among research on many semiconductors as photocatalysts, the general conclusion is that TiO_2 is more effective because of its characteristics. Comparing to other semiconductor powders, TiO2 has maximum quantum yields due to high photocatalytic activity, photo-corrosion resistance, low cost and toxicity (Abbas, 2008).

In 1972, Honda and Fujshima first demonstrated the potential of using TiO_2 based semiconductor in water purification. Compared to other catalyst, photocatalytic activity for TiO_2 in organic waste degradation demonstrated better performance. From different study on the performance of their photocatalytic activity that TiO_2 performs better than other semiconductors in producing •OH (hydroxyl radicals) (Bhatkhande.S Pangarkar, 2001).

TiO_2 naturally exists in three polymorphs namely anatase, rutile and brookite. The structure difference between them is the connectivity of the TiO_6^{2-} octahedral units, which share edges and corners differently depending on the crystal phase. Anatase, rutile and brookite share four, two and three edges, respectively (Chen, 2005).

These three crystalline phases occur in nature as mineral however, brookite is not commonly observed in mineral and is difficult to be synthesised in pure form. In contrast, anatase and rutile can be synthesised in pure form at low temperature. Anatase TiO_2 is accepted to possess the most photocatalytic activity among the three phases. Compared with anatase phase, rutile TiO_2 is less reactive due to its high recombination rate of electron-hole pairs (Alkhateeb, 2005).

Phases, sizes and shapes, as well as synthesis control are responsible for its photocatalytic activity, and have been controlled during the synthesis processes.

2.4.2.2 Mechanism of TiO_2 Photocatalysis

There is a band gap in TiO_2, which is defined as the gap between the valence band (h^+) and conduction band (e^-). Electrons and holes are produced once light energy equal to or greater than the band gap of TiO_2, followed by transfer of electron from TiO_2 surface to adsorbate surface. The band gap of TiO_2 is 3.2 eV the electrons on TiO_2 surface can reduce electron acceptors, while holes can oxidize electron donors. The hole adsorbs the surrounding water molecules and gets oxidized to form a hydroxyl radical (Aguedach, 2005).

Absorption of a photon promotes an electron (e-) from a valence band to a higher energy conduction band. This electronic promotion simultaneously creates a localized electron hole (h^+), which is highly oxidizing and a mobile electron (e-), which is a delocalized reducing agent (Equation 2.1). The electron-hole pair may recombine or be captured by other species in close proximity. For example, molecular oxygen, which is known to be required for this reaction to Proceed, is readily reduced to form superoxide ion (O_2^-), (Equation 2.2).

At the same time, water is oxidized (losses an electron) at the site of the photogenerated electron holes to produce hydroxyl radical (HO•), (Equation 2.3). The hydroxyl radical is a very powerful oxidizing agent and will rapidly mineralize organic compounds, (Equation 2.4). This electron transfer process will be more effective if species can be pre-adsorbed on TiO_2. Meanwhile, some electron-hole recombination takes place, competing with the charge transfer process. This recombination happens either in the volume of TiO_2 particle or on the TiO_2 surface.

$$TiO_2 + hv \rightarrow e^- + TiO_2^+ (h^+) \quad \ldots\ldots \quad (2.1)$$

$$e^- + O_2 \rightarrow O_2^- \quad \ldots\ldots \quad (2.2)$$

$$H_2O + h^+ \rightarrow HO\bullet + H^+ \quad \ldots\ldots \quad (2.3)$$

$$\text{Organics} + HO\bullet \rightarrow \text{Mineralization} \quad \ldots\ldots \quad (2.4)$$

The term mineralization refers to the complete chemical oxidation resulting in the formation of carbon dioxide and water, (Equation 2.5).

$$\text{Organics} + [\text{Oxidation}] \rightarrow CO_2 + H_2O \quad \ldots\ldots \quad (2.5)$$

The generation of hydroxyl radical is a cyclic process and initiates the series of reactions on the TiO_2 surface as shown in the schematic representation in Figure 2.2.

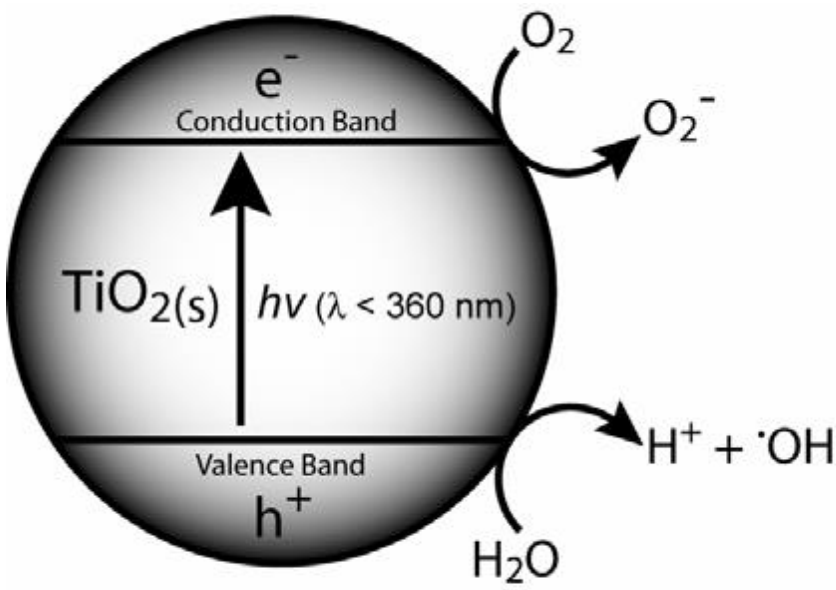


Figure 2.2 Mechanisms of TiO2 Photocatalysis

2.4.2.3 Kinetics in TiO_2 Photocatalysis

The kinetics of photocatalytic oxidation of organics can be described by Langmuir-Hinshelwood (L-H) approach. The following Equation 2.6 derives the rate reaction:

$$r = K_{Overall}\left(\frac{K_{A}K_{D}C_{A}C_{D}}{1+K_{A}C_{A}+K_{D}C_{D}}\right) \quad (2.6)$$

Where r is the reaction rate, the $K_{overall}$ is kinetic rate constant, *Ki* Langmuir adsorption constants, *Ci* concentrations, A and D for the reactants.

The photocatalytic process starts with the interaction of oxygen and water with generated charge carriers on the photoinduced surface of the catalyst. The L-H approach implies that first step is adsorbance of reactants on the catalyst surface. It follows with the reaction that generates products that eventually desorb from the surface.

2.4.2.4 Parameters influencing TiO_2 photocatalysis efficiency for treating textile wastewater

The main parameter which influence efficiency of TiO_2 photocatalysis to treat textile wastewater are pH of aqueous solution, oxygen agent, catalyst dosage and existence of salt and auxiliaries are the main factors affecting the efficiency of TiO_2 photocatalysis process (Akyol, 2004).

The effects of pH on photocatalysis efficiency have been investigated in many researches because of Practical industrial wastewater is not neutral and Surface-charge-properties can be changed by different pH. This means that at different pH, the adsorption of dyes with different charges differs as a result of the charges adsorbed on TiO_2.

In addition to that at low pH, positive holes are the major oxidation species, while at neutral and high pH, hydroxyl radicals are considered as the predominant species. Furthermore, in acidic conditions, TiO_2 particles tend to agglomerate and the available surface area for dye adsorption and photon adsorption would be reduced (Aguedach, 2005).

Oxygen agent is another parameter influencing the photocatalytic efficiency. Specifically, oxygen acts as an electrons scavenger ($O_2+e^- \rightarrow O_2^{-}\bullet$), so the air flow that contains oxygen in the Photocatalytic system should be well controlled.

The catalyst loading for the treatment of textile dyeing wastewater is also responsible for the treatment efficiency. The initial rate of photocatalysis was found to be directly proportional to catalyst concentration. This is simply due to the increased quantity of catalyst increases the active sites on TiO_2 surface, thus increasing the number of hydroxyl and superoxide radicals. However, overloading of catalyst in the treating system may lead to the agglomeration of TiO_2, and may cause the interception of light, resulting in a decrease of treating efficiency (Bizani E., 2006).

Although existence of salts and auxiliaries in wastewater can influence the TiO_2 photocatalytic performance. Parameters mentioned above that influence the photocatalytic performance are External factors. In terms of internal factors, the photocatalytic activity of TiO_2 itself is also vital to the treating efficiency. The main hindrance of utilising the photocatalytic property of TiO_2 is the recombination of electrons and holes, and the wide band gap (Carey, 1992).

2.4.2.5 Benefits and Limitations of TiO_2 Photocatalysis

- ***Benefits of TiO_2 Photocatalysis;***
  - UV/TiO_2 process has been studied for many organic compounds degradation which have an excellent removal performance than the other AOP techniques.
  - Operate at ambient condition.
  - The catalyst is inexpensive, commercially available in various crystalline forms and non-toxic.
  - Removes toxicity from the wastewater which makes it preferable from other AOPs method to use biological treatment.

- **Limitations of TiO_2 Photocatalysis**
  - Pre-treatment of feedstock is required to avoid the fouling of active TiO_2 sites and inhibition of catalyst. Fouling is occurred due to the presence of inorganic particulates and non-organic materials. Presence of alkalinity and anionic species observed to inhibit catalyst activity.
  - With the initially low concentration of dissolved oxygen in feedstock additional oxygen sparging will be required to increase the efficiency of process performance.
  - UV/TiO_2 can perform at a higher wavelength, 300 to 380 nm, than other UV assisted oxidation processes.

CHAPTER THREE

3 MATERIALS AND METHOD

3.1 MATERIALS

3.1.1 Sample Collection and Study Area

Textile wastewater was collected from Ayka Addis textile factory located in Alem Gena around 20 km south west from Addis Ababa city. Ayka Addis textile factory is one of the largest industry in Ethiopia which produces knitted fabric product for men, women, kids and sports with a daily capacity of 30,000-40,000 pieces. The raw wastewater and treated wastewater characterized for the following parameters BOD_5, COD, pH, Total Solid (TS), Total Dissolved solid (TDS), Total Suspended Solid (TSS) and Turbidity. All the analysis was carried out as described in standard methods for the examination of water and wastewater. (APHA - AWWA - WPCF, Washington DC, 1999)

On this study the treatment of wastewater focused mainly on the removal of COD and Color in the effect of pH, irradiation time and catalyst dosage in batch studies. The photcatalysis experiment was done at Addis Ababa Institute of Technology School of chemical and biochemical engineering, in laboratory of biochemical engineering and characterization of raw wastewater and treated wastewater was analyzed at Addis Ababa university collage of natural science at center of Environmental science in Environmental Laboratory.

3.1.2 Chemicals

Chemicals used in this study are Titanium dioxide (TiO_2), sodium hydroxide (NaOH), hydrochloric acid (HCl), BOD_5 reagent, COD reagent, and distilled water.

Table 3. 1 chemicals and their function

Chemicals	**Their function**
Titanium dioxide	Semiconductor used as a photocatalyst
sodium hydroxide	Used to adjust the pH
hydrochloric acid	Used to adjust the pH
BOD_5 reagent	Used to measure 5 day BOD of the wastewater and treated wastewater which measure the effect of pollutant on dissolved oxygen.

COD reagent	Used to measure oxidizable pollutant found in wastewater.
distilled water	Used as for making blank solution, used to wash equipment and as a reagent.

3.1.3 Apparatus

Apparatus used in this study was cylindrical Pyrex glass beakers different in size, flask, laminar flow cabinet with UV-C, magnetic stirrer, pH meter, BOD_5 incubator, COD analyzer, UV-Vis spectrophotometer, analytical balance, spatula, Oven dryer, Turbidometer and desiccators.

Table 3. 2 Apparatus and their function

Apparatus	**Their function**
cylindrical Pyrex glass beakers and Flask	Used as a photo reactor and to hold sample
laminar flow cabinet with UV lamp (UV-C)	as a source of UV light to degrade the pollutant at wavelength of 254 nm
magnetic stirrer	To mix sample
pH meter (HANNA, HI11310)	To measure pH
BOD_5 incubator (TS 606/4-I)	To measure BOD_5
COD analyzer (HI 839800)	To measure COD
UV-Vis spectrophotometer (UVD-3200)	To measure absorbance at 620 nm
analytical balance	To weight mass of titanium dioxide
Desiccators	For cooling sample
Glass fiber Filter disk	To filter sample for TSS analysis
oven dryer (DAS 42000)	For drying the sample for TS and TSS analysis
Turbido meter (2100 NTU)	To measure turbidity

3.2 METHODS

3.2.1 Experimental setup

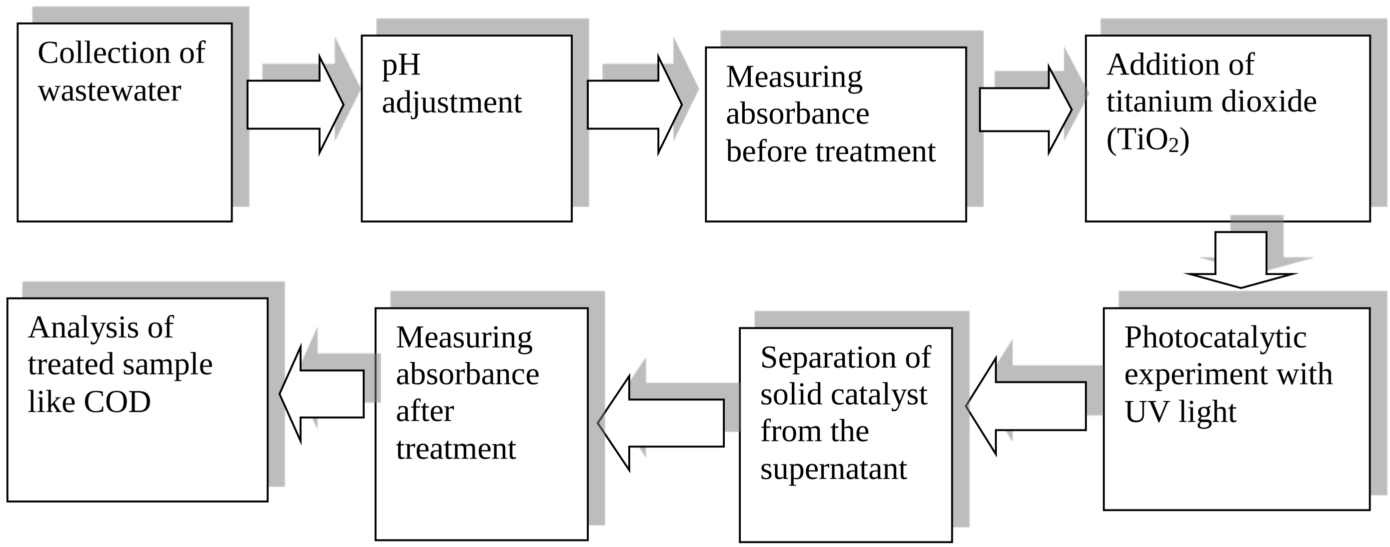


Figure 3. 1 experimental set up of TiO2 photocatalysis

3.2.1.1 Experimental Procedure

Experiments were conducted using titanium dioxide (Anatase 99.99% purity) and samples pH value was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH). Before doing the experiment it is necessary to reduce pH of the wastewater by using 0.1 M of HCl solution because of high alkalinity and then measure of the absorbance before treatment were done then addition of desired amount of titanium dioxide in to 250ml of wastewater samples, the solution was stirred throughout the experiment by magnetic stirrer then each samples inserted in to the laminar flow cabinet by opening UV-C lamp with wavelength of 254nm to degrade textile wastewater dyes and to reduce high COD and color for the desired period of irradiation time for each samples. After treatment, the supernatant and solid catalyst were separated by whatman filter paper 0.45um then absorbance of the supernatant liquid (treated wastewater) were measured at λmax of 660 nm then further analysis of the treated wastewater like COD and color were done.

3.2.2 Analytical Methods

Analytical methods used in this study was measured according to procedures given in standard methods for the examination of water and wastewater (APHA-AWWA-WPCF, 1999).

3.2.2.1 COD Analysis

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. The dichromate ion ($Cr2O7^{2-}$) is the specified oxidant used in this experiment. Chemical oxygen demand (COD) measurements were carried out according to procedures given in standard methods for the examination of water and wastewater, titrimetric method 5220 C (APHA-AWWA-WPCF, 1999).

Apparatus used

a) Digestion vessels: borosilicate culture tubes were used, 16 × 100 mm, 20 × 150 mm, or 25 × 150 mm, with tetra-fluoro-ethylene (TFE) lined screw caps.

b) Block heater which operate at a temperature of 150 ± 2 °C, with holes to accommodate digestion vessels.

c) Microburet

d) Ampule sealer: Use only a mechanical sealer to insure strong and consistent seals.

Reagent used

a) Standard potassium dichromate digestion solution, 0.01667M: Add to about 500 ml distilled water 4.903 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150 ^{0}C for 2 hour, 167 ml H_2SO_4, and 33.3 g $HgSO_4$. Dissolve, cool to room temperature, and dilute to 1000 ml were used.

b) Sulfuric acid reagent: Add Ag_2SO_4, reagent or technical grade, crystals or powder, to H_2SO_4 at the rate of 5.5 g Ag_2SO_4/kg H_2SO_4 were used.

c) Ferroin indicator solution: Dissolve 1.485 g 1,10-phenanthroline monohydrate and 695 mg FeSO4.7H2O in distilled water and dilute this reagent by a factor of 5 (1 + 4) were used.

a) Standard ferrous ammonium sulfate titrant (FAS), approximately 0.10 M: Dissolved 39.2 g Fe $(NH_4)_2(SO_4)_2$ $6H_2O$ in distilled water. 20 ml H_2SO_4 were added, cool, and dilute to 1000 ml.

b) Standardize solution daily against standard $K_2Cr_2O_7$ digestion solution as follows: Pipet 5.00 ml digestion solution into a small beaker.

$$Molarity\ of\ FAS\ solution = \frac{\text{Vol.of 0.01667M K2Cr2O7 solution titrated,ml}}{\text{Vol.of FAS used in titeration,ml}} \ldots\ldots\ldots\ldots\ldots\ldots.. \quad (3.1)$$

c) Potassium hydrogen phthalate (KHP) standard, $HOOCC_6H_4COOK$: Lightly crush and then dry KHP to constant weight at a temperature of 110 ^{0}C. Then Dissolve 425 mg in distilled water and dilute to 1000 ml.

Experimental procedure

a) Culture tubes and caps were washed with 20 % H_2SO_4 before first use to prevent contamination.

b) Tubes or ampules can be placed in block digester preheated to 150 °C and reflux for 2 hrs behind a protective shield.

c) Then it was placed to cool to room temperature and place vessels in test tube rack.

d) Culture tube caps were removed and small tetraflouro ethylene (TFE) covered magnetic stirring bar were added.

e) 0.05 to 0.10 ml (1 to 2 drops) ferroin indicator were added and stirred rapidly on magnetic stirrer while titrating with standardized 0.10 M FAS.

f) The end point is a sharp color change from blue-green to reddish brown, although the blue green may reappear within minutes. In the same manner reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of the sample.

Calculation

Chemical oxygen demand (COD) concentration was calculated using the following formula:

$$\boldsymbol{COD\left(\frac{mg}{l}\right) = \frac{(FASs - FASp)*N*f}{Vs}} \quad \text{.................. (3.2)}$$

where; FASs: used ferrous ammonium sulphate concentration for sample, mg/l, FASp: used ferrous ammonium sulphate concentration for pure water, mg/l, f: dilution factor (8000), N: normality of FAS and Vs: sample volume, ml

3.2.2.2 Color measurement

In this study color removal efficiency were measured in terms of changes in absorption spectra. The absorption spectra were measured by UV-Vis Spectrophotometer (UVD-3200). According to Lambert's Law the proportion of incident light absorbed by a transparent medium is independent of the intensity of the light (provided that there is no other physical or chemical change to the medium) (UV-Visible, 2013). Therefore successive layers of equal thickness will transmit an equal proportion of the incident energy. Lambert's law is expressed by equation 3.3.

$$T = \frac{I}{Io} \quad \text{.................. (3.3)}$$

Where I is the intensity of the transmitted light, Io is the intensity of the incident light, and T is the Transmittance.

According to Beer's Law absorption of light is directly proportional to both the concentration of the absorbing medium and the thickness of the medium in the light path (UV-Visible, 2013).

A combination of the two laws (known jointly as the Beer-Lambert Law) defines the relationship between absorbance (A) and transmittance (T) can be expressed in equation (3.4).

$$A = log\frac{Io}{I} = \log\frac{100}{T} = Ecb \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3.4)$$

Where A is absorbance (no unit of measurement), ε is molar absorptivity ($dm^3 \ mol^{-1} \ cm^{-1}$), c is molar concentration ($mol \ dm^3$), and b is path length (cm). ε is a function of wavelength and so the Beer-Lambert law is true only for light of a single wavelength, or monochromatic light.

A plot of absorbance against concentration will be linear but for this study the concentration is unknown because of textile wastewater have a combination of different dyes so the concentration of each dyes cannot be known so according to Beer-Lambert law it is therefore more convenient to express results in absorbance rather than transmission when measuring unknown concentrations, since linear calibration plots will be available (UV-Visible, 2013) .

An alternative to plotting calibration curves is to make use of the relationship which shown by equation (3.9):

$$C = k\ A \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3.5)$$

Where, C is the concentration of the unknown, A is the measured absorbance of the unknown, and k is a factor derived from the reference or standard solution.

3.2.2.3 UV-Visible Spectrophotometer

Is a method to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through sample solution. The basic principle is that each compound absorbs or transmits light over a certain range wavelength. The extent of decolorization that had occurred during photocatalytic treatment was assessed by measuring the sample absorbance at 660 nm, which is the wavelength that corresponds to the maximum absorbance in the visible region, measured by Spectro UV-VIS 3200 double beam pc spectrophotometer. UV visible spectrophotometer uses light at ultraviolet range (185 – 400 nm) and visible range (400 – 700 nm) of electromagnetic radiation spectrum (UV-Visible, 2013).

Decolorization efficiency (DE) was calculated from a mathematical equation (3.10):

$$DE = \frac{(Absorbance)o-(Absorbance)t}{(Absorbance)o} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.10)$$

Where, $(\text{Absorbance})_o$ is the absorbance measured before treatment, $(\text{Absorbance})_t$ is the absorbance measured after treatment at irradiation time t.

Experimental procedure

a) Spectrophotometer was turned on to warm up for at least 15 minute before running any sample.
b) The cuvettes was cleaned, rinsed thoroughly with distilled water.
c) Proper volume of the sample loaded into the cuvette.
d) Control solution (blank solution) were prepared which has only chemical solvent in which the solute to be analysed is dissolved in.
e) Outside of the cuvette was wiped before placing it into the spectrophotometer to reduce measuring error.

When running the experiment:

- Wavelength of 660 nm were choosed to analyse the textile wastewater which is in the preferred range of (200-800 nm). Using a single wavelength of light (monochromatic Color) make the testing more effective.
- The machine were calibrated by blank solution.
- After the machine calibrated the blank were removed and calibration were tested to make it at 0.
- Absorbance of the wastewater were measured at wavelength of 660 nm (before and after treatment).
- Repeating the test were done with successive wavelength of light to check best wavelength.

Analyzing the absorbance data

a) Calculate the transmittance and absorbance of the sample. The transmittance is found by dividing the intensity of light that passed through the sample solution with the amount that passed through the sample blank were done.
b) Then absorbance value versus the wavelength on the graph were plotted.

3.2.3 Experimental Design and data analysis

In this study experimental design and data analysis was done by using design expert software (version 11.1.0). The experimental data analysis was provided by using Box-Behnken design (BBD), which is one type of response surface methodology (RSM).

RSM is a collection of statistical and mathematical methods that are useful for modeling and analyzing engineering problems (ying, 2011). RSM allows the interaction of the independent variables with the response variables to be monitored using a collection of statistical and mathematical methods. and also the Box-Behnken design has a maximum efficiency for an experiment involving three factors and three levels further, the number of experiments conducted for this is much lesser which is advantage over the other RSM design. Therefore, to determine the effect of the three operating factors for the textile wastewater treatment, response surface methodology (RSM) was used. The operating factors were irradiation time, titanium dioxide dosage and pH and the response variables were COD and color.

Box-Behnken design was used to characterize the process parameters of photocatalysis using the three factors of textile wastewater treatment. Diagnostics and model graph were plotted to represent the results.

This representation showed the relative effects of the three factors. For this factors designs $\alpha = 1$ and all factors are run at the three levels, which are -1, 0 and 1 in terms of the coded values. Three levels, three factors without replication at box-behnken were used and total of 17 experiments were done. The independent factors were irradiation time, pH and TiO_2 dosage these factors were selected to investigate the quality of treated textile wastewater and in order to minimize errors the experimental work was randomized.

The significant effect of treatment was judged with the help of 'F' (Variance Ratio). Calculated 'F' value was compared with the table value of F at 5% level of significance with 95 % CI.

If calculated value Exceed the table value the effect will be considered to the significance. The significance of the Study was tested at 5% level.

Table 3. 3 selected factors and corresponding levels.

Factors	symbols	Levels		
		-1	0	+1
TiO_2 dosage (mg/l)	A	400	475	550
pH	B	7	8	9
Irradiation time (hour)	C	3	4	5

In this study the factors were selected by referring different literature which was done before. The reason of selection was:

- **Irradiation time** (contact time between the UV radiation and the aqueous solution in the treatment process) : irradiation time as a factor was selected because of its effect on the efficiency of photocatalytic process, when the irradiation time increases at the same time it increases the production of hydroxyl radicals which is very powerful oxidizing agent that mineralize organic compounds.
- **pH**: on the treatment of textile wastewater pH is the main factor which plays a great role in the degradation of organic pollutant like dyes, that at different pH the adsorption of dyes with different charge differs as a result of the charges adsorbed on TiO_2 surface.
- **TiO_2 dosage**: catalyst dosage can be another main factor which influence the treatment process of photocatalysis. This is because of increased quantity of catalyst increases the active site on TiO_2 surface, thus increases the number of hydroxyl and super oxide radicals.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characterization of Ayka Addis Textile factory Wastewater

Table 4.1 shows characterization of Ayka Addis Textile wastewater which is taken from the outlet of the dyeing and finishing section, the characterization result implies that the effluent contains high suspended solids (SS), chemical oxygen demand (COD), biological oxygen demand (BOD), highly colored and other organic pollutant which makes the characterization parameter value greater than the value set by Ethiopian environmental protection agency (EPA).

In this study of textile wastewater treatment by using TiO_2 photocatalysis was mainly focused on removing COD and color by selecting TiO_2 dosage, pH and irradiation time as experimental factors which play great role on reducing the value of COD and Color.

Table 4. 1 characterization of Ayka Addis textile factory

Parameter	**Values**
Temperature (^{0}c)	38
pH	11
Chemical oxygen demand (COD) (mg/l)	1150
Biological oxygen demand (BOD) (mg/l)	210.77
Total solid (TS) (mg/l)	2500
Total dissolved solids (TDS) (mg/l)	1650
Total suspended solid (TSS) (mg/l)	850
Turbidity (NTU)	190

4.2 Decolorization efficiency of photocatalytic treatment for textile wastewater

Decolorization efficiency (color removal efficiency) of photocatalytic treatment can be measured by using absorbance value. On this study, absorbance was measured at wavelength of 660 nm maximum absorbance value by using Spectro UV-VIS double beam pc UVD-3200.

$$\text{Decolorization efficiency (\%)} = \frac{(A)o-(A)t}{(A)o} * 100\% \text{................ (4.1)}$$

Where, $(A)_0$ = absorbance value before treatment, $(A)_t$ = absorbance after treatment at irradiation time t

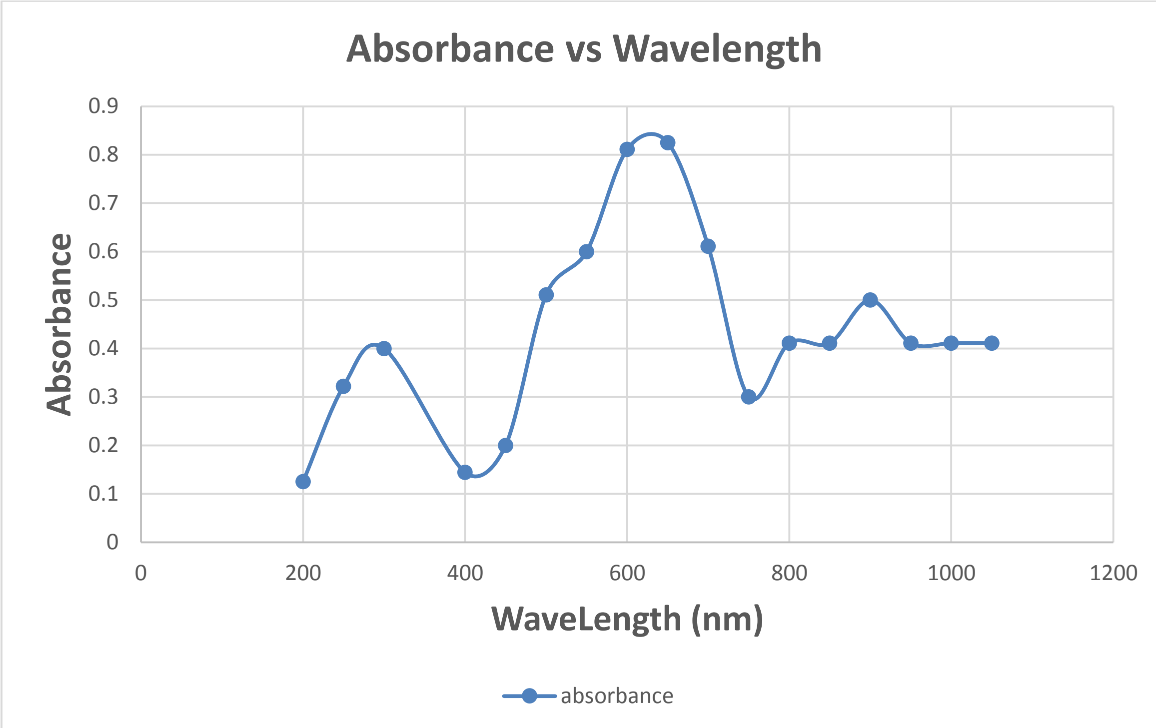
The degradation of dyes present in the textile wastewater for color removal must be monitored by scanning the absorbance at wavelengths ranging from 200-800nm (p.M Andrade M.A.F. Carvalh, 2015).

Table 4.2 shows that the UV-VIS absorbance measurement value before and after treatment at wavelength of 660 nm which shows that photocatalytic treatment of real textile wastewater can remove color effectively, the color removal percentage at optimum value of TiO_2 dosage of 475 mg/l, pH 9 and irradiation time of 5 hour shows 88 % color removal which shows photocatalytic treatment of textile wastewater have a great potential in reducing the color of textile wastewater as a result reduces Environmental as well as aesthetic pollution.

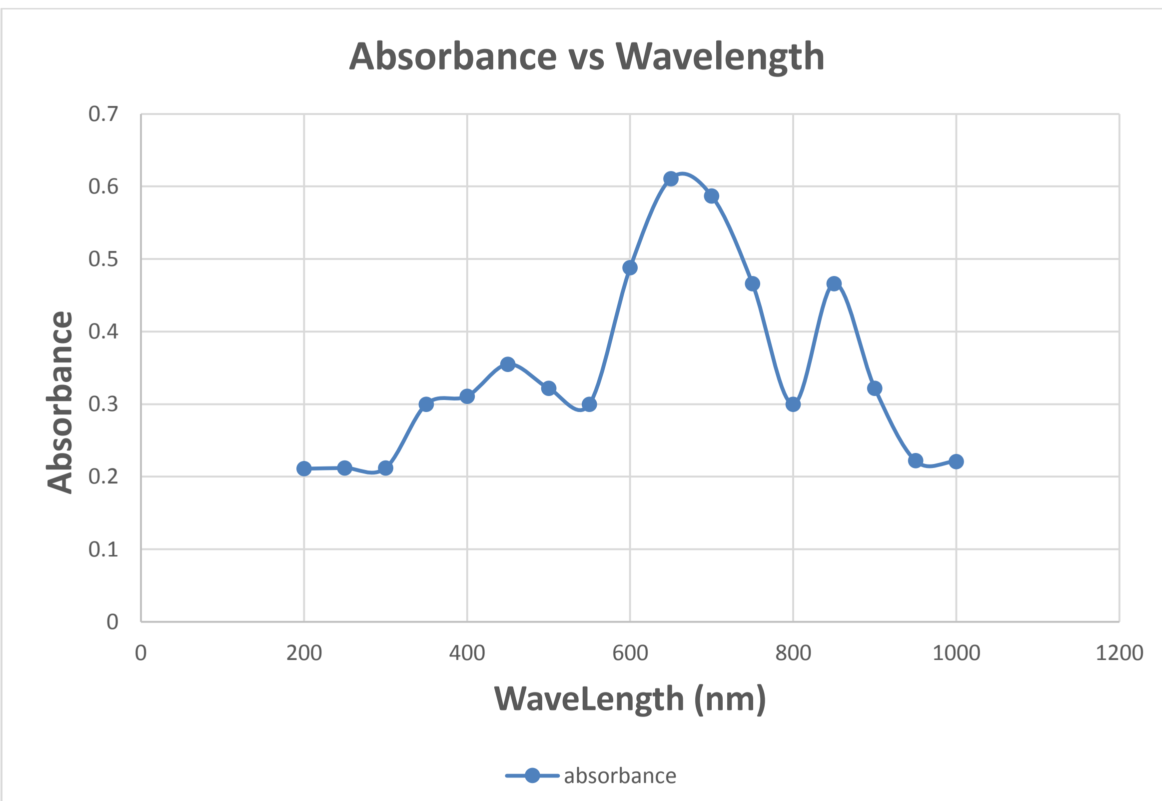
The collected sample wastewater were a mixture of different dyes (basic dye, reactive dye etc.) so, it is difficult to know the concentration of each dyes so the absorbance measured before treatment have a mixture of different dyes and absorbance before treatment for each run were measured instead of taking average value because of the raw wastewater sample shows variation in each run which is the effect of reaction of dyes makes it to vary the value in each run.

Table 4. 2 UV-VIS Absorbance measurement of textile wastewater before and after treatment at 660nm

No.	**TiO_2 dosage (mg/l)**	**pH**	**irradiation time (hr)**	**Absorbance before treatment**	**Absorbance after treatment**	**Decolorization efficiency (%)**
1	475	9	3	1.311	0.551	58
2	475	8	4	1.267	0.443	65
3	400	9	4	1.322	0.594	55
4	550	8	5	1.269	0.456	64
5	475	8	4	1.262	0.426	66.21
6	400	7	4	1.157	0.451	61
7	475	8	4	1.285	0.430	66.53
8	475	7	3	1.124	0.506	55
9	475	8	4	1.231	0.398	67.62
10	475	7	5	1.257	0.503	60
11	550	9	4	1.462	0.366	75
12	475	9	5	1.482	0.178	88
13	400	8	3	1.455	0.80	45
14	550	8	3	1.345	0.336	75
15	475	8	4	1.285	0.419	67.32
16	550	7	4	1.315	0.802	39
17	400	8	5	1.421	0.128	91


Absorbance vs Wavelength
Absorbance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
1200
WaveLength (nm)
absorbance

(a)


Absorbance vs Wavelength
Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
1200
WaveLength (nm)
absorbance

(b)

Figure 4. 1 UV-VIS measured Absorbance value vs. wavelength of raw wastewater (a) and treated wastewater (b).

Figure 4.1 shows UV-VIS Measured Absorbance value vs. Wavelength of raw wastewater and treated wastewater at 660nm which indicate that at wavelength of around 660nm there is a maximum absorbance value for treated wastewater means that there is high removal efficiency of Color and the absorbance value of raw wastewater shows that it is highly colored effluent.

4.3 Analysis of Treated Wastewater

Table 4.3 shows the optimum data for treated textile wastewater which measured at optimum condition of 475mg/l TiO_2 dosage, pH 9 and irradiation time of 5 hour. Textile factory wastewater has been the major environmental pollutant aesthetically as well as aquatic pollution because of lack of effective treatment and lack of attention from the factory owner and the government officials. In this study of photocatalytic textile wastewater treatment mainly focused on the removal of COD and color but to know the effectiveness of photocatalytic treatment the other wastewater parameter were measured so as a result photocatalytic treatment of textile wastewater by using TiO_2 photocatalysis can remove pollutant 90.4% COD, 78.65% BOD, 88% Color, 95.5% TDS, 97.1% TSS and 88.42% Turbidity from the textile wastewater which makes this treatment technology the best option.

Table 4. 3 Optimum data of treated wastewater

Parameter	**Values**
Biological oxygen demand (BOD) mg/l	45
Chemical oxygen demand (COD) mg/l	110
Total dissolved solids (TDS) (mg/l)	74
Total suspended solids (TSS) (mg/l)	25
Turbidity (NTU)	22

4.3.1 Analysis of Treated Wastewater with Response Surface Methodology

4.6.1.1 Development model equation

The mathematical relationship between the response and the independent variables TiO_2 dosage (A), pH (B) and irradiation time (C) in terms of coded and actual factors can be determined by Design Expert software (version 11). The model equation that correlates the response (COD and Color) to the treatment process variables in terms of coded factors after excluding the insignificant terms was given in equation. The model assumed for analysis of variance was quadratic model and ANOVA was performed using partial sum of squares methods with lambda value of 1. Model A: TiO_2 dosage, B: pH and C: irradiation time and, quadratic model factors; pure quadratic terms (A^2, B^2, C^2) and interaction of quadratic terms are (AB, AC, BC) depending on the F and P values.

Table 4.4 Statistical analysis of treated wastewater

Std	**Run**	**Factor 1 A:TiO_2 dosage (mg/l)**	**Factor 2 B: pH**	**Factor 3 C: irradiation time (hour)**	**Response 1 COD (mg/l)**	**Response 2 Color (%)**
13	1	475	8	4	130	65
5	2	400	8	3	250	45
2	3	550	7	4	161	39
8	4	550	8	5	210	64
4	5	550	9	4	155	75
6	6	550	8	3	169	75
12	7	475	9	5	110	88
1	8	400	7	4	201	61
14	9	475	8	4	135.89	66.21
17	10	475	8	4	140.89	67.32
15	11	475	8	4	135.92	66.53
16	12	475	8	4	139.68	67.62
11	13	475	7	5	135	60
3	14	400	9	4	143	55

9	15	475	7	3	162	55
7	16	400	8	5	165	91
10	17	475	9	3	140	58

4.3.2 Analysis of Variance (ANOVA) on the Experimental Variables

The response optimized value for the removal of COD and Color of textile wastewater was based on the three process variables (TiO_2 dosage, pH and irradiation time) described on the response surface methodology. The effect of the independent variables and their mutual interaction on the efficiency of removal COD and color can be seen by analysis of variance ANOVA.

Table 4.5 ANOVA for COD removal

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	18853.76	9	2094.86	106.58	< 0.0001	significant
A-TiO2 dosage	512.00	1	512.00	26.05	0.0014	
B-pH	1540.13	1	1540.13	78.36	< 0.0001	
C-irradiation time	1275.13	1	1275.13	64.87	< 0.0001	
AB	676.00	1	676.00	34.39	0.0006	
AC	3969.00	1	3969.00	201.93	< 0.0001	
BC	2.25	1	2.25	0.1145	0.7450	
A^2	8578.31	1	8578.31	436.43	< 0.0001	
B^2	1162.07	1	1162.07	59.12	0.0001	
C^2	1200.72	1	1200.72	61.09	0.0001	
Residual	137.59	7	19.66			
Lack of Fit	65.25	3	21.75	1.20	0.4159	not significant
Pure Error	72.34	4	18.09			
Cor Total	18991.35	16				

The Model F-value of 106.58 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 1.20 implies the Lack of Fit is not significant relative to the pure error. There is a 41.59% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.6 Fit Statistics for COD removal

Std. Dev.	4.43	R^2	0.9928
Mean	157.85	Adjusted R^2	0.9834
C.V. %	2.81	Predicted R^2	0.9391
		Adeq Precision	41.5034

The Predicted R^2 of 0.9391 is in reasonable agreement with the Adjusted R^2 of 0.9834; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 41.503 indicates an adequate signal. This model can be used to navigate the design space.

Final Equation in Terms of Coded Factors

$COD = +136.48* - 8.00*A - 13.88*B - 12.63*C + 13.00*AB + 31.50*AC - 0.7500*BC+45.14*A^2-16.61*B^2 + 16.89*C^2$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Final Equation in Terms of Actual Factors

COD = +2798.76456* - 10.79647*TiO_2 dosage + 172.59967*pH - 341.22100*irradiation time

+0.173333*TiO2 dosage * pH + 0.420000*TiO2 dosage * irradiation time - 0.750000*pH * irradiation time + 0.008024*TiO2 dosage² - 16.61300*pH² + 16.88700*irradiation time²

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

Table 4.7 ANOVA for Color removal

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	2778.20	9	308.69	287.91	< 0.0001	significant
A-TiO2 dosage	0.1250	1	0.1250	0.1166	0.7428	
B-pH	465.13	1	465.13	433.81	< 0.0001	
C-irradiation time	612.50	1	612.50	571.26	< 0.0001	
AB	441.00	1	441.00	411.31	< 0.0001	
AC	812.25	1	812.25	757.56	< 0.0001	
BC	156.25	1	156.25	145.73	< 0.0001	
A^2	32.26	1	32.26	30.09	0.0009	
B^2	165.42	1	165.42	154.28	< 0.0001	
C^2	104.51	1	104.51	97.47	< 0.0001	
Residual	7.51	7	1.07			
Lack of Fit	3.25	3	1.08	1.02	0.4727	not significant
Pure Error	4.26	4	1.06			
Cor Total	2785.70	16				

The Model F-value of 287.91 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case B, C, AB, AC, BC, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 1.02 implies the Lack of Fit is not significant relative to the pure error. There is a 47.27% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.8 Fit Statistics for Color removal

Std. Dev.	1.04	R^2	0.9973
Mean	64.63	Adjusted R^2	0.9938
C.V. %	1.60	Predicted R^2	0.9789
		Adeq Precision	65.6349

The Predicted R^2 of 0.9789 is in reasonable agreement with the Adjusted R^2 of 0.9938; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 65.635 indicates an adequate signal. This model can be used to navigate the design space.

Final Equation in Terms of Coded Factors

$$Color = +66.54* + 0.1250*A + 7.63*B + 8.75*C + 10.50*AB - 14.25*AC + 6.25*BC - 2.77*A^2 - 6.27*B^2 + 4.98*C^2$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Final Equation in Terms of Actual Factors

$$Color = -91.72322* + 0.109151*TiO2\ dosage + 16.41300*pH + 9.14400*irradiation\ time + 0.140000*TiO2\ dosage * pH - 0.190000*TiO2\ dosage * irradiation\ time + 6.25000*pH * irradiation\ time - 0.000492*TiO2\ dosage^2 - 6.26800*pH^2 + 4.98200*irradiation\ time^2$$

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

4.6.3 Diagnostics plots and Model graph of response COD and Color on the Experimental Variables

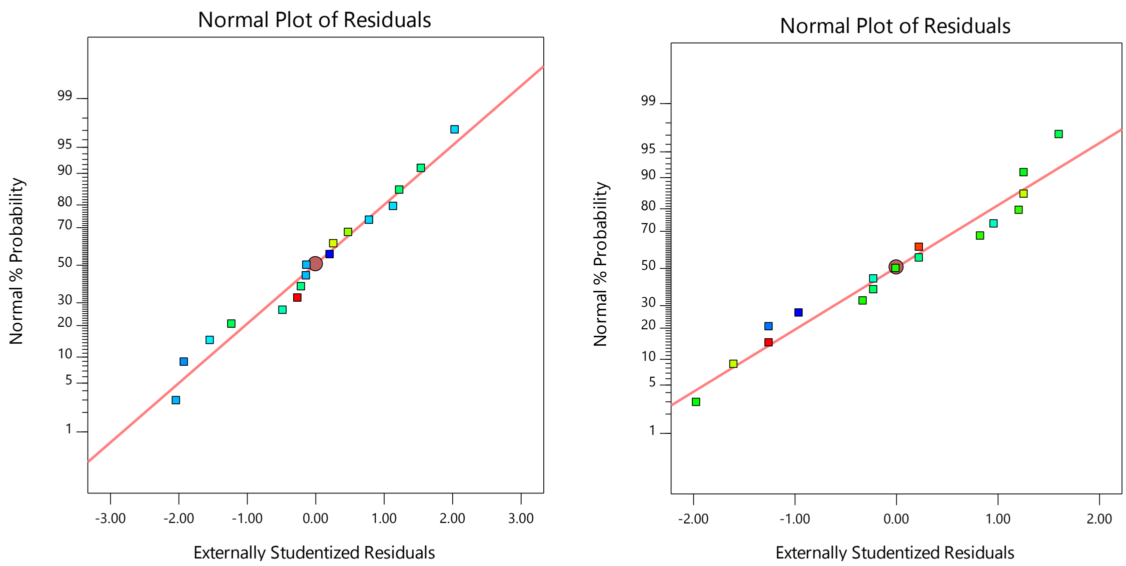
4.6.3.1 Diagnostics plots for the response of COD and Color

The normal probability plot of residuals is shown in Figures 4.2. If data from experiments form a normal distribution, the residuals fall on a straight line, which implies that the errors are spread in a normal distribution. Here a residual means difference in the observed value (obtained from the experiment) and the predicted value or fitted value (value that can be predicted by the developed model equation). Hence, observing this normal plot, it can be noticed that all the points line up well and the deviation of points from normality is insignificant, which means that the COD and Color removal is precisely modeled.

This can also be confirmed by the variations between the residuals and model predicted values analyzed through residual graphs as presented in Figure 4.3. The plot is a random scatter (constant range of residuals across the graph). Thus, the model does not need any form of transformation as it is well fitted which can be shown by the Box-cox plots in Figure 4.6. In which if the data is normal it cannot need any transformation other than it can suggest the best model transformation. On the other hand, Figure 4.4 shows the plot of residuals versus the experimental run order. It checks for lurking variables that may have influenced the response during the experiment. The plot shows a random scatter and thus no more blocking or any other solutions were needed.

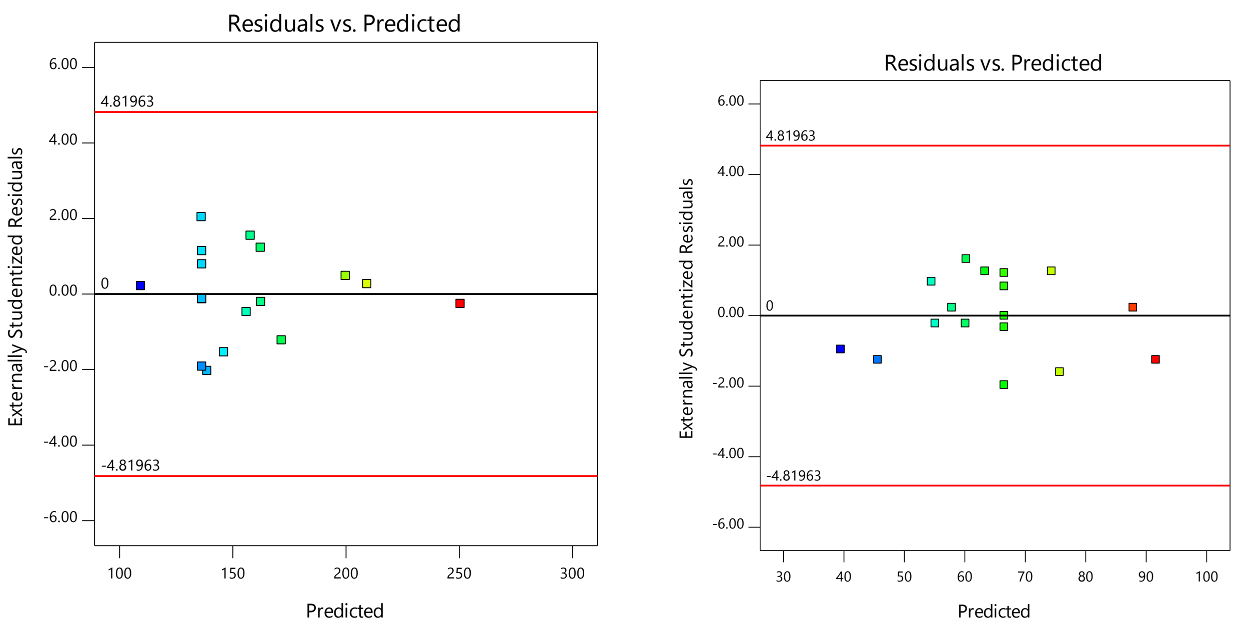
The plot of predicted versus actual (Figure 4.7), which is the graph of the predicted response values versus the actual response values, is also another important diagnostics plot that should be taken into consideration. The purpose is to detect a value, or group of values, that are not easily predicted by the model. . Looking into the graph, all values fall along the straight line, which shows the high power of prediction of the model developed.

Figure 4.5 shows residual vs. any selected factor to check whether the variance is not accounted for by the model, the graph exhibit a random scatter.



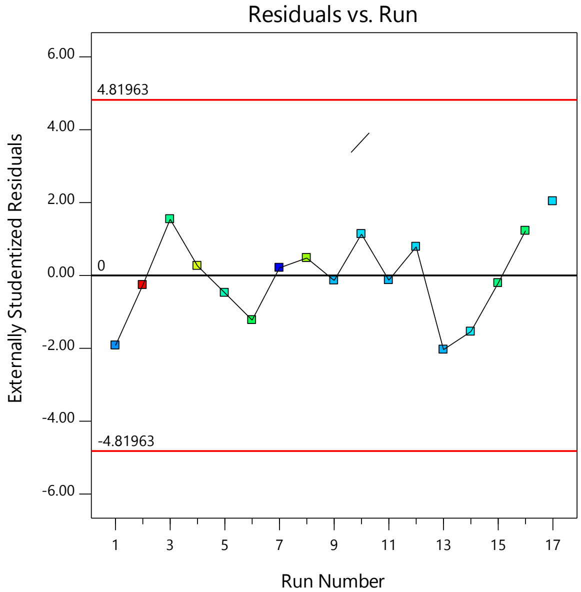
(a) (b)

Figure 4.2 Normal plots of response COD and Color

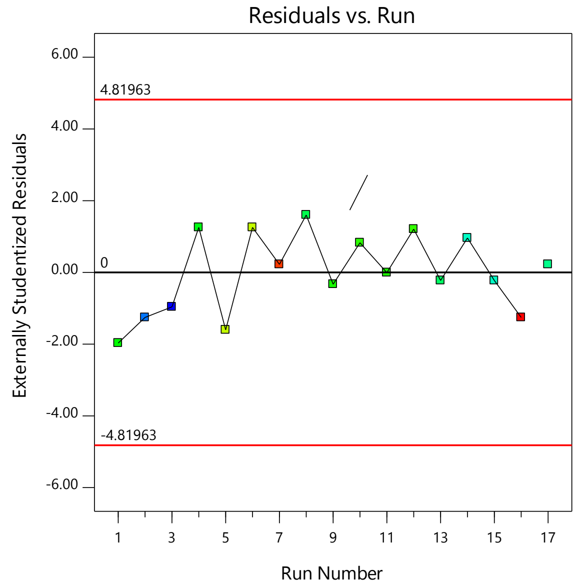


(a) (b)

Figure 4.3 Residual vs. predicated plots of response COD (a) and Color (b)

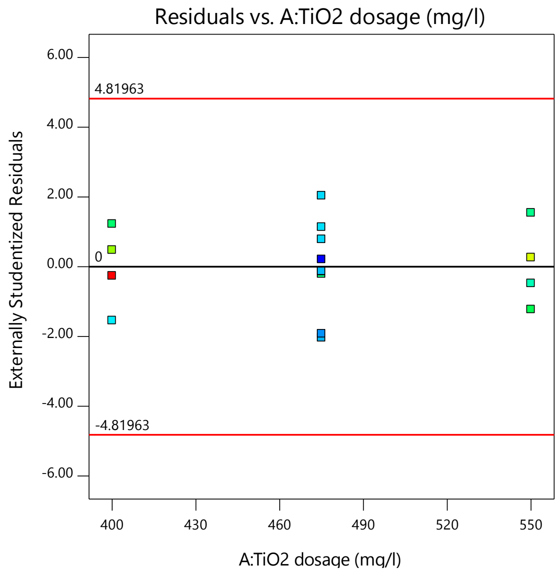


(a)

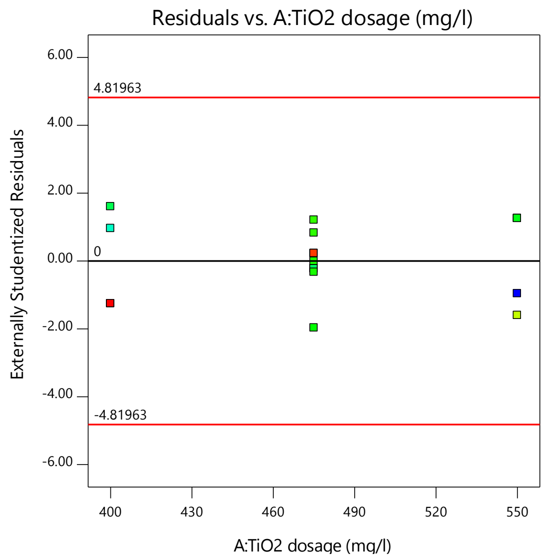


(b)

Figure 4.4 Residual vs. run plots of response COD (a) and Color (b)

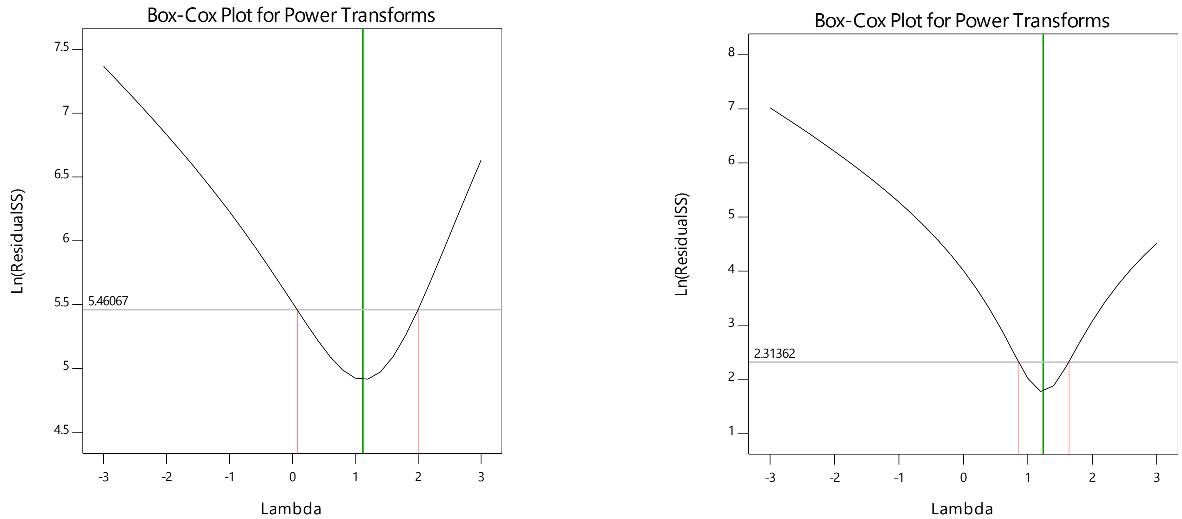


(a)



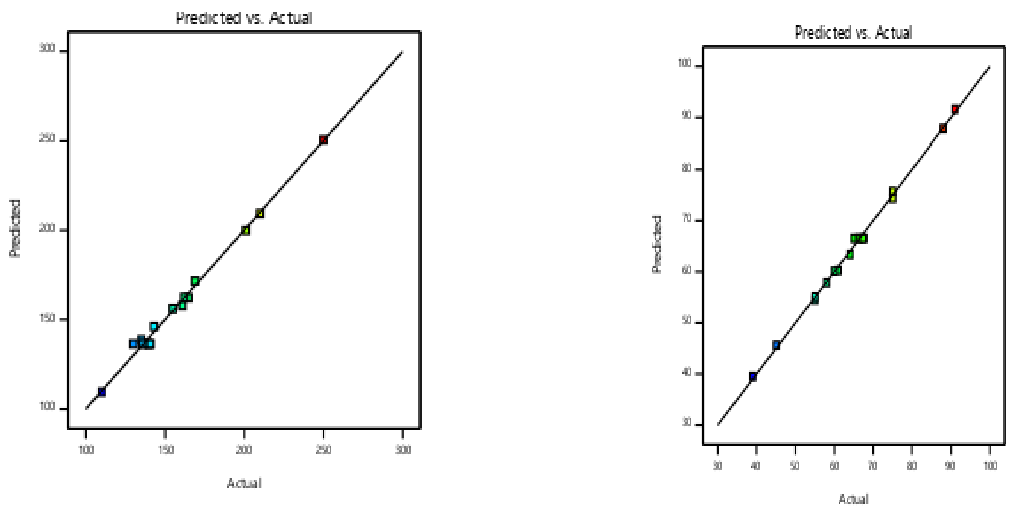
(b)

Figure 4.5 Residual vs. factor plots of response COD (a) and Color (b)



(a) (b)

Figure 4.6 Box-cox plots of response COD (a) and Color (b)



(a) (b)

Figure 4.7 predicted vs. actual plots of response COD (a) and Color (b)

4.6.3.2 The effect of Effect TiO_2 dosage, pH and irradiation time on the removal of COD and Color

The effect of TiO_2 dosage, pH and irradiation time with the response COD and Color can be seen in Figure 4.8 which shows a direct relationship, when the value of TiO_2 dosage, pH and irradiation time increases then COD and Color removal efficiency as well increase the optimum value of TiO_2 dosage, pH and irradiation time where at 475 mg/l, 9 and 5 hour respectively.

When the amount of TiO_2 dosage increases from 400-550 mg/l then the removal of COD and Color increases as well it increases the active site on TiO_2 surface, thus increases the number of hydroxyl and super oxide radicals which is responsible for the degradation of organic pollutant.

When the value of pH increases from 7-9 then the removal of COD and Color increases as well which shows a positive relationship between the response value and the selected factor, that at different pH the adsorption of dyes with different charge differs as a result of the charges adsorbed on TiO_2 surface when the pH is higher it is favorable condition for the removal of both COD and Color in which low value of pH causes aggregate of the catalyst (AL-Kdasi, 2004).

Irradiation time can also have a direct relationship with the removal of COD and Color as the duration of irradiation time increases it increase the production of hydroxyl radical which is responsible for the mineralization of organic pollutant (Akyol, 2004).

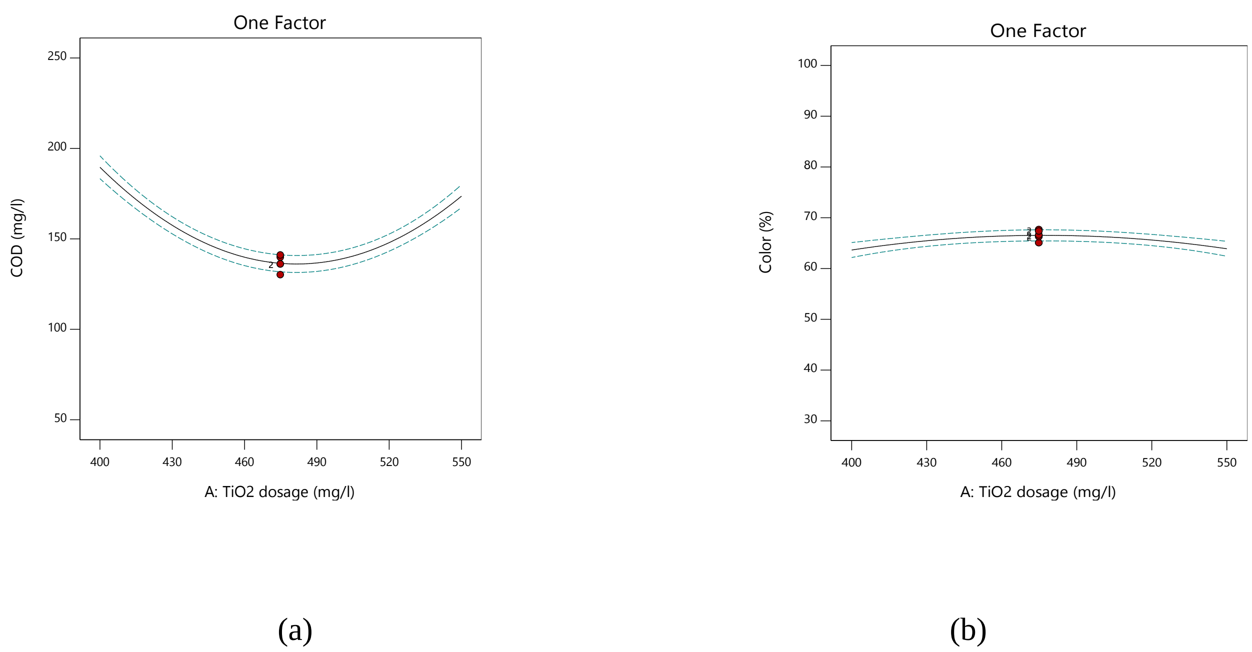
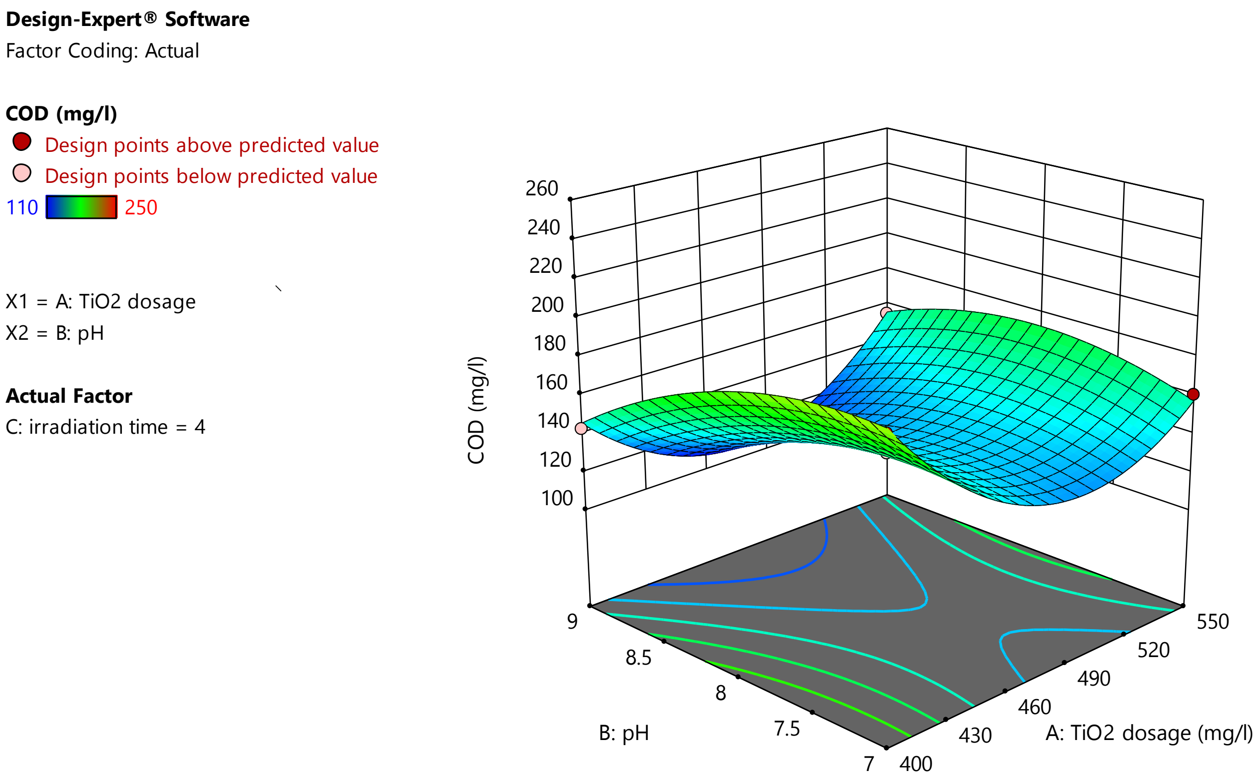
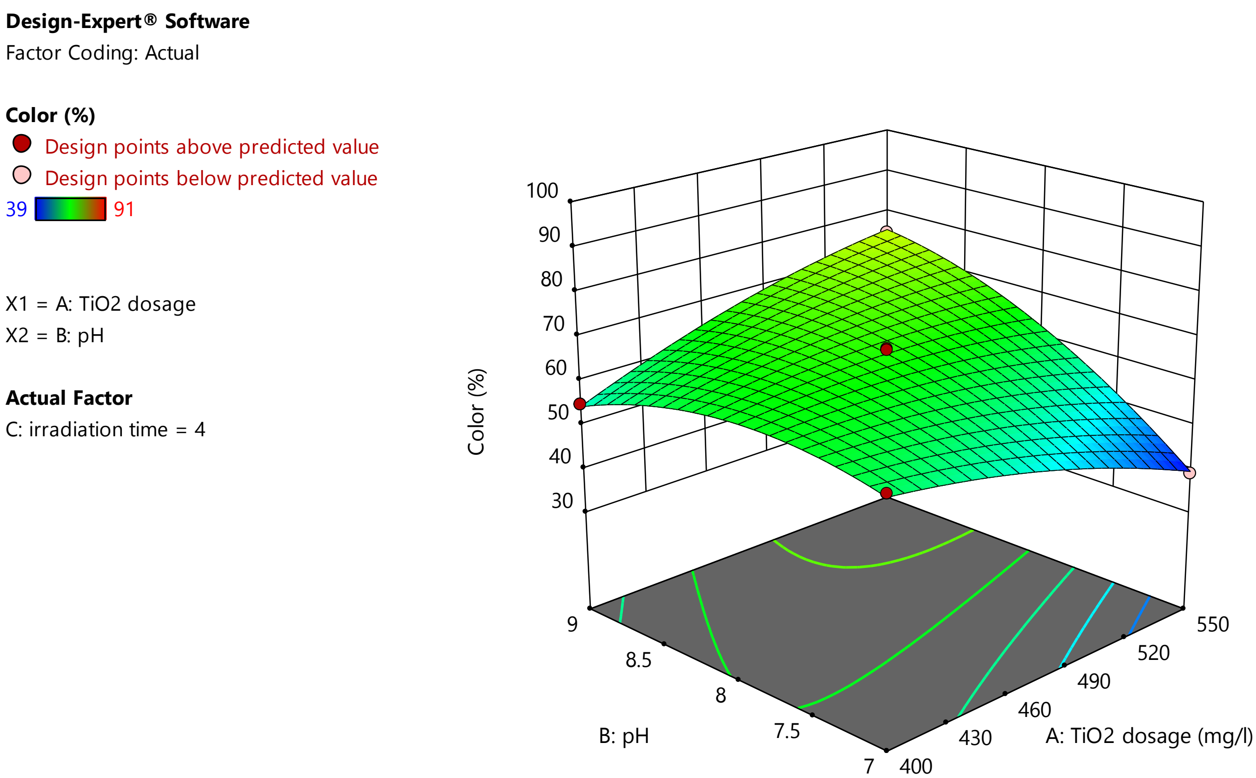


Figure 4.8 Model graph on the interaction of one factors for the response COD (a) and Color (b)



(a)

3D response surface for the response COD shows direct relationship that when the TiO_2 dosage increases COD removal also increases as the catalyst dosage increase it increases the active surface on titanium dioxide surface which is responsible for the production of hydroxyl radicals.



(b)

Figure 4.9 3D surface plot for the response of COD (a) and Color (b)

3D response surface for the response Color shows that a direct relationship between pH value in which increase in the value of pH increases the production of hydroxyl radicals which is responsible for the degradation of organic pollutant.

4.6.3.3 Optimization Solution plots for the Response COD and Color

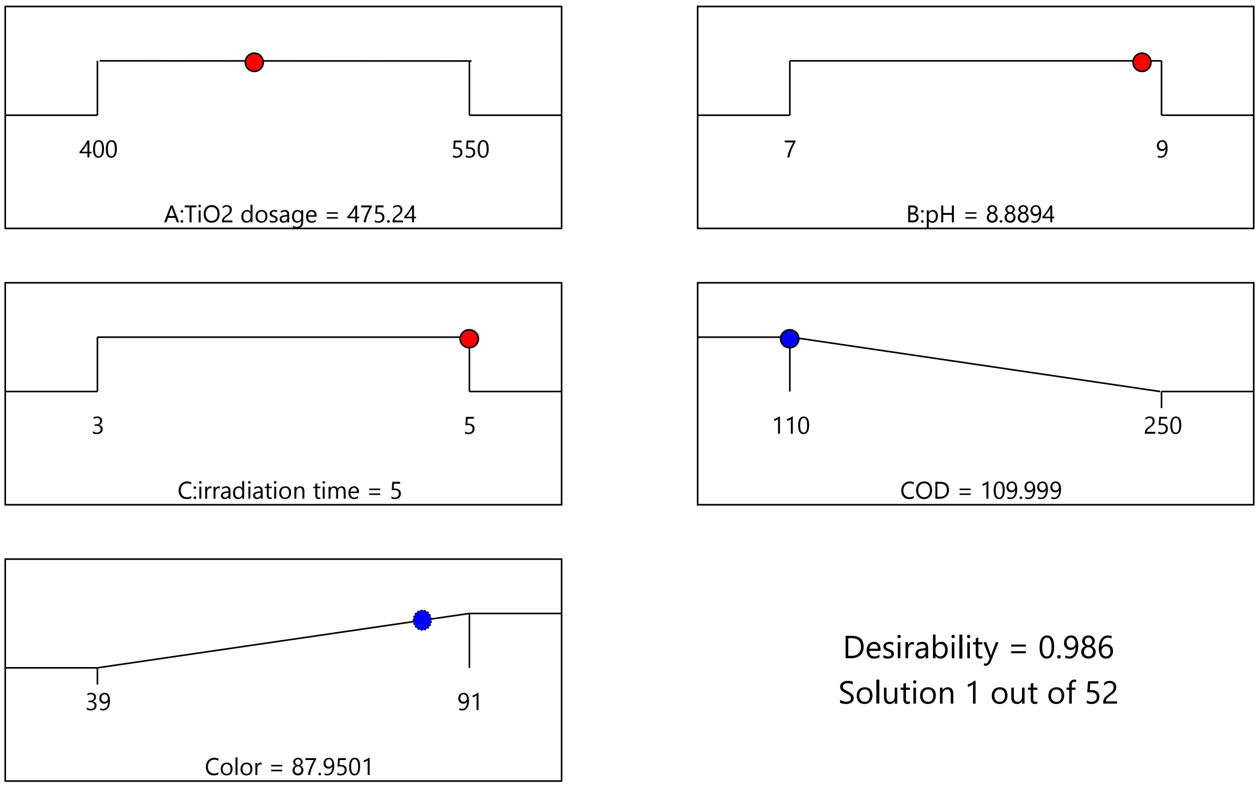


Figure 4.10 optimization solution for the response COD and Color

Figure 4.10 shows that optimum value for the photocatalytic treatment of textile wastewater in which the selected factor TiO_2 dosage, pH and irradiation time are 475.24 mg/l, 8.8894 and 5 hour respectively in which maximum COD and Color removal were obtained.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Heterogeneous photocatalysis degradation using TiO_2 remains a viable alternative for the degradation of recalcitrant organic contaminant like textile wastewater dyes. This promising treatment option solves the problem of environmental pollution both in aquatic as well as human being by reducing the pollutant load such as COD and Color.

The experimental result indicated that the optimum conditions for removal of COD and color were obtained at TiO_2 dosage 475 mg/l, pH 9 and irradiation time 5 hour. In this conditions the Efficiency of photocatalysis treatment by using semiconductor TiO_2 on the removal of COD and Color were obtained 90.43 % and 88 % respectively.

According to the results of analysis of variance (ANOVA) it can be concluded that the parameters TiO_2 dosage, pH and irradiation time is more significant variable on the removal of COD and Color. The experimental result indicated that the effect of TiO_2 dosage, pH and irradiation time have a significant effect on the removal of COD whereas, pH and irradiation time have a significant effect on the removal of color.

Ayka Addis textile factory has Biological wastewater treatment plant (Activated sludge) which have a significant effect in reducing environmental pollution by removing degradable organic pollutant but it is not effective treatment option in reducing recalcitrant organic pollutant like textile dyes so it must be upgraded to advanced oxidation treatment plant such as TiO_2 photocatalysis which is effective and efficient means of treatment technology.

In general from an environmental point of view, photocatalytic treatment of textile wastewater can be effective and efficient means of treatment option to overcome the issues of environmental pollution it is cost effective, environmentally friendly doesn’t have any waste after treatment and the treated wastewater can be used as a recycle in same factory as well as for other industry which uses low quality water.

5.2 Recommendations

Based on the result of this study the following recommendations are forwarded,

- ✓ Attention by the government must be increased in order to overcome the health and environmental effect of the discharge from the textile wastewater, in which by controlling industry to regulate the discharge limit set by Ethiopian environmental protection authority (EPA).
- ✓ Doping of the catalyst Titanium Dioxide with metals or non-metals can increase the effectiveness of the semiconductor by reducing the band gap increases its photocatalytic activity.
- ✓ Future work should focus on the effectiveness of these technologies in combination with other efficient treatment options such as biological treatment which comprehensively remove different kinds of pollutants in the textile dyeing wastewater where, each technology by itself may not be sufficiently effective for the degradation of organic pollutant completely so coupling of two treatment option can enhance the efficiency of removing bio-recalcitrant organic compound.
- ✓ Applying of the photocatalysis treatment technology in large scale can be appropriate treatment option for textile wastewater which is the fastest growing industry in Ethiopia Further study should focus on economic evaluation of such established system to achieve real industrial applications.
- ✓ Future work should focus on the removal of Nano particles from the treated wastewater.

REFERENCES

A review of Engineering Developments of Aqueous Phase Solar Photocatlytic Detoxification and Disinfection Process, D.Y.Goswami., Journal of Solar Energy Engineering, Vol 119(2), 101-107, 1997.

Abbas, J. A., Kadhim, S. H., Hussain, H. F. 2008. Photocatalytic degradation of textile dyeing wastewater using Titanium dioxide and Zinc Oxide, *E*-Journal of Chemistry, 5, 219-223.

Aguedach, A., Brosillon, S., Morvan, J., Lhadi, E., 2005. Photocatalytic degradation of azo-dyes reactive black 5 and reactive yellow 145 in water over a newly deposited titanium dioxide. Applied Catlysis B: Environmental, 57, 55-62.

Akyol, A., Yatmaz, H. C., Bayramoglu, M., (2004). Photocatalytic decolorization of Ramazol Red in aqueous ZnO suspensions. Appl. Catal. B: Environ. 54, 19-24.

Alkhateeb, A. N.,Hussein, F. H., Asker, K. A.,(2005). Photocatalytic decolorization of industrial wastewater under natural weathering conditions. Asian J Chem., 17, 1155-1159.

Al-Kdasi, A., Idris, A., Saed, K., Guan, C. T., (2004). Treatment of textile wastewater by advanced oxidation processes- A review. Global Nest: the Int. J., 6, 222-230.

Allègre, C., Moulin, P., Maisseu, M. and Charbit, F. (2006) Treatment and reuse of reactive dyeing effluents. Journal of Membrane Science 269(1–2), 15-34.

APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Wastewater, ASTM D1252-00, 17th ed., APHA-AWWA-WPCF, Washington, DC, 1999.

Arslan, I.,Balcioglu,I. A., Tuhkanen, T.,Bahnemann, D.,(2000). H2O2/UV-C and Fe2+/H2O2/UV- A versus TiO2/UV-A treatment for reactive dye wastewater. J. Environ. Engg. 126, 903-909.

Baran W, Makowski A, Wardas W. 2003. The influence of FeCl3 on the photocatalytic degradation of dissolved azo dyes in aqueous TiO2 suspensions. Chemosphere. 53:87-95.

Bahnemann, D., Cunningham, J., Fox, M.A., Pelizzetti, E., Pichat, P. and Serpone, N.I.N. (1994) Photocatalytic treatment of waters. In: Helz, G.R., Zepp, R.G. and Crosby, D.G., Eds., Aquatic and Surface Photochemistry, Lewis Publishers, Boca Raton, FL, 261.

Bizani, E., Fytianos, K., Poulios, I., Tsiridis, V., (2006). Photo catalytic decolorization and degradation of dye solutions and wastewaters in the presence of TiO2. Journal of Hazardous Materials, 136, 85-94.

Carey J H. An introduction to AOP for destruction of organics in wastewater. Water Pollution Research Journal Canadian, 1–21, 1992.

Cleaner Production Program (CPP) (2002). Textile Processing Sector. Environmental Report. Karachi. URL: http://www.cpp.org.pk.

Cabral, K., Gallo, J., Salim, C., Hinode, H., Borja, J., & Gallardo, S. (2010). Optimization of process parameters using Box-Behnken experimental design for the photocatalytic decolorization of methyl orange in aqueous medium. In the Proceedings of 5th ERDT Conference: *P*hilippine Competitiveness through ERDT. Manila, Philippines.

Chong M N., Jin B., Chow W K., Saint C. Recent developments in photocatalytic water treatment technology. A review. Water Research, 44, 2997-3027 (2010).

C.S. Turchi, D.F.Ollis, “Photocatlytic Degradation of organic water contaminants: mechanisum involving hydroxyl radical attack”, Journal of catalysis, vol 122,1990, 178-192.

Chen, S., Cao, G., (2005). Studyon the photocatalytic reduction of dichromate and photocatalytic oxidation of dichlorvos. Chemosphere, 60, 1308-1315.

Daneshvar, N., Solari, D., Khataee, A. R.,(2003). Photocatalytic degradation of azo acid red 14 in water on ZnO as an alternative catalyst to TiO2. Photochem. Photobiol. *A: Chem.,* 157, 111-116.

Diriba Dadi, Till Stellmacher, Feyera Senbeta, Steven Van Passel, Hossein Azadi (2014). Environmental and Health Impacts of Effluents from Textile Industries in Ethiopia: The Case of Gelan and Dukem, Oromia Regional State. 22-24.

EPA (1996). Best management practices for pollution prevention in textile industry, manual.625R96004, Washington DC, USA.

Gallo, J., Borja, J., Salim, C., Ngaotrakanwiwat, P., Hinode, H., and Gallardo S. 2012. “Optimization for Photocatalytic Color Removal of Turquoise Blue Dye C.I. 199 in Immobilized AC/TiO2 and UV System using Response Surface Methodology” Asean Engineering Journal.

Georgiou, D., Melidis, P., Aivasidis, A., Gimouhopoulos, K., (2002). Degradation of azo-reactive dyes byultraviolet radiation in the presence of hydrogen peroxide. Dyes Pigments, 52, 69-75.

Glaze W H., Kang J W., Chapin D H. The chemistry of water treatment processes involving ozone, hydrogen peroxide and UV-radiation. Ozone: Science and Engineering, 335-352, 1987.

Herney-Ramirez J., Vicente M A., Madeira L M. Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review. Applied Catalysis B, 10–26, 2010.

K. Sarayu & S. Sandhya (2012).Current Technologies for Biological Treatment of Textile Wastewater.

Kusic H., Koprivanac N., Bozic L. Minimization of organic pollutant content in aqueous solution by means of AOPs: UV and ozone-based technologies, Chemical Engineering Journal, 127–137, 2006.

Kabra, K., Chaudhary, R. and Sawhney, R.L. 2004 Treatment of Hazardous Organic and Inorganic Compounds through Aqueous-Phase Photocatalysis: A Review. Industrial & Engineering Chemistry Research, 7683-7696.

Legrini, O., Oliveros, E. and Braun, A.M. 1993 Photochemical Process for Water Treatment. Chemical Reviews, 671-698.

Lech Kos, Jan P. Discoloration of Real Textile Wastewater with Advanced Oxidation Processes.

Mariano, M., Kho, M and Lucanas A. Pilot Scale Investigation of the Solar Photodegradation of Wastewater Containing TBD using Nanotitania-Activated Carbon Composite Catalyst, 2012. BS Thesis De La Salle University. Manila.

Metcalf, Eddy, Inc. (2003), Wastewater Engineering Treatment and Reuse, 4th Ed., McGraw-Hill, New York.

Mojtaba A., Pegah A., and Negar A. 1327-1332(2014***).***Combination of TiO2-photocatalytic process and biological oxidation for the treatment of textile wastewater.

Munter R., Advanced Oxidation Processes Current status and prospects. Proceedings of the Estonian Academy of Sciences, 50, 59-80 (2001).

Mattioli D., Malpei F., Bortone G., Rozzi A. (2002). Water Minimization and Reuse in Textile Industry. In: Lens P., Pol L.H., Wilderer P., Asano T. (Eds.). Water Recycling and Resource Recovery in Industry: Analysis, Technologies and Implementation. IWA publishing, London, UK.

Maleki A., Mahvi A H., Alimohamadi M., Ghasri A. Advanced Oxidation of phenol by Ultraviolet Irradiation in Aqueous System. Pakistan Journal of Biological Sciences, 2338-2341 (2006).

Mills, A. and Le Hunte, S. 1997 an Overview of Semiconductor Photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 1-35.

Maroga Mboula, V., Héquet, V., Gru, Y., Colin, R. and Andrès, Y. 2012 Assessment of the Efficiency of Photocatalysis on Tetracycline Biodegradation. Journal of Hazardous Materials, 209-210, 355-364.

Morphology of a TiO2 photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases; Ohno, T., Sarukawa, K., Tokieda, K., Matsumura, M.; Journal of Catalysis vol. 20; pp 82-86; 2001.

Ollis, D.F., Pelizzetti, E. and Serpone, N. 1991 Photocatalyzed Destruction of Water Contaminants. Environmental Science and Technology, 1523-1529.

O.T. Can, M. Kobya, E. Demirbas, M. Bayramoglu(2005).Treatment of the textile wastewater by combined electro-coagulation 181–187.

Pera-Titus M., Garcia-Molina V., Banos M. A., Gimenez J., Esplugas S., Degradation of chlorophenols by means of Advanced Oxidation Processes: A general review, Applied Catalysis B: Environmental, 219-256.

Photocatalytic degradation for environmental applications - a review; Bhatkhande, D.S., Pangarkar, V.G., Beenackers, A.A.C.M.*;* Journal of Chemical Technology and Biotechnology vol. 77; 102-116;2001.

Pollution research group (PRG) waste minimization guide for the textile industry (1998),a step towards cleaner production , university of Natal, draft volume 1 and 2.

Punzi, M. (2015) Treatment of Textile Wastewater by Combining Biological Processes and Advanced Oxidation.

P. M. Andrade[1], M. A. F. Carvalho, A. S. Miranda[2], H. R.Marques, S. R. Campos[2] e N. N. Brito (2015) Remidation of Textile Dyes Mixtures Using TiO_2/VIS Photocatalysis Fenton Fe^{2+}/H_2O_2 328-338.

Ramtake P., Gogate P. Treatment of real industrial wastewater using the combined approach of advanced oxidation followed by aerobic oxidation. Environ. Sci. Pollut. Res.

Rizzo, L., Meric, S., Guida, M., Kassinos, D. and Belgiorno, V. 2009 Heterogeneous Photocatalytic Degradation Kinetics and Detoxification of an Urban Wastewater Treatment Plant Effluent Contaminated with Pharmaceuticals. Water Research, 4070-4078.

Segneanu A E., et al.Wastewater treatment methods Chapter 4 in Elshorbagy W., ed., “Water Treatment”, InTech, 53-71, 2013.

Sharmila Pokharna, Rupali Shrivastava 2013. Photocatalytic Treatment of Textile Industry Effluent Using Titanium Oxide 2277 – 8322.

Spacek, W., Bauer, R., Heisler, G. Heterogeneous and homogeneous wastewater treatment Comparison between photodegradation with TiO2 and the photo-Fenton `reaction. Chemosphere, 30, 1995.

Tapp, J.F., Hult, S.M. and Wharfe, J.R. 1996 Toxic Impact of Wastes on the Aquatic Environment. Royal Society of Chemistry, London.

WHO. (2008). Water pollutants: biological agents, dissolved chemicals, non-dissolved chemicals, sediments, heat. WHO CEHA, Amman.

Yahiat, S., Fourcade, F., Brosillon, S. and Amrane, A. 2011 Removal of Antibiotics by an Integrated Process Coupling Photocatalysis and Biological Treatment Case of Tetracycline and Tylosin. International Biodeterioration & Biodegradation, 997-1003.

Yerkinova A. (2017), Photocatalytic Degradation of Organic Pollutants in Wastewater.

Ying li, Response surface methodology a review, December 6, 2011

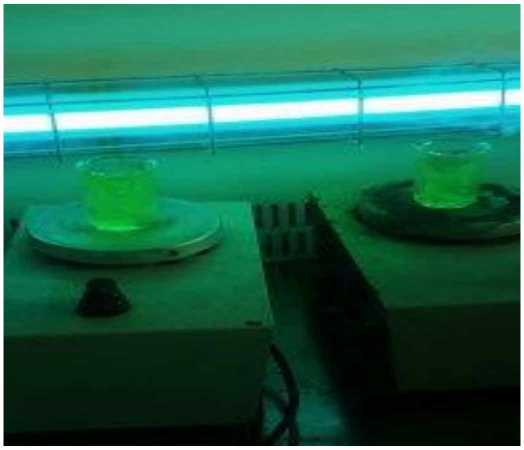
ANNEXES

Annex 1. Table A: Textile wastewater limit Values for discharges to Water bodies Source (Ethiopia EPA, 2003)

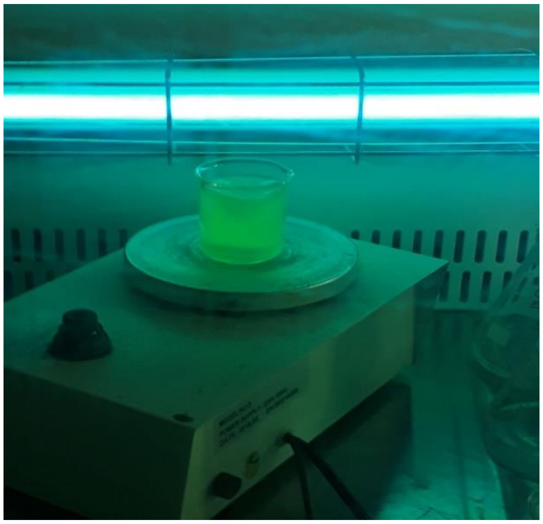
Parameters Limit values (MPL)	**Limit values (MPL)**
pH	6-9
Temperature (^{0}C)	40
Total Dissolved Solids (TDS)	80 mg/l
Conductivity (EC)	1000 µS/Cm (at 20 ^{0}C)
Sulfide (S^{-2})	2 mg/l
BOD_5 at 20 ^{0}C	50 mg/l > 90 % removal
COD	150 mg/l > 80% removal
Ammonia (NH_{3-N})	30 mg/l
Nitrate (NO_3)	50 mg/l NO_3
Total phosphorus (as P)	10 (>80% removal)
Total Nitrogen (as N)	40 mg/l >80% removal
Sulfate (SO_4)	200 mg/l SO_4
Total Suspended solids (TSS)	30 mg/l
Nickel (as Ni)	2 mg/l
Chromium (as total Cr)	1 mg/l
Cadmium (as Cd)	1 mg/l
Lead (as Pb)	0.5 mg/l
Copper (Cu)	2 mg/l
Iron (Fe)	1.0 mg/l dissolved Fe
Zinc (Zn)	5 mg/l

Annex 2. Sample picture of raw wastewater, treated wastewater and photocatalysis experiment in laboratory scale.

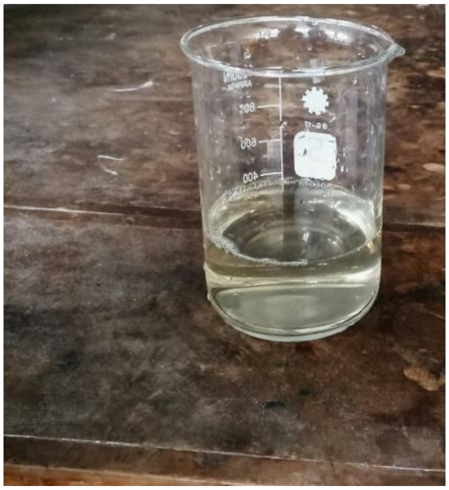
Raw wastewater



Photocatalysis experiment with UV-C



Photocatalysis experiment with UV-C



Treated wastewater

COD reactor

UV-VIS spectrophotometer

Drying oven (105 ^{0}c)

Annex 3. Table B: UV-VIS Absorbance measurement.

No.	Absorbance before treatment	K *Abs	Absorbance after treatment	K*Abs
1	1.311	13.112	0.551	5.511
2	1.267	12.671	0.443	4.435
3	1.322	13.221	0.594	5.941
4	1.269	12.691	0.456	4.562
5	1.262	12.623	0.426	4.261
6	1.157	11.572	0.451	4.512
7	1.285	12.855	0.430	4.304
8	1.124	11.241	0.506	5.061
9	1.231	12.313	0.398	3.981
10	1.257	12.572	0.503	5.032
11	1.462	14.625	0.366	3.662
12	1.482	14.824	0.178	1.783
13	1.455	14.552	0.80	8.100
14	1.345	13.452	0.336	3.362
15	1.285	12.854	0.419	4.191
16	1.315	13.150	0.802	8.021
17	1.421	14.212	0.128	1.284

Annex 4. Table C: COD removal efficiency in percent (%).

Std	Run	Factor 1 A:TiO_2 dosage (mg/l)	Factor 2 B: pH	Factor 3 C: irradiation time (hour)	Response 1 COD (mg/l)	COD removal efficency (%)
1	12	400	7	4	201	82.5
2	7	550	7	4	161	86
3	16	400	9	4	143	87.6
4	4	550	9	4	155	86.5
5	13	400	8	3	250	78.3
6	8	550	8	3	169	85.3
7	3	400	8	5	165	85.7
8	2	550	8	5	210	81.7
9	1	475	7	3	162	85.9
10	14	475	9	3	140	87.8
11	9	475	7	5	135	88.3
12	15	475	9	5	110	90.4
13	5	475	8	4	130	88.7
14	11	475	8	4	135.89	88.2
15	10	475	8	4	135.92	88.21
16	17	475	8	4	139.68	87.85
17	6	475	8	4	140.89	87.74

COD removal efficiency (%) = $\frac{COD\ infulent - COD\ effulent}{COD\ infulent} * 100$

Annex 5. Table D Statistical Report of diagnostic graph for the Response of COD and Color.

A, COD removal statistical report

Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals	Cook's Distance	Influence on Fitted Value DFFITS	Standard Order
1	130.00	136.48	-6.48	0.200	-1.633	-1.922	0.067	-0.961	13
2	250.00	250.63	-0.6250	0.750	-0.282	-0.263	0.024	-0.455	5
3	161.00	157.88	3.13	0.750	1.410	1.542	0.596	2.671[(1)]	2
4	210.00	209.38	0.6250	0.750	0.282	0.263	0.024	0.455	8
5	155.00	156.12	-1.12	0.750	-0.508	-0.479	0.077	-0.829	4
6	169.00	171.62	-2.62	0.750	-1.184	-1.226	0.421	-2.123	6
7	110.00	109.50	0.5000	0.750	0.226	0.210	0.015	0.363	12
8	201.00	199.88	1.13	0.750	0.508	0.479	0.077	0.829	1
9	135.89	136.48	-0.5860	0.200	-0.148	-0.137	0.001	-0.069	14
10	140.89	136.48	4.41	0.200	1.113	1.136	0.031	0.568	17
11	135.92	136.48	-0.5560	0.200	-0.140	-0.130	0.000	-0.065	15
12	139.68	136.48	3.20	0.200	0.808	0.786	0.016	0.393	16
13	135.00	138.75	-3.75	0.750	-1.692	-2.037	0.859	-3.528[(1)]	11
14	143.00	146.13	-3.13	0.750	-1.410	-1.542	0.596	-2.671[(1)]	3

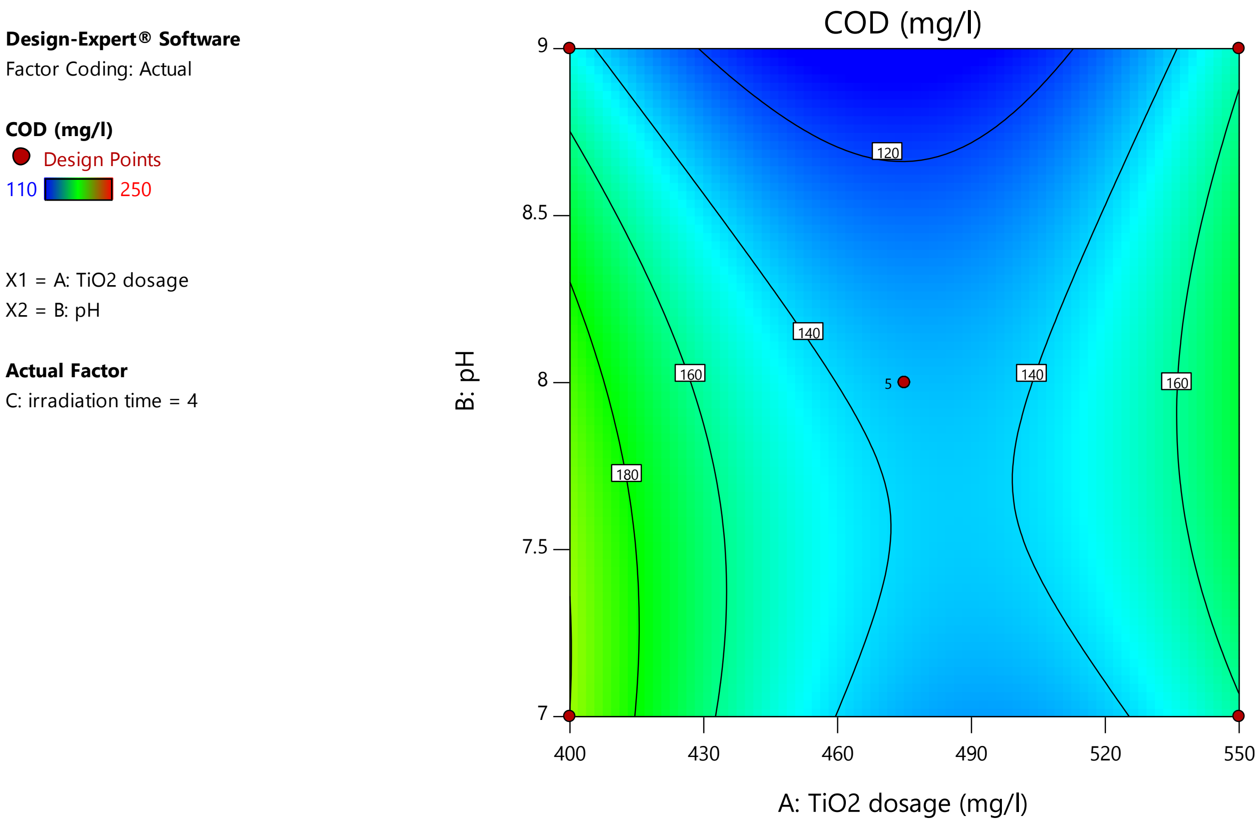
15	162.00	162.50	-0.5000	0.750	-0.226	-0.210	0.015	-0.363	9
16	165.00	162.37	2.63	0.750	1.184	1.226	0.421	2.123	7
17	140.00	136.25	3.75	0.750	1.692	2.037	0.859	3.528[1]	10

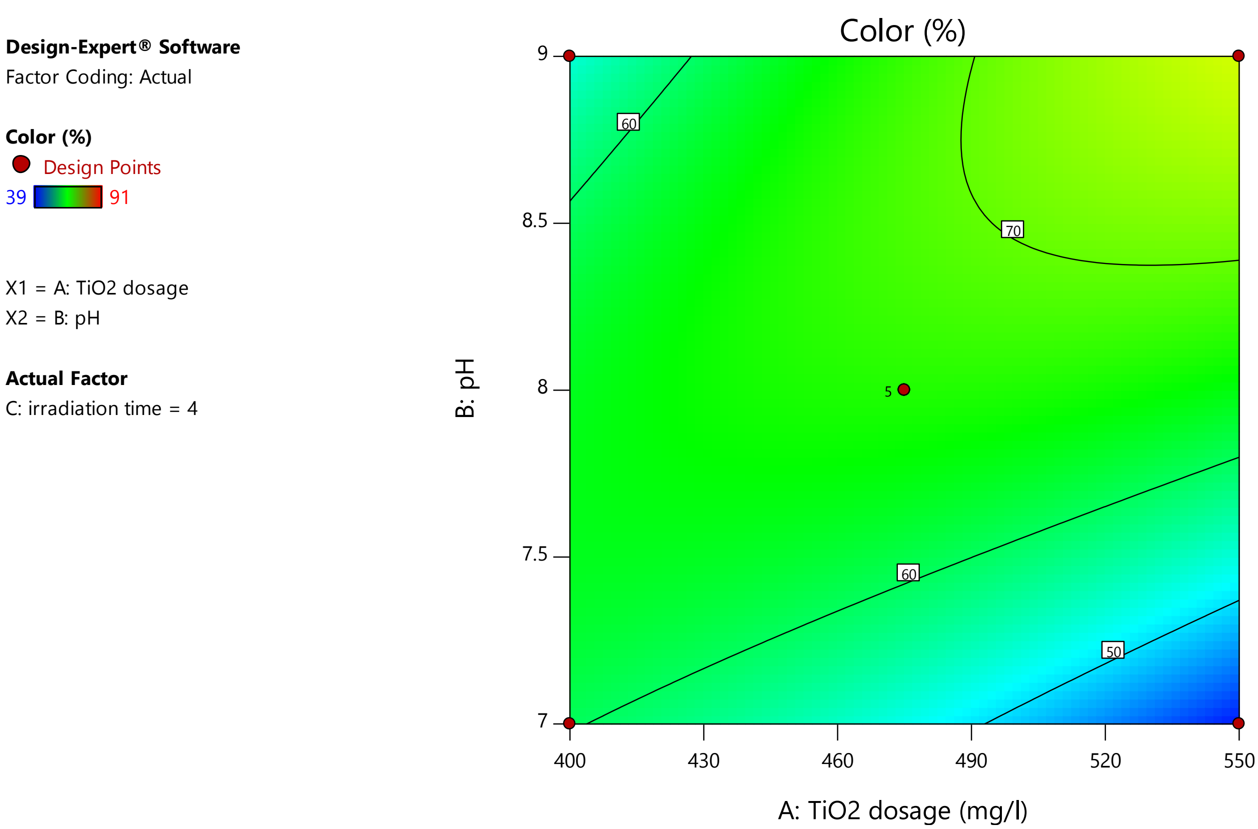
B, Color removal statistical report

Run Order	**Actual Value**	**Predicted Value**	**Residual**	**Leverage**	**Internally Studentized Residuals**	**Externally Studentized Residuals**	**Cook's Distance**	**Influence on Fitted Value DFFITS**	**Standard Order**
1	65.00	66.54	-1.54	0.200	-1.658	-1.971	0.069	-0.985	13
2	45.00	45.62	-0.6250	0.750	-1.207	-1.256	0.437	-2.175	5
3	39.00	39.50	-0.5000	0.750	-0.966	-0.960	0.280	-1.663	2
4	64.00	63.37	0.6250	0.750	1.207	1.256	0.437	2.175	8
5	75.00	75.75	-0.7500	0.750	-1.449	-1.603	0.630	-2.776[1]	4
6	75.00	74.38	0.6250	0.750	1.207	1.256	0.437	2.175	6
7	88.00	87.88	0.1250	0.750	0.241	0.224	0.017	0.389	12
8	61.00	60.25	0.7500	0.750	1.449	1.603	0.630	2.776[1]	1

9	66.21	66.54	-0.3260	0.200	-0.352	-0.329	0.003	-0.164	14
10	67.32	66.54	0.7840	0.200	0.847	0.827	0.018	0.414	17
11	66.53	66.54	-0.0060	0.200	-0.006	-0.006	0.000	-0.003	15
12	67.62	66.54	1.08	0.200	1.170	1.208	0.034	0.604	16
13	60.00	60.13	-0.1250	0.750	-0.241	-0.224	0.017	-0.389	11
14	55.00	54.50	0.5000	0.750	0.966	0.960	0.280	1.663	3
15	55.00	55.13	-0.1250	0.750	-0.241	-0.224	0.017	-0.389	9
16	91.00	91.63	-0.6250	0.750	-1.207	-1.256	0.437	-2.175	7
17	58.00	57.88	0.1250	0.750	0.241	0.224	0.017	0.389	10

Annex 6. Contour graph for the Response of COD and Color.





Annex 7 Laboratory Procedures for Water and Wastewater Analysis (APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Wastewater)

Five Day BOD Test (BOD_5)

Five days biological oxygen demand (BOD_5) measurements were carried out according to procedures given in standard methods for the examination of water and wastewater, 5 days BOD test 5210 B.

Apparatus used

a) Incubation bottles: Use glass bottles having 60 ml or greater capacity (300 ml bottles having a ground glass stopper and a flared mouth are preferred). Clean bottles with a detergent, rinse thoroughly and drain before use.

b) Air incubator or water bath, thermostatically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

Required reagent

Prepare reagents in advance but discard if there is any sign of precipitation or biological growth in the stock bottles.

a) Potassium hydroxide (KOH) to absorb carbon dioxide gas (CO_2)

b) Nitrification inhibitor, 2-chloro-6-(trichloromethyl) pyridine.to avoid nitrification

c) Dilution water: Use demineralized, distilled, tap, or natural water for making sample dilutions

d) Acid and alkali solutions, 1 N of NaOH and HCl, for neutralization of caustic or acidic wastewater samples.

Experimental procedures

Preparation of the sample

a) Select the volume for the wastewater sample

b) The sample volume is related to the expected BOD_5 value. The BOD_5 incubator is designed to operate with the following BOD_5 ranges and sample volume allowing BOD_5 measurement.

i) BOD_5 range 0 - 400 mg/l use the sample without dilution

ii) BOD_5 range 0 - 2000 mg/l, the expected sample volume is 56 ml with 3 drop of nitrification inhibitor and 3 - 4 drop of potassium hydroxide (KOH) addition.

iii) BOD_5 range 0 - 4000 mg/l the expected sample volume is 21.2 ml with 1 drop of nitrification inhibitor and 3 - 4 drop of potassium hydroxide (KOH) addition.

c) Carry out the necessary pretreatment of the wastewater sample, setting pH between 6.5 -7.5, if higher or lower adjust by HCl and NaOH and mix well and allow the sample to settle and filtrate of the sample

d) Measure the wastewater sample precisely using appropriate overflow and if necessary add nitrification inhibitor

e) Insert magnetic stirring rod

f) Place 3 - 4 drop of KOH solution into the seal gasket and insert gasket in the neck of then bottle, screw the BOD sensors to the sample bottle and then place the bottle in the bottle rack

g) Finally, incubate the sample for 5 days at a temperature of 20 ^{0}C.

Calculation

For each test bottle meeting the 2.0 mg/l minimum dissolved oxygen (DO) depletion and the 1.0 mg/l residual DO, calculate BOD_5 as follows:

$$BOD_5, mg/l = \frac{D_1 - D_2}{P}$$

Where;

D1 = DO of diluted sample immediately after preparation, mg/l,

D2 = DO of diluted sample after 5 day incubation at 20 °C, mg/l,

P = decimal volumetric fraction of sample used,

Total solids (TS), Total suspended Solid (TSS) and Total dissolved solids (TDS) Analysis

a) Total Solids (TS): Total solids Measurements were carried out according to procedures given in standard methods for the examination of water and wastewater 2540 B.

b) Total Suspended Solids (TSS): Apparatus used in analysis of total suspended solid is the same as total solid measurement except for evaporating dishes and drying oven measurements were carried out according to procedures given in standard methods for the examination of water and wastewater 2540 D.

Apparatus used (TS)

a) Evaporating dishes

b) Desiccators, provided with a desiccant containing a color indicator of moisture

c) Drying oven operating at a temperature of 103 – 105 ^{0}C, for total and suspended solid analysis.

d) Analytical balance

e) Graduated cylinder and beaker

Experimental procedure (TS)

Preparation of evaporating dish:

a) Heat clean dish at a temperature of 103 – 105 ^{0}C for 1 hr for total solid analysis

b) Store and cool dish in desiccators at room temperature until needed

c) Weigh the dish immediately before use

Sample Analysis (TS):

a) Add a measured volume of well mixed sample to a pre-weighed dish

b) Evaporate to dryness on drying oven for 24 hrs

c) If necessary add successive sample portions to the same dish after evaporation

d) Cool dish in desiccators to balance temperature and weigh it immediately

e) Ignite the residue produced in a muffle furnace for 3 hrs

f) Transfer to a desiccators for final cooling in a dry atmosphere

Experimental procedure (TSS)

Preparation of glass fiber filter disk:

- For this step there is pre-prepared glass fiber filter disk are used.

Sample analysis (TSS):

a) Assemble filtering apparatus and filter and begin suction.
b) Stir sample with a magnetic stirrer at a speed to shear larger particle.
c) While stirring pipet a measured volume on to the seated glass fiber filter.
d) Wash filter with successive 10 ml volume of distilled water, allowing complete drainage between washing and continues suction for about 3 minute after filtration complete.
e) Dry for at least 1 hr at 103-105 ^{0}c in an oven, cool in a desiccators and weigh the sample.

Calculations

The amounts of total solid and total suspended solid in the sample can be computed using Equation,

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

Where;
A = weight of dried residue + dish, mg, and B = weight of dish, mg.

$$\text{mg total suspended solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

Where;
A = weight of filter + dried residue, mg and B = weight of filter, mg.

Total dissolved Solids (TDS): Measurements for analysis of TDS were carried out according to procedures given in standard methods for the examination of water and wastewater 2540 C.

Apparatus used (TDS)

Apparatus used for TDS analysis were the same as that used for total solid analysis except,

a) Glass-fiber filter disk

b) Membrane filter funnel which used as a filtration apparatus.

c) Drying oven operating at a temperature of 103 – 105 ^{0}C, for total and suspended solid analysis.

d) Suction flask

Experimental procedure (TDS)

a) Preparation of glass fiber filter disk were done by applying vacuum and washing the disk with 20 ml volume of distilled water.

b) Preparation of evaporating dish were done by heating clean dish to 180 ^{o} c for 1 hr. in an oven and then it is stored in a desiccator.

c) Sample volume were choosed to yield between 2.5 and 200 mg dried residue.

Sample Analysis (TDS):

a) sample were stirred with magnetic stirrer and pipet a measured volume on to a glass fiber filter with applied vacuum.

b) Washing with 3 successive 10 ml volume of distilled water, then the sample was allowed to complete drainage and continue suction for about 3 minute after filtration is complete.

c) Total filtrate were transferred to a weighted evaporating dish and evaporate to dryness.

d) The evaporated sample were dried in an oven for 1 hr. and then cooled in a desiccator.

e) Repeating of drying, cooling, desiccating and weighing was continued until weight change is less than 4%.

Calculations

The amounts total dissolved solid in the sample can be computed using Equation,

$$\text{mg of total dissolved}\frac{\text{solids}}{\text{L}} = \frac{(\text{A} - \text{B}) * 1000}{\text{sample volume, ml}}$$

Where; A = weight of dried residue + dish, mg, and B = weight of dish, mg.

pH Measurements

pH measurements were carried out by using 890 MD pH meter. The pH meter was calibrated by using suitable buffer solution.

Turbidity

Turbidity is the cloudiness or haziness of a fluid caused by large number of individual particles that are generally invisible to the naked eye, similar to smoke in air. Turbidity can be measured by the device called Turbidometer for this study of textile wastewater treatment the turbidity were measured by Turbidometer (2100 NTU) before and after treatment.

Experimental procedure to measure Absorbance

a) Turn on the spectrophotometer to warm up for at least 15 minute before running any sample.
b) Clean the cuvettes, rinse each cuvettes thoroughly with distilled water.
c) Load the proper volume of the sample into the cuvette.
d) Prepare a control solution (blank solution) which has only chemical solvent in which the solute to be analysed is dissolved in.
e) Wipe the outside of the cuvette before placing it into the spectrophotometer.

When running the experiment:

- Choose and set the wavelength of light to analyze the sample with. Use a single wavelength of light (monochromatic color) to make the testing more effective.
- Calibrate the machine with the blank.
- Remove the blank and test the calibration.
- Measure the absorbance of your experimental sample.
- Repeat the test with successive wavelength of light.

Analyzing the absorbance data

f) Calculate the transmittance and absorbance of the sample. The transmittance is found by dividing the intensity of light that passed through the sample solution with the amount that passed through the sample blank.
g) Plot the absorbance value versus the wavelength on the graph.

h) Compare your absorbance spectrum plot to known plots of specific compounds.

Annex 8 Biological wastewater treatment plant (Activated sludge) of Ayka Addis Textile factory