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Removal of Methylene Blue Dye Using Titanium Dioxide Photocatalyst.

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THESIS WORK

ON

Removal of Methylene Blue Dye Using Titanium Dioxide Photocatalyst

By: Tigabu Halefom

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 Masters of Science in Chemical Engineering (Environmental Engineering Stream).

Advisor: Dr. Shimels Kebede.

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Declaration

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for degree at this or any other university, and that all resources of materials used for this thesis have been duly acknowledged.

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Signature: ---

Date of Submission: ---------------------------------

This thesis has been submitted for examination with my approval as a university advisor.

Name: Dr. Shimels Kebede

Signature: -------------------

Date: ------------------------

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LIST OF ABBREVIATIONS

AOP	Advanced oxidation process
RSM	Response Surface Methodology
Kpp	Apparent rate constant
MB	methylene blue
UV	Ultraviolet
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
XRD	X-ray diffraction
ANOVA	Analysis of variance
Abs	Absorbance
FTIR	Fourier Transform Infrared Radiation
SEM	Scanning electron microscope
BET	Brunauer-Emmett-Teller
BJH	Barett-Joyner-Halenda

Abstract

The application of dyes in different process industries will cause environmental impact. Thus, the need for removal of dyes using an Advanced oxidation process is a vital issue to decrease the effect of dyes. An Advanced oxidation process works based on the generation of hydroxyl radicals as an intermediate to takes place the photocatalytic process under UV irradiation. Titanium dioxide was used in the photocatalytic decolorization study of a dye i.e., methylene blue (MB). During Usage of this semiconductor as a photocatalyst for removal of dye, physiochemical characteristics of the photocatalyst, the effect of the various process parameters like initial dye concentration, catalyst loading, and UV irradiation time on the photodegradation of MB were investigated using surface Response methodology. We obtain that the photocatalyst material has anatase composition of 100%, the specific surface area 55.64 m^2/g *and crystallite size of 39.93 nm respectively. In addition to this, analysis on degradation of methylene blue (MB) as an organic dye pollutant upon photocatalytic oxidation of* TiO_2 *nanoparticles under UV-light (393 nm) irradiation was optimized. According to analysis of variance numerical optimization 94.89 % removal efficiency were predicted through adjusting the selected parameters under specified or bounded conditions. Furthermore, the rate of dye degradation (reaction) kinetics were also studied. The result indicates from first order Languier-Hinshewood kinetics model, is good fitting with regression coefficient of 97.93 %.*

1. INTRODUCTION

1.1. Background

All life forms are dependent on water for their existence and it is believed that, even the first life starts in water. Thus, quality of water is the most important natural resource of the world and plays a vital role in the development of communities. Around 70% and above the earth is covered with water. However, majority of it is not appropriate to sustain human life and only limited amount of potable water resource is available [1]. The different application area of chemicals for various purposes in day-to-day life and the growing industrialization directed to unwanted contamination of our existing natural resources by the release of diverse organic and inorganic pollutants into water system. Nowadays, the public has become more sensitive towards the safeguard of the environment and general awareness has now increased about the potential adverse effects of industrial effluents contaminate with various pollutants, including dyes on the environment [2].

Dyes are produced every year in millions. Today there are more than 100,000 commercially available dyes exist with over 7×10^5 metric tons' dyestuffs annually produced in the world. Some of them are used in textile dying process in Ethiopia and have good water solubility and easily hydrolyzed into insoluble forms. Textile dyes wastewater, in particular characterized by intense color, high level of chemical oxygen demand (COD), dissolved solids highly fluctuating pH [3]. It is estimated that 2 % of dyes produced annually are discharged in effluent from different manufacturing operations. While in the textile industry, it is estimated that 10% to15% of the dye used during the manufacturing of textile products is released into the environment worldwide annually [4]. Most of these dyes are found to be toxic and carcinogenic to aquatic animals and plants. Usage of them for different purpose results an increase in the pollution of water which affects the entire ecosystem of plants, animals and humans. Now a day the release of colored dye effluents into water bodies has been an environmental problem of increasing concern. Dyes are being used in a lot of industries, worldwide, including textile, chemicals, pharmaceuticals, foods, cosmetics and laboratories. Discharge of colored waste waters from such industries results serious environment problem. Decolorization of textile dyeing effluents has been the target of great attention because of their toxicity and aesthetic effect on the environment [5]. Therefore, it is desirable to remove dyes from colored effluents for safe discharge in receiving water bodies to keep the environment sustainable.

Removal of these dyes can be accomplished using physical, chemical and biological (aerobic and anaerobic) methods. Both chemical like (Ozonation and chlorination) as well as physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for decolorization of dyes from textile effluents [6, 7].

But they have their own limitation. The disadvantages of these con-ventional methods are sludge formation, waste disposal problem, high operation cost, time consuming and ineffectiveness in cases where complicated aromatic compounds are presented [8, 9]. Consequently, there is considerable driving interest in the utilization of advanced oxidation processes (AOP, s) for the complete degradation of dyes used in textile industry. The heterogeneous photo catalytic oxidation processes have been extensively used in the literature for the degradation of dyes [10, 11]. Photo catalytic treatments are based on the generation of highly reactive hydroxyl radicals. These radicals are high oxidant species; they attack the most of organic molecules. They are also characterized by low selectivity of attack which is useful characteristic for an oxidant used in wastewater treatment. In the last decade, most attention has been given to titanium dioxide due to its high photo catalytic activity, low cost, nontoxicity and high stability in aqueous solution [12]. Many studies have been reported titanium dioxide is generally considered to be a better photo catalyst and has the ability to detoxificate water from a number of organic pollutants. However, it has negative side only activated by UV- light [13, 14].

The release of dyes and their products in the environment cause toxicity problems. So an attempt has been made to study the degradation of dyes. In this research an (AOPs), a semiconductor photo catalyst Titanium dioxide was used for the degradation efficiency of aqueous solution of these dyes (MB). Photo catalyst experiments were conducted to investigate the effects of various process parameters (catalyst loading, initial dye concentration and irradiation time) on the process performance.

Advanced oxidation processes (AOPs) results in an intermediate products of hydroxyl radicals in driving the processes of oxidation. There are different ways for production of hydroxyl radicals in AOPs. Ozone, hydrogen peroxide, ultraviolet radiation, etc are some methods of AOPs that can be used individually or in different combination forms to generate the hydroxyl radicals [15,16]. when the aqueous suspension of titanium dioxide irradiated by photon energy higher than the band gap the conduction band electrons (e-) and the valence band holes (h+) are formed.

Photodegradation process starts when titanium dioxide absorbs a UV radiation of energy equal to or higher than its band gap. During this time the formation of free electrons in the conduction band and holes in the semiconductor valence band occurred. This results the energized electrons can either recombine with the holes (and then dissipate the absorbed energy as heat) or the electron-hole pairs can participate in redox reactions. A reaction will take place between them and electron acceptors/donors adsorbed on the surface of the photocatalyst. On the other hand, the solid side at the semiconductor/liquid junction creates an electrical field that separates the electrons-holes pairs that fail to recombine. This electron field allows the holes to migrate to the illuminated part of the titanium dioxide and the electrons to migrate to the unlit region of the titanium dioxide particle surface. At the end the initial steps of photocatalytic degradation of a species is the reaction with extremely reactive but shortlived hydroxyl radicals or direct hole trapping. The hydroxyl radicals are formed either in the highly hydroxylated semiconductor surface or by direct oxidation of the pollutant molecules under UV radiation. There is also a possibility that both methods of forming hydroxyl radicals occur in these situations simultaneously. Thus, reduction of adsorbed oxygen species occurs immediately ones this process is completed. The amount of Dissolved oxygen molecules (in the aqueous system), or other electron acceptors available in the aqueous system can cause this reduction [17, 18].

1.2. Statement of the Problem

Water is an important necessity for the survival of human beings. Treating waste water is a vital issue to decrease environmental contaminants and problems. In addition to this, Wastewater recycling and reuse are very important to meet the water requirements for irrigations, industry and domestic uses due to increasing in population and development in many parts of the world.

The three main types of methods for water treatment are biological, chemical and physical. Biological water treatments involved the use of microorganisms to biodegrade the pollutants in the water [19]. But, the efficiency of biological treatment is insufficient because of the non-biodegradability of dyes. Thus, the biodegradation will be time consuming and incomplete. Physical wastewater treatment methods, they involve trapping and separating the pollutant and water through physical means. Even though the water is free of dye after the treatment processes, the pollutants still existed and are not eliminated due to the non-destructive nature of the processes. This will result in secondary pollution which is undesirable in the long run. In addition, there are other limitations such as the high cost and the carbon adsorption required disposal of spent carbon [20]. On the other hand, the chemical water treatments mainly involve the reactions between the selected chemicals and the pollutant polluted by disinfection with chemicals. Examples of such treatments are chlorination and Ozonation. However, the methods have disadvantages such as potentially hazardous chlorinated by-products can be produced as well as ozone's toxicity and instability [21,22].

However, the photocatalytic degradation method can potentially mineralize the dye completely and with no need of post treatment which is environmentally friend. Thus, photocatalysis can be a good alternative way to eliminate the dye pollutants. Among the different semiconductors, titanium dioxide was considered as one of the most popular catalysts because of its high activity, good chemical stability, non-toxic, biologically inert and water insolubility [20].

1.3. Objective

The main objective of this study is to investigate dye removal efficiency of photocatalyzed titanium dioxide from aqueous solution.

1.3.1. Specific Objective

- To investigate the physiochemical characteristics of the photocatalyst (TiO_2)
- To study the effects of parameters like (dye concentration, irradiation time and catalyst dosage) on the degradation of MB using titanium dioxide photocatalyst and to find the optimal point.
- To investigate the degradation kinetics of methylene blue in presence of UV light using commercial Titanium dioxide catalyst.

1.4. Significance of the Study

Discharging of dyes into the river as the whole to the environment results serious environmental problems. Therefore, removal of color (dyes) from textile wastewater is necessary because of their environmental problems and health risks. This study can ensure the alternative method to remove dyes and also to show that titanium dioxide can be low cost and efficient photocatalyst based on effectiveness of the treatment means.

The advantages of this method (heterogeneous photocatalysis) over other conventional methods is:

- Almost complete mineralization of all organic pollutants including hydroxyl radical resistant, such as carbon tetrachloride.
- The process is named as green technology because degradation products (carbon dioxide and water) are environmentally harmless.
- Atmospheric oxygen is used as oxidant, and no other oxidant is necessary so there is no consumption of expensive and hazardous oxidizing chemicals (H_2O_2 and O_3)
- The photocatalysts are cheap, non-toxic, stable, non-hazardous, biologically and chemically inert, insoluble under most conditions and recyclable.
- Minimum energy UV light is used for photocatalyst activation and even solar light can be used [23].
- Economic Viability is comparable with activated carbon adsorption method for medium and large capacities [24].

Hence, this research definitely contributes for economical alternatives as well as aesthetic value of the environment.

The most widely used and effective method for removal of dyes using adsorption in industry is activated carbon, although the running costs are expensive. When the removal material used cheaper cost and does not require any expensive additional pretreatment step the method of heterogeneous photocatalyst (photodegradation of dye using titanium dioxide) become feasible and advisable for removal of these wastes because it doesn’t form sludge.

1.5. Scope of the Study

This study focused on the photocatalytic degradation of MB using titanium dioxide as the photocatalysts under Uv light. The photocatalyst is characterized by BET, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). In addition, the effect of selected operating parameters such as catalyst loading, concentration of pollutant, irradiation time and rate of kinetics for dye degradation will also be investigated

2. LITERATURE REVIEW

2.1. Over View of Phtocatalysis

Photocatalysis comes from two words: light and catalysis which means a chemical reaction enhanced by the absorption of light (photo-absorption) by a solid material or semiconductor. That is why semiconductor is called a photocatalyst. The photocatalyst reaction occurs at the surface of the semiconductor and the catalyst remains unchanged during and after the reaction takes place. In this study, the application of Advanced oxidation process for treatment of dyes was investigated using a semiconductor Titanium dioxide under UV irradiation instead of the conventional methods. This is due formation of sludge, sludge disposal problem, time consuming and ineffectiveness of these existed methods for degradation or removal of very toxic and complex organic pollutants or recalcitrant. In addition to this, an AOP method is environmentally friend and with no need of waste disposal problem.

Semiconductor photocatalysis has received much attention during last three decades as a hopeful solution for both energy generation and environmental problems. Semiconductor photocatalysis is began by electron-hole pairs after bandgap excitation. When a photocatalyst is irradiated by light with energy equal to or greater than band-gap energy, the valence band electrons can be excited to the conduction band, leaving a positive hole in the valence band. The excited electron-hole pairs can recombine, liberating the input energy as heat, with no chemical effect. However, if the electrons and holes are migrating to the surface of the semiconductor without recombination, they can participate in various oxidation and reduction reactions with adsorbed species such as water, oxygen, and other organic or inorganic species. These oxidation and reduction reactions are the basic mechanisms of photocatalytic waste treatment(remediation) means in photocatalysis.

Photocatalysis can takes place in liquid or gas phase. Generally, heterogeneous photocatalyst process can be divided into the following independent activities [25].

- Diffusion of the reactants to the surface of the photocatalyst.
- Adsorption of reactants on the surface of the photocatalyst
- Reaction in the adsorbed phase, which is the heart of the photocatalytic process that is degradation of pollutants takes place. It is frequently a charge transfer between adsorbed reactants and the semiconductor. UV- light is absorbed by the semiconductor.
- Desorption of the products of the redox reaction (i.e. release of the products from the surface of the photocatalyst).
- Draining of the products from the region close to the semiconductor to free the access to its surface for the remaining reactants.

Dyes can be occurred from wastes of different process industries specially textile processing. This part describes the different methods for dye removal and a review on classification of dyes, and characteristics of titanium dioxide. In addition, research on color removal of waste waters with a special emphasis on methylene blue photocatalyst decolorization(photodegradation) and the factors affecting it are discussed.

2.2. Dyes and Remediation Techniques

In this section, dyes, the classification of different conventional waste water remediation techniques (dye removal techniques), and advanced oxidation process are discussed. In addition to this, the mechanism of photodegradation and the factors affecting it is also list out. Further, the effect of dyes on environment specially on healthy of humans are reviewed.

2.2. Dyes

Dyes are toxic, coloured and aromatic organic compounds, which show special compatibility towards given substrate. The colour of dyes is due to the particular absorption of wavelength of light and the atoms exist in the dye. Group of atoms called chromophores or auxochromes are responsible for the colorant of dyes. Dyes have various applications such as textile, paint, paper, dyeing, leather, plastic etc so, the application of dyes is consistent in our day to day activity and it is difficult to avoid them in most area of human movement. On the other hand, they also have an effect on the environment during their application. One thing they cause a risk to the environment like, toxicity, water coloration, carcinogenetic, mutagenicity which causes water pollution and eutrophication in eco-system. The discharge of dye effluent from the various industries into river waters, lakes, water reservoirs leads to severe environmental problems and increases BOD content and decreased oxygen level in aquatic ecosystem. Even the very less amount of concentration of some of the dyes is highly toxic, which is difficult to degrade or considered as recalcitrant and causes skin allergies and leads to carcinogenic problems [26]. Thus, the dye pollution is not only a source to water pollution but also affects the human health and thus it is very important to degrade the dye contaminants to decrease their effect on the environment.

Generally, dyes can be described as a colored substance that has an affinity to the substrate to which it is being applied. They can be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Though, the classification of dyes on basis of structure is an appropriate system and has many advantages, like it readily identifies dyes as belonging to a group and having characteristic properties. In addition to this, there are a number of different classes of dyes based on their applications. Examples of the dyes classes are reactive dyes, direct dyes, disperse dyes, vat dyes anthraquinone dyes, sulfur dyes, cationic azo dyes, cationic methine dyes, acid dyes, solvent dyes, metal-complex dyes, naphthoquinone and benzoquinone dyes [27].

Discharged of industrial wastewater containing high concentration of coloured toxic compounds. This results a risk of harm to the health in the population as the whole to the environment.

The existence of dye in wastewater:

- Obstruct light penetration
- Highly visible and unacceptable
- Stable to light irradiation and heat
- Become as a toxic to microorganisms
- Difficult to remove due to their complex structure and synthetic origins in which they synthesized

2.2.1. Methylene Blue

Methylene Blue (methylthionine chloride) is a heterocyclic aromatic chemical compound with molecular formula ($C_{16}H_{18}ClN_3S$, $3H_2O$). It is (MB) a cationic thiazine dye. MB in commercial purity was used without further purification.

Table 1: physical and chemical property of MB [28, 29, 30]

Physical and chemical properties	Value
Melting temperature	180
Solubility in water	35.5 g/L
PH value	3
Molecular weight	319
Color	Dark blue-green in oxidized form, colorless in reduced form
Chemical formula	$C_{16}H_{18}N_3ClS$

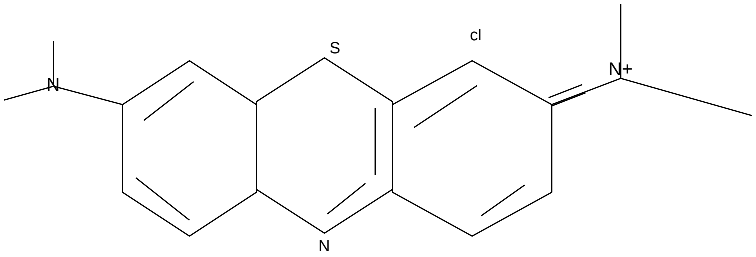

Figure 1: Structure of methylene blue

2.3. Review of Available Treatment Methods

Wastewaters from dyeing processes industries are discharged into nearby land or rivers due to inefficient, and ineffectiveness of the treatment systems. The treatment technologies(methods) can be divided into three categories: physical, chemical and biological [31]. All of them have pros and cons. Most of the treatment systems are simple to use and their disadvantage is Because of the high cost and disposal problems, so the conventional methods for treating dyes wastewater have not been widely functional on a large scale in the textile and paper industries [32].

All the time processing(chemical) industrial wastes have their own organic and inorganic matter in varying degrees of concentration and quantity. These wastes could be acids, bases, toxic materials, and matter high in biological oxygen demand, color, and low in suspended solids. A lot of materials in the chemical industry are toxic, mutagenic, carcinogenic and difficult to degrade either their nature or synthetic origin. For example, Surfactants, emulsifiers and petroleum hydrocarbons that are being used in chemical industry reduce performance efficiency of many treatment unit operations [33]. Caring and following a material safety data sheet is important during usage of such like chemicals in the industry or anywhere else. The best way or strategy to clean highly contaminated and toxic industrial wastewater is in general to remediate them at the source and sometimes by applying onsite treatment within the production lines with recycling of treated effluent following the safety data sheet [34, 35].

2.3.1. Physical methods

There are many physical methods available for textile wastewater treatment. One of the classes of such methods is the membrane processes and they are being increasingly used in the dye removal process for the recovery of valuable compounds from the wastewater and the recycling of the water [36]. The membrane technology mainly revolved around the trapping or filtering the pollutant through physical means and thus, separating them with the effluent. The factors that determine the type and porosity of the filter are the specific temperature and chemical composition of the wastewaters [37].

There are also additional different physical methods that are used for removal of dyes from waste water, Coagulation and flocculation are physical methods that are used for the decolorization of waste water comprising disperse dyes. These methods have low decolorization efficiency and highly generation of sludge [38].

2.3.2. Chemical methods

Chemical methods for removal of dyes are takes place by the addition of chemicals like lime aided with aluminum sulfate which have a disadvantage of additional cost of a chemical. But they are the most common methods for decolorization of textile waste water due to their ease to use. These treatment methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with Fe (II)/Calcium hydro oxide, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical developments. These treatment techniques are often expensive, and even the dyes are removed, accumulation of concentrated sludge creates a disposal problem. During application of this method for dye removal the probability of a secondary pollution problem to occur is high because of excessive chemical use [39]. Now a day, other developing technologies(techniques), known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation.

2.3.3. Biological methods

Biological treatment methods for removal of textile waste water are dependent on the amount of dissolved mater(waste) and their efficiency is affected by micro-organisms load, temperature and the amount of organic loading rate etc. [40]. This treatment is carried out in activated sludge and rotating biological contactor. As compared to physical and chemical methods biological systems for treatment of wastewater is an alternative and most economical method because of its low-cost method. Biodegradation methods such as adsorption by (living or dead) microbial biomass, fungal decolorization, bioremediation systems and microbial degradation are commonly used in the treatment of manufacturing and industrial effluents. Microorganism such as yeasts, bacteria, fungi and algae are able to accumulate and degrade different pollutants [41]. In this method, the selected microorganisms familiarize themselves to the pollutant and eventually develop new resistant strains. The strains are able to let the microorganisms to transform the toxic wastes into less harmful forms. Microorganisms such as bacteria, fungi, algae, actinomycetes, yeasts and plant can decolorize the dye effluent [42].

However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity near diurnal variation as well as toxicity of some chemicals, and less flexibility in design and process operation [43]. This method of treatment is unable to obtain satisfactory colour elimination with current conventional biodegradation processes.

Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin.

Table 2: Advantage and disadvantage of dye removal methods [44]

Dye removal method	Advantage	Disadvantage
Coagulant Flocculent	Simple, economically Feasible	High sludge production, handling and disposal problems
Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirement
Adsorption on activated carbon	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dye, the regeneration is expensive and result in loss of the adsorbent, non-destructive process
Membrane separation	Remove all dye types, produce a high-quality treated effluent	High-pressure, expensive, incapable of treating large volumes
Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dye
Oxidation	Rapid and efficient Process	High-energy, cost, chemical required
Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
Selective Bio adsorbents	Economically attractive, Regeneration is not necessary, high selectivity	Requires chemical modification, nondestructive process

photocatalysis by applying titanium dioxide nanoparticles will be used for the photodegradation of polluted water over the last two decades. This technology has a lot of advantages such as complete mineralization of organic pollutants like aliphatic, aromatics, polymers, dyes, surfactants, pesticides and herbicides to carbon dioxide, water and mineral acids, no waste solids to dispose of at given atmospheric pressure and temperature conditions. The photocatalysis process methodology works with two kinds of reaction systems.

These reactions are suspension and immobilized systems [45]. These methodologies have their own limitation. Suspension system are energy intensive to recycle the catalyst and difficulty to apply in large system where as immobilized systems have mass transfer limitation and reduction in surface area to volume ratio which results an overall reduction in pollutant removal [46, 47].

Titanium dioxide powders have higher photocatalytic efficiency due to their higher specific surface area. However, it has difficulty in the separation of powder from the liquid state applied in waste treatment and recycling processes. This is because of the formation of aggregates, and the depth of penetration of UV light is limited because of strong absorption by both catalyst particles and dissolved organic species. These problems can be overcome, and the application of titanium dioxide nanoparticles can also be expanded through doping or inserting various materials as substrates [48].

During the application of this catalyst as waste treatment different materials like Glass beads or fiberglass having mesh structures will enhance the surface area available by the catalyst for efficient photodegradation. In addition to this, coating transparent film of titanium dioxide on beads of silica gel was developed for photocatalytic activity [49]. This is due to the available reaction area was so large and it will help to have highly efficient decomposition of harmful organic substances, unpleasant odors and colored matters present in wastewater.

In recent years, several published papers indicating that waste water treatment based on photocatalytic activities are familiar with sufficient results and accepted the potential of photocatalytic oxidation treatment means or technology for neutralizing very diverse groups of toxic compounds in waste water [50]. Before this technology (AOP) a lot of researches are studied removal of dyes from textile waste water using different adsorbent, bio-sorbent and absorption. Adsorption is a means of the separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. It is the process that takes place when a liquid or most commonly a gas known as the adsorbate accumulates on the surface of a solid adsorbent and forming a molecular film. An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substances onto its surface by intermolecular forces. But this methodology for treatment of dye wastes will produce sludge and cause environmental problem. As the result an advanced oxidation process is selected for study.

2.4. Advanced Oxidation Process

Different group of chemical oxidative technologies for remediation of waste water are classified as advanced oxidation processes (AOPs) has been investigated as a significant level of study either academically or industrially over a few decades. These oxidation process technologies are characterized by the generation of highly reactive and non-selective hydroxyl radicals, which are very active oxidants in an aqueous medium. These active and reactive radicals are capable of oxidizing almost all organic compounds to water, carbon dioxide, and mineral salts through a process called mineralization [51]. Advanced oxidation process technologies can be categorized into two general categories. These that used UV in conjunction with other chemical additives, examples of such are like: UV with hydrogen peroxide, titanium dioxide and Fenton. On the other hand, those which are not used UV source can be classified as a dark oxidative process, such as: Ozonation (O_3), Fenton's reagent, ultrasound, and microwaves. Different researchers have been done study on each of these AOPs with respect to reactor design, optimization, and modeling. Along with, reaction kinetics of many pollutants have also been investigated, which are essential and significant for large-scale application.

2.4.1. Ozonation

Remediation of waste water using ozone is most applicable relative to other AOPs and has been used for disinfection, odor control, and colour removal [52]. Degradation of pollutants using Ozonation occurs through two types. These are the direct oxidation by ozone, which is a highly selective process with low reaction rates [53]. The other is the indirect mechanism through producing of hydroxyl radicals. The first step of this process is the decomposition of ozone by hydroxide ions. The formed hydroperoxyl radical is in an equilibrium state. The superoxide anion radical and ozone then react to form ozonide anion radical, which then immediately decomposes into oxygen and hydroxyl radicals [54]. The overall reaction is:

$$3O_3 + OH^- + H^+ \rightarrow 2OH + 4O_2 \qquad (2)$$

The drawback of Ozonation is the formation of potentially harmful by-products which can react with other compounds in water, one of which, bromate, is regulated and is considered a possible human carcinogen [55, 56].

2.4.2. UV/H_2O_2

Photolysis is a common practice for waste treatment by applying UV irradiation. But this technology alone is not efficiently degrading the majority of organic pollutants. Thus, the addition of hydrogen peroxide in conjunction with UV irradiation cleaves apart the O-O bond to generate hydroxyl radicals [57].

The advantages of UV/H_2O_2 are that it has high reaction rates and no formation toxic by-products like Ozonation and chlorination. However, it has high operational cost.

$$H_2o_2 + hv \rightarrow OH + OH \qquad (2.1)$$

$$OH + H_2o_2 \rightarrow Ho2 \qquad (2.2)$$

ultraviolet irradiation

Light is a form of the electromagnetic energy. Ultraviolet lights are those having a wavelength of 100-400 or less than 400 cm^{-1}. However, the forms of light that having a wavelength of greater than 400 or from 400-700 cm^{-1} are called Visible light. The shorter the wavelength of light the higher will be the photon energy as shown in table below.

Table 3: Wavelength and energy emitted by different type Ultraviolet light

Name	Abbreviation	Wavelength(nm)	Photon energy(eV)
Ultraviolet A	UVA	315-400	3.1-3.94
Ultraviolet B	UVB	280-315	3.94-4.43
Ultraviolet C	UVC	100-280	4.43-12.4
Vacuum Ultraviolet	VUV	10-200	6.2-12.4

Source: ISO 21348 spacenvironment@spacenvironment.net

2.4.3. Principle of AOP

The technology of advanced oxidation process has been used for degradation of waste water containing dyes specially for decolorization of textile wastes and it works based on the generation of very reactive and oxidizing free hydroxyl radicals that have been used with an increasing interest due to their high oxidant power. The principle of advanced oxidation process is in terms of the participation of hydroxyl radicals that are assumed to be fundamental and operative during the reaction process. Even though, there are other species involved during the advanced oxidation process, the active species which are responsible for the destruction of contaminants in most cases seems to be the hydroxyl radical which are unstable and quite reactive. Because of the instability of these radicals and their high reactivity, it must be generated continuously within the system chemical or photochemical reactions described in the literature [58].

2.5. Photocatalytic Mechanism of Titanium Dioxide

Titanium dioxide in the anatase and rutile phase has different band-gaps. When the energy of a photon from the light source exceeds this gap, $\lambda < 388$ nm, a photoexcited electron will be promoted to the conduction band, leaving a positive hole in the valence band, this is called the electron – hole pair (e^-, h^+). The charged particles can recombine to produce heat, become trapped or migrate to the surface to participate in a series of redox reactions. During UV irradiation into an aqueous solution for degradation the catalyst remains in an electrostatic equilibrium, where at steady-state there is an equal rate of electron and hole migration to the surface [59]. Surface trapped holes are responsible for the mineralization of organic micropollutants by either direct oxidation between the pollutant and hole or by reacting with surface adsorbed molecular water and hydroxide ions to produce hydroxyl radicals. As the holes are involved in the oxidative reactions, the surface electrons must also react to maintain the charge equilibrium and to minimize recombination. Oxygen is used as an electron scavenger due to the minimal processing cost of sparging the solution with air. Dissolved oxygen will adsorb onto the catalyst surface and be reduced by the surface rapped electron. Even though hydrogen peroxide is produced, its contribution to the reactive hydroxyl radicals towards mineralization is deemed minimal.

Usage of titanium dioxide was shown to be generally effective as a catalyst for photobleaching or photodegradation of many structural classes of organic dyes in aqueous solution, using UV-light. However, results from study of 15 dyes indicate that photobleaching rates differ significantly from families of dyes with different functionalities and are dependent on the light source and crystalline form of titanium dioxide used [60]. The average bleaching rate of anionic dyes is faster than cationic dyes, and neutral dyes were the slowest to be bleached using titanium dioxide and visible light photocatalyst [61].

However, in this study the investigation is carried out by using UV-light, titanium dioxide as a catalyst and methylene blue as model pollutant. Of the different type of dyes methylene blue is selected for the investigation, because it has more affinity to adsorption and due to the fact that MB is being positively charged can be easily adsorbed onto the catalyst through electrostatic reaction, resulting into effective degradation and it is cationic dye can highly bind to the catalyst [62].

The general mechanism for this treatment process will be:

- Light absorption and generation of electron hole pair
- Separation of charge carriers
- Oxidation reduction reaction at the surface of semiconductor [63]

Organic pollutants + i) TiO_2 → $CO_2 + H_2O$ + others (phosphate, nitrate etc...)

ii) Oxygen

ii) UV- light

2.5.1. Titanium (IV) dioxide (TiO_2)

Titanium dioxide, also called titanium (IV) oxide or Titania, was discovered in 1821 and commercialized in the early 20th century [64]. It is the seventh abundant metal in the earth crust. Since its discovery, titanium dioxide has been widely used as white pigment, later used in paints, plastics such as in carrier bags, in papers, synthetic fibers and ceramics [65]. It is also used as a photocatalyst.

In 1960s, Fujishima and Honda starts to investigate the photoelecrolysis of water using a single crystal titanium dioxide electrode. Their investigation was decomposing of water using titanium dioxide and UV-light into hydrogen and oxygen without an external voltage. The findings of Fujishima and Honda were reported in nature in 1972[66]. Starting from that, purification of water, air and surface from organic and inorganic impurities using titanium dioxide semiconductor photocatalysis has been under extensive research.

All the time titanium dioxide is not found in the pure state. Rather it is found in an oxide form, in the minerals ilmenite ($FeTiO_3$), rutile (TiO_2) or sphene ($CaO–TiO_2–SiO_2$) [67, 68]. During its application as a pigment titanium dioxide is used to scatter light photons. This light scattering process can take place by three mechanisms: reflection from the surface of a crystal, refraction within a crystal, and diffraction, whereby light is bent as it passes near a crystal. Due to its high refractive index value titanium dioxide is considered as a good pigment [69].

2.5.2. Fundamental Properties

Alibaba's titanium dioxide products are white powders with high specific surface areas. These products are pure titanium dioxide with an Anatase content of 80 – 90 % by weight with a small portion of rutile. During their usage as a catalyst they are not surface treated. As mentioned above, they are excellent photocatalyst. This is due to their high surface.

2.5.3. Photocatalytic Applications

Titanium dioxide is considered as a good semiconductor. Due to its light-sensitive semiconductor, it absorbs electromagnetic radiation in the near UV region. The difference in Energy between the valence band and the conductivity bands in the solid state is 3.05 eV for rutile and 3.29 eV for anatase, corresponding to an absorption band at < 415 nm for rutile and < 385 nm for anatase [70]. The first step for occurrence of photodegradation by semiconductor photocatalyst is adsorption. The need for absorption of light energy is to promote electrons from the valance band to conduction band (Figure 1). These electrons and similarly created positive electron hole can move on the surface of the solid and redox reaction will takes place [71].

For oxidation reaction to occur, the valance band must have a higher oxidation potential than the material under consideration.

Table 4: Wavelength and energy emitted by different type Ultraviolet light [72]

Oxidants	Oxidation potential(V)
·OH(hydroxyl radical)	2.8
O_3(ozone)	2.07
H_2O_2(hydrogen peroxide)	1.77
ClO_2(hypochlorous acid)	1.49
Cl(chlorine)	1.36

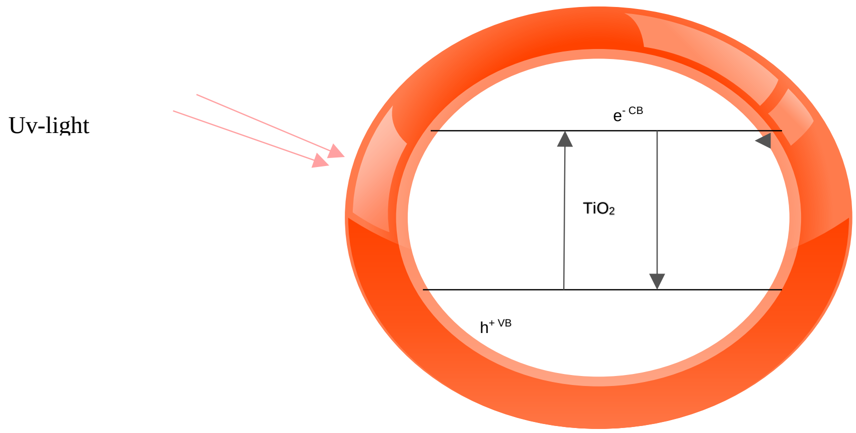

Figure 2 : Photocatalytic activity of titanium (IV) dioxide.

$$TiO_2 \text{ catalyst} + hv \rightarrow e^-_{cb} + h^+_{vb} \qquad (2.3)$$

Where, e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can drift to the catalyst surface, where they can enter in a redox reaction with other species existing on the surface. Most of the time, $h+_{vb}$ can react easily with surface bound H_2O to produce $OH^\bullet$ radicals, whereas, e^-_{cb} can react with O_2 to produce superoxide radical anion of oxygen.

$$H_2O + h^+_{vb} \rightarrow OH^\bullet + H^+ \qquad (2.4)$$

$$O_2 + e^-_{cb} \rightarrow O_2^- \qquad (2.5)$$

The above reaction prevents the combination of the electron and the hole which are produced in the first step. The hydroxyl radicals and superoxide radical anion of oxygen can then react with the dye to form other species and are thus responsible for the decolorization of the dye [73].

$$OH^{\bullet} + \text{dye} \rightarrow \text{dye}_{ox} \qquad (2.6)$$

$$\text{Dye} + e^{-}_{cb} \rightarrow \text{dye}_{red} \qquad (2.7)$$

Due to the non-biodegradability nature of synthetic dyes, conventional biological treatment processes are ineffective. Adsorption and coagulation practices result in secondary pollution. Consequently, a more promising technology based on advanced oxidation processes (AOPs) has been studied extensively for decolorization and degradation of textile dyes. The heterogeneous photocatalytic oxidation process developed in the 1970's is of special interest especially when solar light is used. The photocatalytic decolorization of a dye is held to take place according to the following mechanism. when a Tio_2 catalyst is exposed to UV radiation, electrons are promoted from the valence band to conduction band and an electron- hole pair is produced. For example, Water molecules which are adsorbed on the surface of titanium dioxide catalyst will be oxidized at the surface and producing hydroxyl radicals. The hydroxyl radicals are highly stronger oxidizing agent than either ozone or chlorine, both known as strong oxidants.

On the other hand, reduction of oxygen forming superoxide anions is takes place in the conduction band. All these oxidizing species can cause complete oxidation of organic compounds to carbon dioxide and water [74]. The anatase form requires higher light energy than the rutile form but shows a stronger photoactivity. This can be explained with the longer lifetime of the excited state in anatase and the well adsorption of oxygen in anionic form at the anatase surface [75].

2.5.4. Chemical structure of titanium dioxide

Titanium belongs to the family of transition metal oxides. There are four commonly known polymorphs of titanium dioxide found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 (B) (monoclinic) [76].

2.5.5. Titanium dioxide as a photocatalyst

There are different materials used as a photocatalyst. Of which titanium dioxide is one that is considered as the best photocatalyst. The primary reason for an efficient semiconductor photocatalyst is that the redox potential of the charge couple, electron hole pairs lies within the band gap domain of the photocatalyst. In addition to possessing a suitable band gap energy, an ideal semiconductor should also be easy to produce and use, cost effective, photostable, nonharmfull for humans and the environment [76].

Most of the recommended photocatalyst semiconductors have their own limitations. For example, GaAs, PbS, and CdS are not sufficiently stable for catalysis in aqueous media as they freely undergo photocorrosion and are also toxic [77]. Zink oxide is also unstable due to its ability to form Zn $(OH)_2$ when it gains and dissolving in water [78]. Titanium dioxide is considered as an ideal photocatalyst. it is cheap, and nontoxic. Its holes are strongly oxidizing and redox selective. The drawback is that it does not absorb visible light, difficulty in recycling and only activated by UV- light [79]. To overcome this problem, several approaches including dye sensitization, doping, coupling and capping of TiO_2 have been studied extensively.

Most of the simple metal oxide photocatalysts, are primarily active under UV irradiation (100-400 nm wave length), present in only a small portion of solar light. For example, (Table 5), TiO_2 has a wide band-gap energy of 3.0 -3.2 eV, which prevents the utilization of visible-light that accounts for most of solar energy. Recently, significant studies have also been made to develop new or modified semiconductor photocatalysts that are capable of using visible-light (400–700 nm wave length) including metal ion doping, nonmetallic element doping, and sensitization with organic dyes or small band-gap semiconductors such as CdS.

Table 5: Band-gap energies for several common semiconductor materials [80, 81]

Semiconductor	Band-gap energy(eV)
Diamond	5.4
TiO_2	3-3.2
WO_3	2.7
ZnO	3.2
SnO_2	3.5
$SrTiO_3$	3.4
Fe_2O_3	2.2
CdS	2.4
ZnS	3.7
CdSe	1.7
Gap	2.3
GaAs	1.4
Sic	3

2.6. Dye Adsorption

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, gas–solid, or liquid– solid interface or simply using a solid solvent. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The properties of adsorbate and adsorbents are reasonably specific and depend upon their constituents. This process is different from absorption since in absorption, the substrate which is usually in the form of fluid percolates into the absorbent or liquid solvent.

In this study the adsorption affinity of the dyes was determined by placing 0.1 g of nanoparticles in 100 mL of synthetic solution of the specific dye. This solution was then stirred at a constant speed for 30 min in the dark to determine the adsorption of the dye. Photodegradation is then takes place by applying Uv light. Liquates of a Samples were taking, centrifuged and tested via a spectrophotometer for the concentration determination.

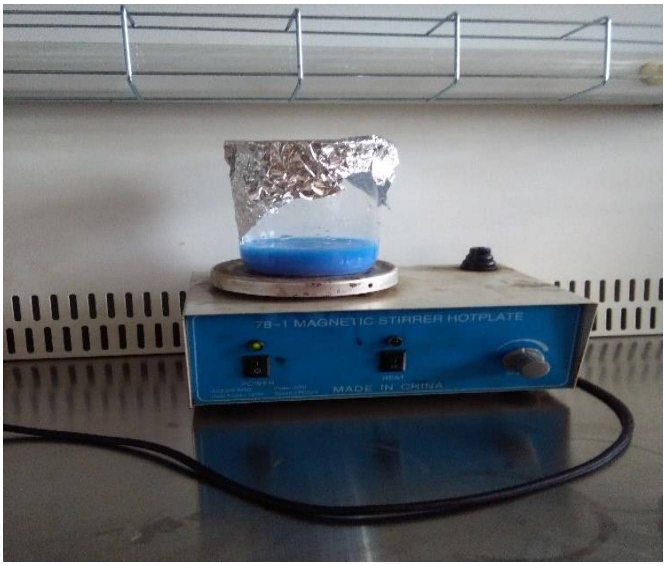

Figure 3 : Adsorption of MB on titanium (IV) dioxide in the dark

2.7. Dye Degradation

The degradation of the dyes was determined in a batch type process after exposure for 30 min in the dark to separate the adsorption from the degradation process. Samples were taken at specified times of 60 min, 90 min and 180 min. These samples were centrifuged and the concentration of the remaining dye was determined by using UV spectrophotometer. The data obtained was then interpreted for degradation efficiency and kinetic reaction rates over titanium dioxide photocatalyst.

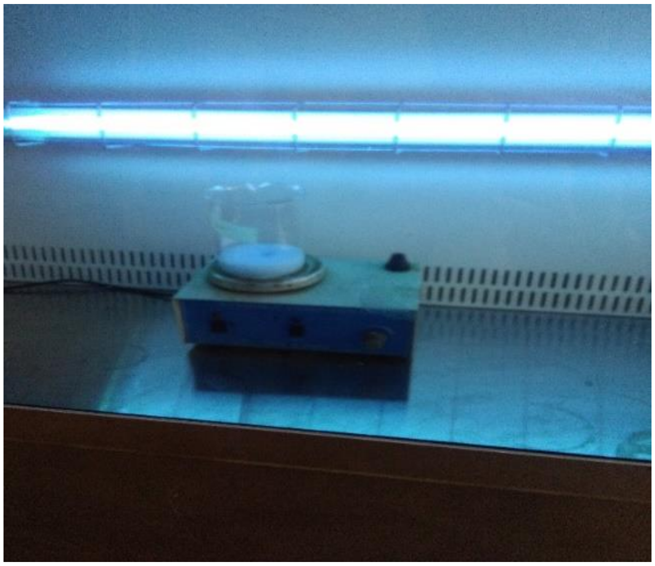

Figure 4 : Photodegradation of MB under UV light

2.8. Environmental and Healthy Impact of Dyes

Dyes have great impact on the environment and healthy of human beings. Any industrial activities cause pollution either directly or indirectly to the environment specially textile industries. Wastewater is the most environmentally damaging, and the wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as its variety of composition. The dyestuff lost through the processes of dying cause problem [82]. This part will discuss the effect of these wastes in the environment and specifically on the health of human beings as well as environmental regulations that has to be taken to minimize the impact of dyes.

2.8.1. Environmental Impact

Colour is usually the first contaminant to be recognized in a wastewater because a very small amount of synthetic dyes in water (< 1 ppm) are highly visible, affecting the aesthetic value, transparency and gas solubility of water bodies. They adsorb and reflect the sunlight entering into water, thus interfering with the aquatic species growth and hindering photosynthesis. Additionally, they can have acute and /or chronic effects on organisms depending on their concentration and length of exposure. Removal of colour from dye-containing wastewater is the first and major concern, but the point of degrading dyes is not only to remove colour, but to eliminate, or substantially decrease, the toxicity (i.e. detoxification) [83].

2.8.2. Healthy impact

dyes and their degradation products are quite carcinogenic, teratogenic, and harmful to human health. Many laboratory experiments on animals have shown mutagenic and carcinogenic effects due to the release of amines. These carcinogenic amines make the dyes as potential health hazards [83].

2.8.3. Environmental Regulation

Government legislation regarding the removal of dyes from industrial effluents is becoming increasingly stringent, especially in the more developed and developing countries [84]. Enforcement of the law will continue to ensure that textile and other dye-utilizing industries treat their dye-containing effluent to the required standards. In Ethiopia, colour limits in industrial waters have also been set and have been made more stringent in the last few years. Table 6. presents an example of the environmental management standard of mojo tannery industry.

Table 6: Environmental management standard for mojo tannery industry

Parameter	Limit value
Temperature	40 c^0
pH	6-9
BOD	200 mg/L
COD	500 mg/L
Suspended solids	50 mg/L
Total Ammonia	30 mg/L
Total Nitrogen	60 mg/L
Oils and fats	15 mg/L
Chromium (as total Cr)	2 mg/L
Chromium (Cr VI)	0.1 mg/L
Chloride (Cl)	1000mg/L
Sulphide(s)	1 mg/L

Different process industries discharge wastes which have great impact on the environment specially textile industries. Due to the toxicity of textile wastewater, many countries have made an agreement and passed regulations to control these effluent outputs. One country that has enacted such regulations is the United States. In 1972, the U.S Environmental Protection Agency (EPA) created the Clean Water Act to restore and maintain the chemical, physical, and biological integrity of the nation’s waters. As a result of this act, all toxic pollutants were to be identified and arrangements were to be created for the removal and appropriate disposal of materials [85].

Starting from 1972 to 1975, research on wastewater treatment was performed at the Cracow Water Protection Section at the Water Economy Research Institute in Warsaw, Poland as part of an agreement with the EPA. The focus of the research was to analyze the various techniques for waste water treatment like, physical, chemical and biological Treatment Methods [86], to treat wastewater (removal of color, detergents, other refractory pollutants) and determine the most effective and economic solution. Initially, the following technologies were studied: rapid filtration on single and multi-media beds, adsorption on granular activated carbon, ion exchange on anionic and cationic resins, coagulation with the use of typical coagulants and with the application of auxiliary chemicals, oxidation with ozone and chloride, and reverse osmosis results were used to create regulations [87].

2.9. Factors Affecting Photodegradation

The degradation rate ands and efficiency of the photocatalytic systems are highly dependent on a number of operational parameters that govern photodegradation process and its kinetics. This section will discuss the effect of each operational parameters and their significance.

Temperature

Temperature is one of the factors which affects the rate of photodegradation of dyes. The effect of it on the removal of dye using semiconductor photocatalyst is an increase in reaction temperature generally results increased photocatalytic activity however reaction temperature larger than 80 °C promotes the recombination of charge carriers and disfavour the adsorption of organic compounds on the Titania surface [88]. The optimum range of operational temperatures for decolorization for AOP was found to be in the range 40–50 ^{o}C. When the temperature is low, desorption of the products formed limits the reaction because it is slower than the degradation on the surface and the adsorption of the reactants. On the other hand, at a higher temperature, the limiting stage becomes the adsorption of the dye on TiO_2 surface. The reduction of the adsorptive capacity associated with the organics and dissolved oxygen at higher temperatures results a decrease in the rate constant [89, 90].

Inorganic ions

Waste water contains different inorganic anions and cations. These various inorganic ions such as magnesium, iron, zinc, copper, bicarbonate, phosphate, nitrate, sulphate and chloride present in wastewater can affect the photocatalytic degradation rate of the organic pollutants due to their absorbed ability on the surface of the catalyst [91]. The cations present in waste water such as copper, iron and phosphate can decrease the photodegradation efficiency if they are present at certain concentrations whereas calcium, magnesium and zinc have little effect on the photodegradation of organic compounds which is associated to the fact that these cations are found at their maximum oxidation states that results in their inability to have any inhibitory effect on the degradation process [92]. The other inorganic anions such as nitrate, chlorides, carbonates and sulphates are also known to inhibit the surface activity of the photocatalyst. The presence of salts can diminish the colloidal stability, which results an increase in mass transfer and reduces the surface contact between the pollutant and the photocatalyst [93]. Some anions such as chlorides, carbonates, phosphate and sulphates also scavenge both the hole and the hydroxyl radicals so that they reduce the photoactivity [94].

Morphology of the photocatalyst

The surface morphology like particle size and structure are an important factor to be considered in photocatalytic degradation process because there is a direct relationship between organic compounds and surface coverage of the photocatalyst [95]. The photon reaching to the photocatalyst controls the rate of reaction which implies that the reaction takes place only in the absorbed phase of the photocatalyst [96].

Light intensity

The intensity of light affects photodegradation and it determines the extent of light absorption by the semiconductor catalyst at a given wavelength. The degradation efficiency of dyes using a semiconductor photocatalyst depends on the intensity of light [97]. An increase in the intensity of light will result in increased photocatalytic reaction rates. However, the initiation of semiconductor TiO_2 photocatalysis reaction rates is not highly dependent on light intensity, where a few photons of energy can sufficiently induce the surface reaction [98]. In order to obtain, a high photocatalytic reaction rate, particularly in waste water treatment, a relatively high light intensity is required to adequately provide each TiO_2 surface active sites with sufficient photons energy required, which means, higher light intensity provides higher energy for more titanium dioxide nanoparticles to produce electron-hole-pairs [99, 100].

3. MATERIALS AND METHODS

3.1. Materials

Chemicals

- Anatase TiO_2 catalyst
- Distilled water
- Methylene Blue ($C_{16}H_{18}ClN_3S\cdot 2H_2O$) was used as a model pollutant in order to evaluate the photocatalytic performance of the catalyst.

3.2. Method

The photocatalytic activity of titanium dioxide nanoparticles was investigated using MB as a model chemical in batch photo reactor using Uv-light irradiation. A 500-ml beaker was used as photo reactor for all experiments in which Uv-light will be provided by Plexiform lamp (Pk526) with a wavelength of 100-400 nm. During this process, 0.1 gram of titanium dioxide powder was prepared and suspended in 100 ml of 10 ppm MB solution to determine the time required for complete decolorization. The solution is continuously stirred with a magnetic stirrer to ensure homogenous mixing during 3-h irradiation period. Prior to proceeding to photo activity test, the solution will be stirred further for additional 30 min in dark environment to create adsorption-desorption equilibrium. After which, 60 ml of aliquots will be taken from the reactor and filtered using centrifuges. The concentration of MB will be then analyzed with UV-Vis spectrophotometer (UVD-3200) at 664 nm wavelength absorbance. The MB decolorization efficiency (R (%)) will be calculated using the following formula:

$$R(\%) = \frac{initial\ concentration - final\ concentration}{initial\ concentration} * 100\% \qquad (3)$$

Then determination of effect of different parameters likes (pollutant concentration, dosage of catalyst, and irradiation time) were evaluated using ANOVA by making fixed rotational speed and temperature respectively. In order to find optimum operating conditions, the experiment is done for different times according to the experimental design operational parameters based on Rsm.

3.3. Central Composite Design

The experiments were designed according to central composite design method with the selected three important process parameters as mentioned earlier. Central composite design is used to test the effect of each factor. In factorial experiment, all possible combination of factor levels was tested. And it was determined the effects of individual factors and assessed the effect of change of variables for dye removal. Central composite is selected because it is easy to find the optimum point in which the photodegradation occurred with simple number of experiments.

The required responses (decolorization efficiency of methylene blue) under UV-light were optimized after studying the influences of these independent parameters and their interaction effects.

Table 7: experimental levels of selected variables for CCD

Level					
Abbreviation	Variable	Units	Low (-1)	Medium (0)	High (1)
A	Dosage	Gram	0.1	0.3	0.3
B	Concentration	Mg/L	10	20	30
C	Time	Min	60	120	180

The factors and levels are given in Table 3. The factors, (dosage of catalyst, concentration of pollutant, and irradiation time) were designated as A, B, and C respectively.

The analysis of regression and estimation of coefficients were performed with statistical software package Design expert version. 7. The adequacy of the model equations was evaluated using analysis of variance(ANOVA). Model equation quality fitting and statistical significances were investigated using F-test, coefficients of determination(R^2), coefficients of prediction and determination (Pred - R^2), adjusted coefficient of variance determination(adj-R^2).

The general flow mechanism for the photodegradation of MB using titanium dioxide photocatalyst can be summarized in the following figure.

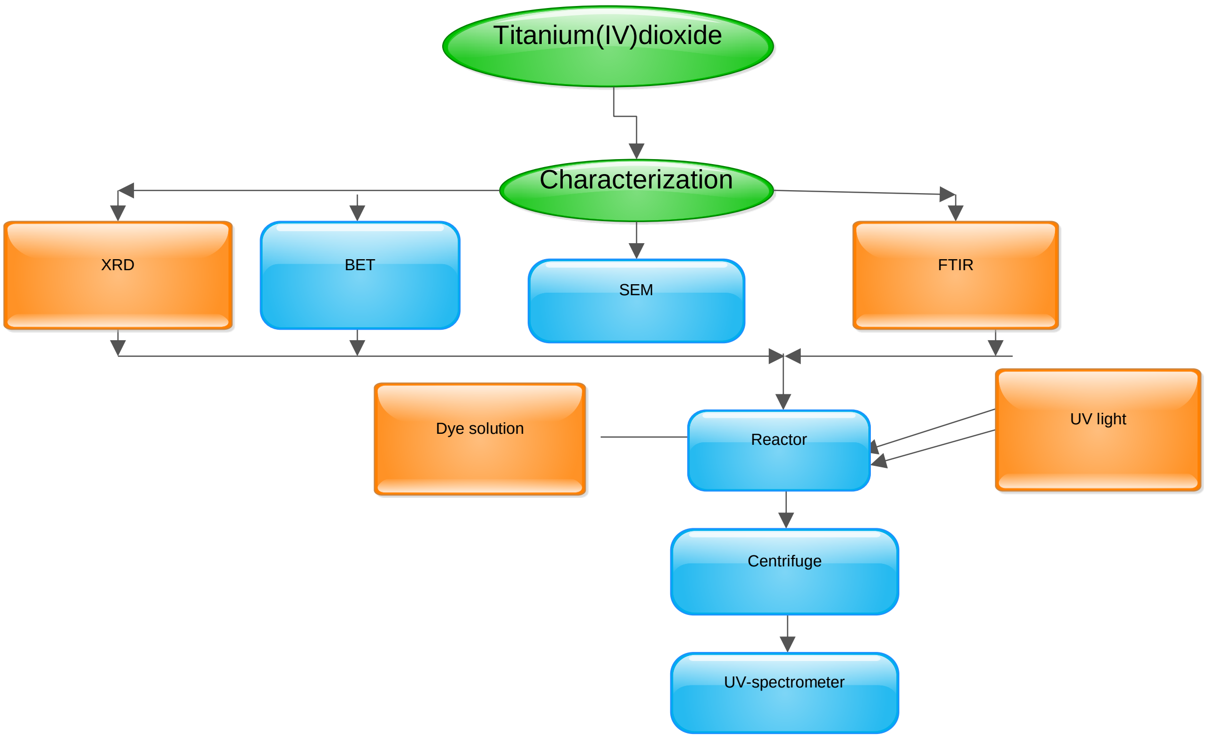

Figure 5 : Flow chart of experimental frame work

3.4. Characterization of the Photocatalyst

Characterization tests were carried out on the titanium dioxide photocatalyst so as to describe its features. The tests were Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), Uv-vis-spectrophotometer and BET surface area. Basic understanding of the characteristics affecting photocatalytic activities is important to make efficient use of existing catalyst and to provide design criteria for the preparation of a new catalyst.

Analysis of function groups were performed using Fourier Transmission Infrared (varian 640-IR) FT-IR spectrometer, from 4000-400 cm^{-1} wavenumber. The crystallite size and phase compositions were obtained from the x-ray diffraction (XRD) measurement on PANalytical X'pert PRO-MPD diffractometer with x-ray char-kα radiation(λ=0.154059), accelerating voltage (40kv) and current(15mA). The crystal size was determined according to scherrer equation. The specific surface area, pore volume and pore diameter were obtained from nitrogen adsorption-desorption isotherm by using Brunauer-Emmett-Teller (BET) and Barett-Joyner-Halenda

(BJH) methods with micrometertics Tristar II 3020. UV-Vis spectra of the sample were scanned using UV/Vis/NIR spectrophotometer (Hitachi, U-4100) in the range of 200-800 nm. The surface morphology of the sample was also examined using field emission scanning electron microscope, (FE-SEM (JOL, JSM-7610F).

Photocatalytic activity

Measuring solution of MB at different concentration through the UV-spectroscope a calibration plot was made. The concentration of methylene blue was varied between 5 and 30 mg/l. The calibration plot was taken in a region linear according to the beer-lambert law and was used to convert the absorbance of the yield in the photodegradation experiments to MB concentration as shown from annexes part.

The final Concentration of the dye was related to absorbance using:

$$C = \frac{A - intercept}{Slope} \qquad (3)$$

Where C is the outlet concentration and A, The measured absorbance at 664 nm.

3.5. Photodegradation Reaction Kinetics

The present photodegradation process assisted by a titanium dioxide semiconductor was studied by varying the rate determining parameters like concentration of the dye (MB), dosage of catalyst and UV- irradiation time. Photocatalytic degradation of dyes generally follows first order kinetics. Though, the process of photocatalytic oxidation is complicated, and it is complex to get the exact reaction kinetics from the elementary reaction steps, the rate reaction depends on the light irradiance and the dosage of catalyst. To describe the kinetics of photocatalysis on waste treatment, the most famous model, which is widely used, is the Langmuir-Hinshelwood (LH) kinetic model of pseudo-first order photocatalytic reactions [101, 102].

The Langmuir-Hinshelwood (L-H) model was initially developed to quantitatively describe gaseous-solid reactions and recently it is employed to describe solid-liquid reactions [103, 104]. In this model, the rate of reaction (r) is proportional to the fraction of surface covered by the substrate (θ).

$$r = -\frac{dc}{dt} = kr\theta \qquad (3.1)$$

Considering the Langmuir-Hinshelwood equation

$$\theta = \frac{KC}{(1 + KC)} \qquad (3.2)$$

$$r = -\frac{dc}{dt} = \frac{krKC}{(1 + KC)} \qquad (3.3)$$

Since kr is the true rate constant, which takes into account several parameters such as the catalyst's mass, efficient photon flow etc., K is the constant of adsorption equilibrium(L/mg) of the Langmuir constant. In photocatalytic studies, the value of K is obtained empirically through a kinetic study in the presence of light and is better than that obtained in the darkness [105, 106]. starting from Langmuir's isotherm. C is the concentration of the organic substrate(mg/L) at any time (min). The above eq. (3.3) will be of zero order when the concentration C (mol/l) is relatively high, (C >5 x 10^{-3}) and KC >>1, in which case the reaction rate will be maximal, on the other hand when the solution is highly diluted, C (mol/l) (C<10^{-3}), the term KC becomes <<1, in this case the denominator of eq (3.3) is neglected and the reaction is essentially an apparent first order reaction [107]:

$$r = -\frac{dc}{dt} = krKC = kappC \qquad (3.4)$$

where ka_{pp} is the apparent rate constant of a pseudo first order reaction (min^{-1}). Thus, integrating eq. (3.4) can be simplified to a first order reaction when C_o is very small, in which case one has:

$$\ln\left(\frac{Co}{C}\right) = Kapp\ x\ t \qquad (3.5)$$

By plotting ln(C_0/C) versus t, the apparent rate constant (kapp) can be determined from the slope of the curve obtained. In addition to this, the kinetic constant kr (mg/L min) and the adsorption constant K(L/mg) were calculated using the L-H model, considering the initial reaction rate and concentration, thus following eq. (3.3) and transforming it into:

$$\frac{1}{ro} = \frac{1}{krK}\ x\,\frac{1}{Co} + \frac{1}{k} \qquad (3.6)$$

Plotting of 1/ro versus 1/Co, the values of the kinetic constant (kr) and the adsorption constant (K) are obtained using eq. (3.6).

4. RESULT AND DISCUSSION

In this part the statistical analysis of surface response methodology, central composite design optimization for the selected parameters and the physiochemical characteristics of the photcatalyst is discussed. The performance of the photocatalyst was investigated using methylene blue as a model pollutant and the factors that affect photocatalyst.

4.1. XRD- Analysis

The phase composition and the crystallite size of titanium dioxide were determined by using X- ray diffraction analysis. From Fig 6, XRD peaks, the width of $2\theta = 25.58^0$ is useful peak since it has high intensity which is used to determine crystals size and the sharp peak show the crystallinity and purity of titanium dioxide nanomaterial. According to JCPDS card number-84-1286 from fig 6, the peaks representing $2\theta = 25.58^0$ confirms that an anatase structure and at $2\theta = 27.36^0$ the instrument does not show any peak that is assigned to rutile phase.

The average crystallite size of the samples was calculated from the most intense diffraction peak of anatase TiO_2 using the Scherrer formula [108] below Equation (4.1):

$$D = \frac{0.9 * \lambda}{(\beta) cos\theta} \qquad (4.1)$$

From the above equation, *D* is the crystallite size in (nm), λ is the radiation wavelength used ($\lambda = 0.15406$ nm), θ is the Bragg angle and β is the full width at half-height of the diffraction peak in radian($\beta = 0.2394$) as shown in the Figure 6 and based on origin pro software analysis. Thus, the crystal size(D) of the material is 39.93nm.

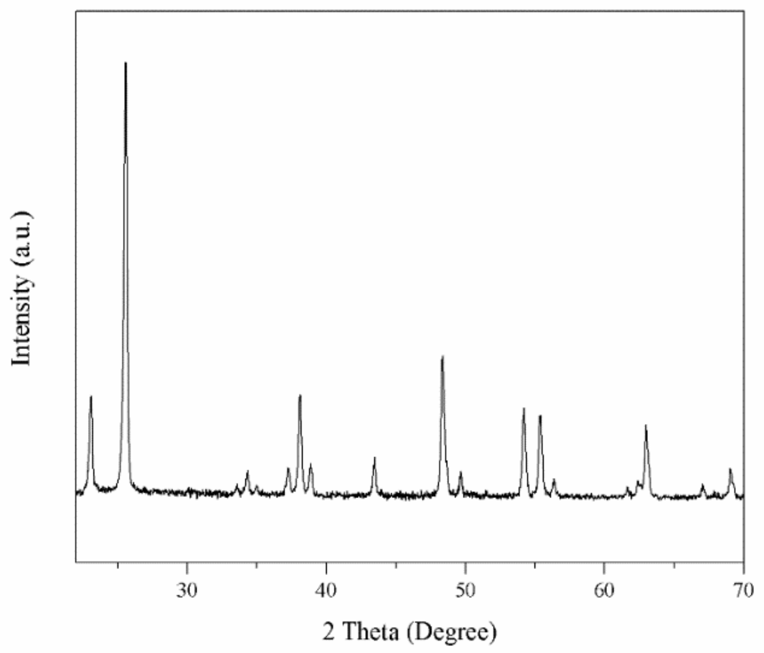

Figure 6: XRD- spectra of titanium (IV)dioxide

4.2. Specific Surface Area Analysis

The Brunauer–Emmett–Teller (BET) method continues to be the most widely used method for evaluating the specific surface area of porous and finely-divided materials. In the 1985 IUPAC recommendations physisorption isotherms were grouped into six types [109]. Based on this classification titanium oxide is grouped under type IV isotherms which are given by mesoporous adsorbents (e.g., many oxide gels, industrial adsorbents and mesoporous molecular sieves) as shown in Fig 8. From Nitrogen adsorption-desorption data. The average surface area of the catalyst is 55.64 m^2/g according to BET method. It is true that, a large surface area will improve the photocatalytic activity because of the availability of more active sites on the surface of the photcatalyst and this results better mass transfer [110, 111]. The hysteresis cycle for titanium oxide catalyst corresponds to the H1 type, according to the IUPAC classification, characterized by having almost vertical and nearly parallel branches of adsorption-desorption over a considerable range of relative pressures as shown in the figure 7. The materials that develop this type of hysteresis are characteristic of solids consisting of particles crossed by nearly cylindrical channels or made up of aggregates (consolidated) or agglomerates of spheroidal particles [112]. Along with, the material showed in (Figure 8) is a monomodal pore size distribution centered in the mesoporous region. The pore size of the material is 9.78 nm according to BJH method, and this result indicates that they are small in their pore size.

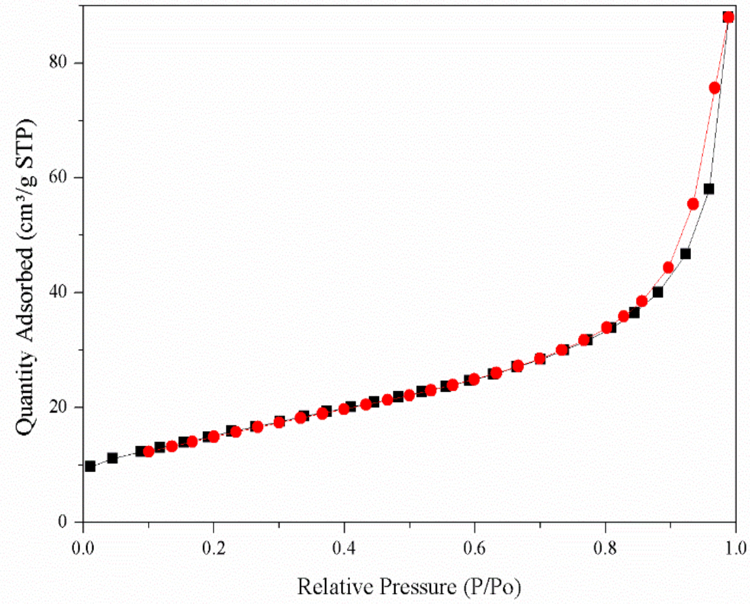

Figure 7: Nitrogen adsorption-desorption isotherms of titanium dioxide

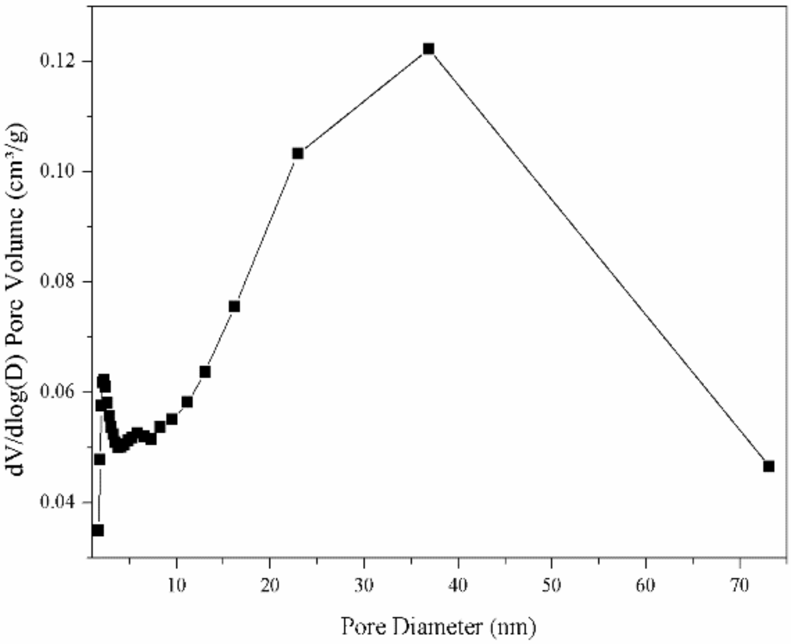

Figure 8 : Pore size distribution of titanium (IV) dioxide

4.3. UV/Vis Analysis (UV-Visible Absorption Spectrum)

The UV-vis absorption spectra for a sample is shown in Figure 9, in between 300 and 700 nm. The Sample has got a peak in 393 nm. Thus, this result indicates that titanium dioxide is activated under Uv region. It is clear that as the size of particles decreases, peaks become sharper and the absorbance increases. The band gap energy was calculated as per the literature report [113] using the following equation:

$$Band\ gap\ Energy\ (E) = \frac{1240}{\lambda}. \tag{4.2}$$

where λ is the wavelength (nm) According to this equation the bandgap of a sample is 3.16 eV, and these results confirm that when the size is smaller, the bandgap will be bigger (Figure 9).

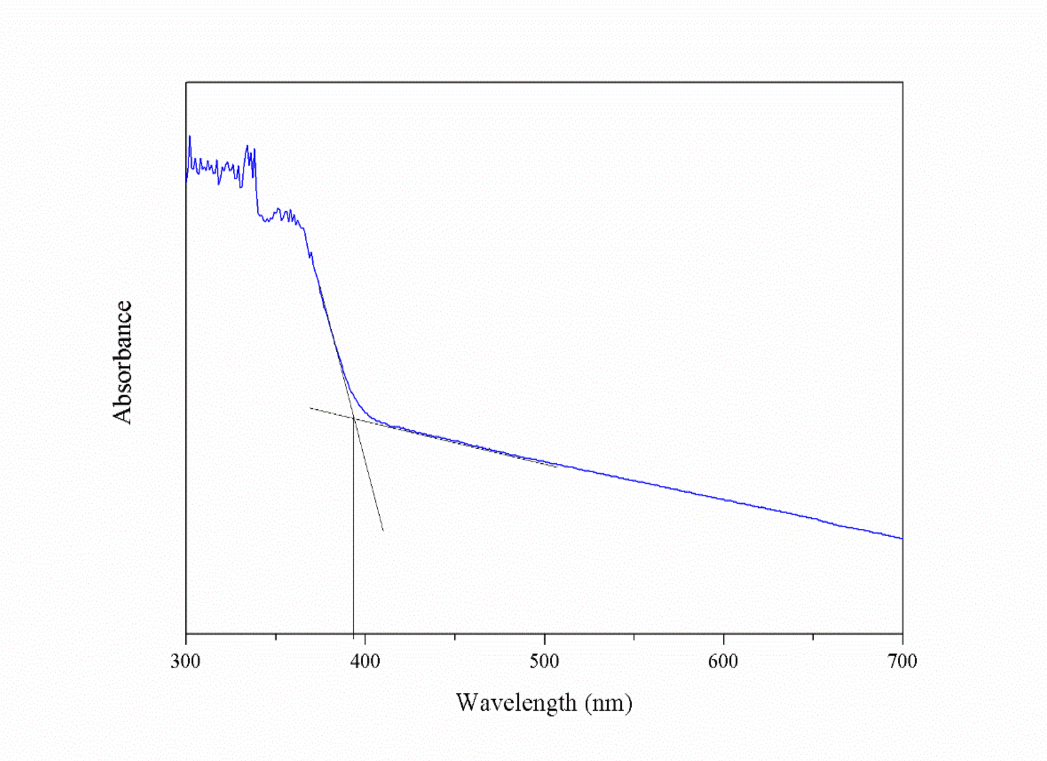

Figure 9 : UV-vis spectra of titanium (IV) dioxide

4.4. SEM Analysis

The surface morphology of the sample was characterized by field emission scanning electron microscope (FE-SEM, JEOL, Model: JSM 7610). Figure 10. shows the scanning electron microscopy images obtained for titanium dioxides, taken with a magnification of 5000x. This analysis was important since the photocatalyst oxidation mechanism is described in terms of surface-oriented adsorption of substrates and hydroxyl radicals. As it can be seen from the figure 10, the Nano particles appeared to be small and agglomerated, showed different morphologies ranging from spherical shapes of various sizes to amorphous shapes [114].

Therefore, the result obtained from BET analysis and being small for nanoparticles as shown from Fig 10, are consistent in which the catalyst is mesopores structure.

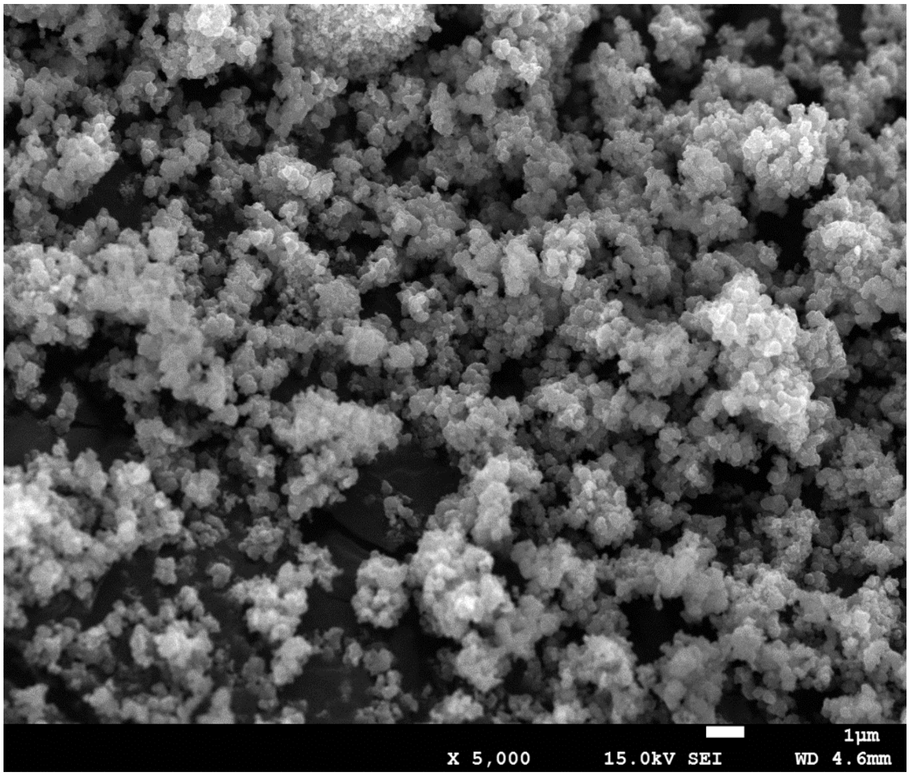

Figure 10: SEM image of titanium (IV) dioxide

4.5. FT-IR Analysis

Fourier Transform Infrared Spectroscopy (FTIR). Figure 11. shows the spectra of titanium dioxide in the range of 400–4000 cm^{-1} to identify the functional groups present in the sample.

Many absorption bands belong to the organic groups such as O-H and alkane were appeared. In the sample TiO_2, between the peaks 3800 to 3000 cm^{-1} a broad band was observed which related to stretching hydroxyl (O-H) groups, representing the water as moisture [115].

In addition to this, the peaks that are found at 584 cm^{-1} and 676 cm^{-1} are for O-Ti-O stretching band in anatase morphology [116, 117]. The adsorption peaks which are located at around 3100-3500 and 1630-1645 cm^{-1} assigned to stretching and bending vibrations of O-H bond in hydroxyl group and absorbed water on the surface of the titanium dioxide [118, 119]. In this study, these peak intensities were found at 3427 cm^{-1} and 1640 cm^{-1} and were broad and weak. The adsorbed OH groups are helpful to improve photocatalytic activity of titanium dioxide by serving as an oxidizer for degradation of organic pollutants and giving better charge transfer by interacting the photogenerated holes [119,120].

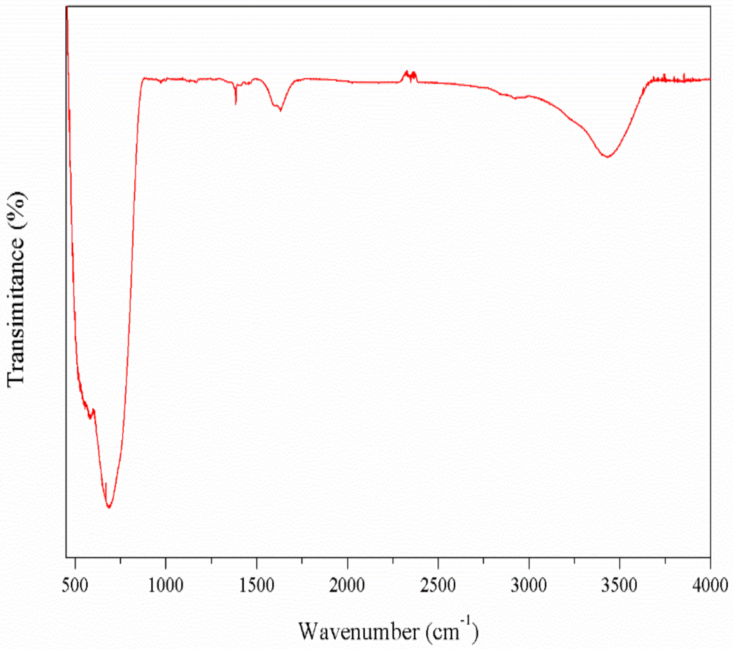

Figure 11: FT-IR spectra of Titanium (IV) dioxide

Table 8: Analysis of variance (ANOVA) CCD quadratic model

Source	Sum of square	DF	Mean Square	F Value	P-value Prob>F	
Model	4247.68	9	471.96	15.14	0.0001	Significant
A-Dosage	*534.94*	1	*534.94*	*17.16*	*0.0020*	
B-Concentration	*2292.69*	1	*2292.69*	*73.56*	*<0.0001*	
C-Time	*808.01*	1	*808.01*	*25.92*	*0.0005*	
AB	*23.46*	1	*23.46*	*0.75*	*0.4060*	
AC	*100.11*	1	*100.11*	*3.21*	*0.1034*	
BC	*219.45*	1	*219.45*	*7.04*	*0.0242*	
A^2	*0.68*	1	*0.68*	*0.022*	*0.8853*	
B^2	*26.59*	1	*26.59*	*0.85*	*0.3774*	
C^2	*37.23*	1	*37.23*	*1.19*	*0.3000*	
Residual	311.68	10	31.17			
Lack of Fit	*235.815*	47.16	*3.11*		*0.1194*	not significant
Pure Error	*75.87*	*5*	*15.17*			
Cor Total	4559.36	19				

The Model F-value of 15.14 implies that the model is significant. There is only a 0.01% chance a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Table 9: model summery statics

Source	Std DV.	R-square	Adjusted R-square	Predicted R-square	PRESS	
Linear	7.60	0.7974	0.7594	0.5747	1938.93	
2FI	6.68	0.8726	0.8139	0.1499	3875.80	
Quadratic	5.58	0.9316	0.8701	0.8152	842.41	Suggested
Cubic	3.56	0.9833	0.9471		+	Aliased

Determination of the model

The statistical summary for each model is shown in Table 9, that was the output by Design Expert7. A quadratic model was suggested, nevertheless it has lower R^2 and adjusted-R^2 (Adj-R^2) values than a cubic model. This is because the cubic model is aliased, which means that the effects of each variable that results dissimilar signals become not distinguishable. For example, a linear relationship, the R^2 and Adj-R^2 values are 0.797 and 0.759, respectively. Therefore, it is clear that the linear relationship is not adequate for the experimental data. Thus, the quadratic model was selected to fit the experimental data for the selected condition.

Model fitting and analysis of variance (ANOVA)

Experiments were performed using CCD or the central composite experimental design. The experimental and predicted removal efficiencies are shown along with the experimental conditions below in Table 10. Based on the model analysis in the model statics part, a quadratic model was chosen to fit the data. The relationship between the removal efficiency and the three chosen actual factors is given below.

$$R(\%) = 36.56 - 2095.03A - 118.78B - 23.03C - 1.71AB - 0.59AC - 8.73E - 003BC - 4770.89A^2 - 2.89B^2 + 0.098C^2$$

Where: A is dosage of catalyst

B concentration of pollutant

C Time required for irradiation

The coefficient of determination (R^2) is well-defined as the ratio of the explained variation to the total variation and is a measure of the degree of fit [121]. A good model fit must have a coefficient of regression at least 0.8 [122]. This means that the response model evaluated in this study can describe the reaction very well, with R^2 of 0.93 and an Adj-R^2 of 0.87 at a confidence level of 95%. In addition, the model is very significant, as it is evident from its F-value ($F_{model} = 15.14$) and very low probability value ($p = 0.0001$) as shown from table 8 above.

A p-value lower than 0.05 indicates that the model is statistically significant, whereas a value greater than 0.1000 indicates that the model is not significant.

Table 10: Experimental and predicted response under different condition

Standared Order	A	B	C	Actual value	Predicted Value
1	0.1	10	60	49.00	48.70
2	0.3	10	60	75.00	75.54
3	0.1	30	60	29.00	28.79
4	0.3	30	60	49.00	48.77
5	0.1	10	180	86.10	86.33
6	0.3	10	180	98.80	99.01
7	0.1	30	180	46.00	45.46
8	0.3	30	180	51.00	51.30
9	0.19	20	120	44.00	52.32
10	0.21	20	120	62.00	53.95
11	0.2	19	120	59.00	52.33
12	0.2	21	120	42.00	48.95
13	0.2	20	114	54.00	56.13
14	0.2	20	126	60.00	58.14
15	0.2	20	120	48.00	53.61
16	0.2	20	120	55.00	53.61
17	0.2	20	120	50.00	53.61
18	0.2	20	120	55.00	53.61
19	0.2	20	120	58.00	53.61
20	0.2	20	120	56.50	53.61

A: Dosage of catalyst

B: Pollutant concentration

C: UV irradiation time

Model accuracy

An accuracy check is important to obtain an adequate and exact model as shown in Fig. [12, 13 and 14]. In addition to this, the model accuracy was checked by comparing the actual(experimental) and predicted values for removal efficiency. Table 10, shows the values of the actual and predicted removal efficiencies for a given condition. In addition to this, a normal plot of residuals between the normal probability (%) and the internally studentized residuals was also obtained. In this way, the residuals can be checked to determine how well the model satisfies the assumptions of ANOVA, and the internally studentized residuals can be used to measure the standard deviations separating the experimental and predicted values [123]. Fig. 12, shows the relationship between the normal probability (%) and the internally studentized residuals. The straight line means that no response transformation was required and that there was no apparent problem with normality.

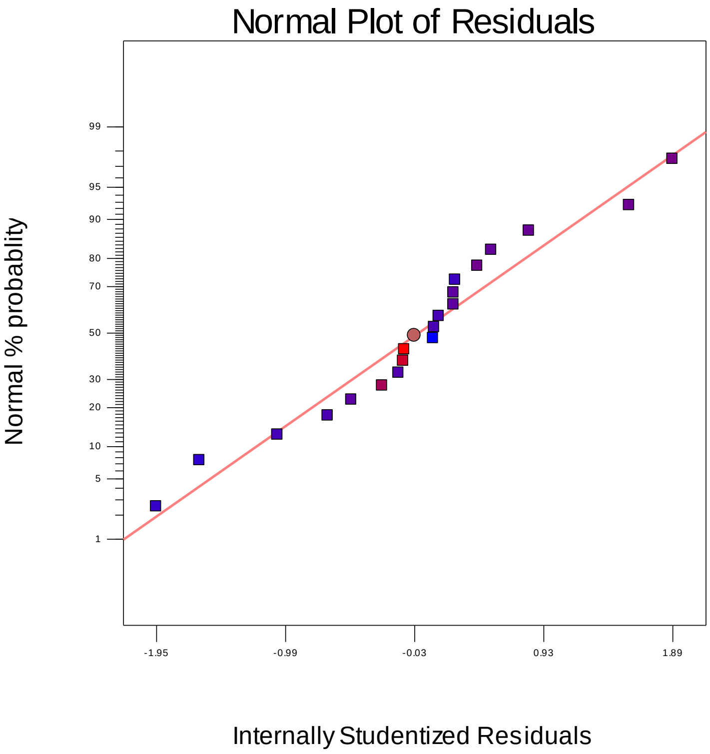

Figure 12: Normal plot of residuals experimental value for MB decolorization

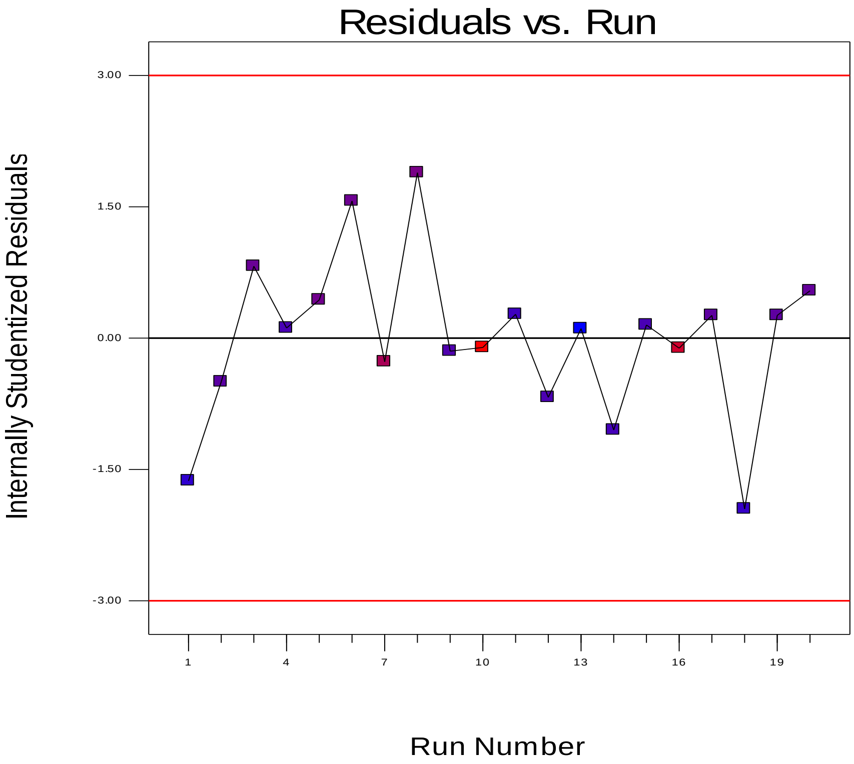

Figure 13: Residual vs experimental value for MB decolorization

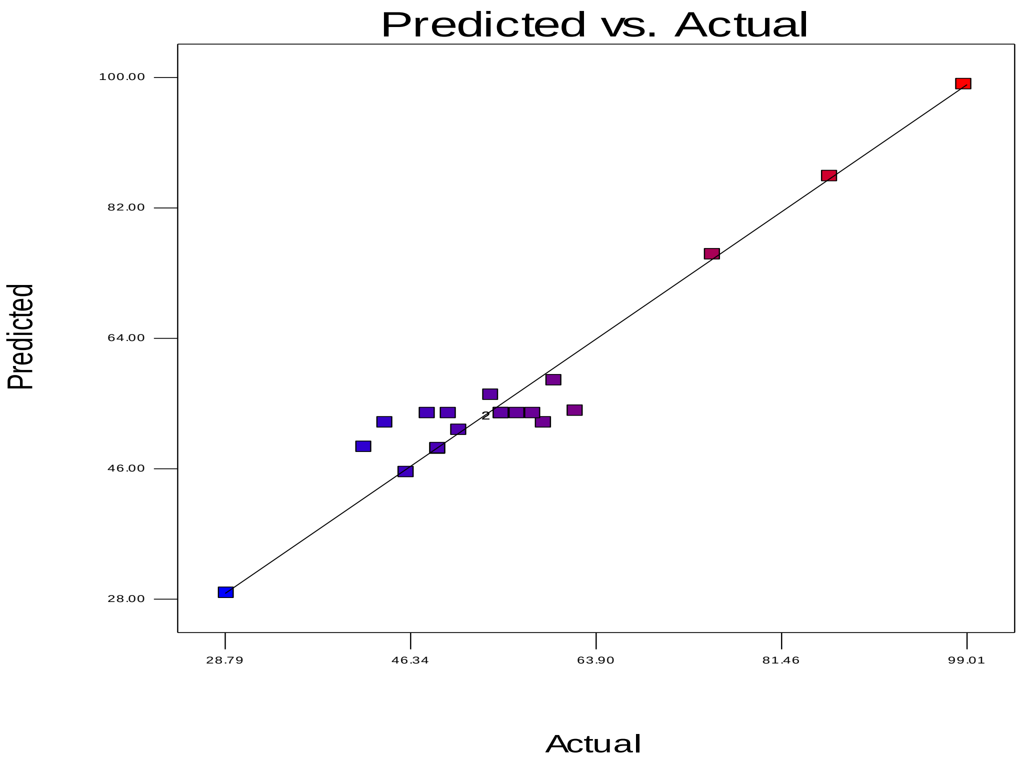

Figure 14: Predicted vs actual value for MB decolorization

4.6. Effect of Parameters on Photodegradation

In this section we will try to discuss the different process variables(factors) that are influencing the photodegradation of dyes according to the outcomes obtained from design expert software version 7. These parameters can be dosage of catalyst, concentration of pollutant and UV irradiation time based on the specified condition.

4.6.1. Dosage of catalyst

The amount of catalyst was varied from 0.1 gram to 0.3 gram per 100 ml of constant dye solution of 10 ppm concentration. The effect is graphically depicted in Fig 15. Photodegradation is affected by the amount or dosage of catalyst. The increase catalyst dosage results an increase in the removal efficiency due to an increase in the number of active sites and these causing the increase in hydroxyl radicals which results an increase in the degradation of MB dye.

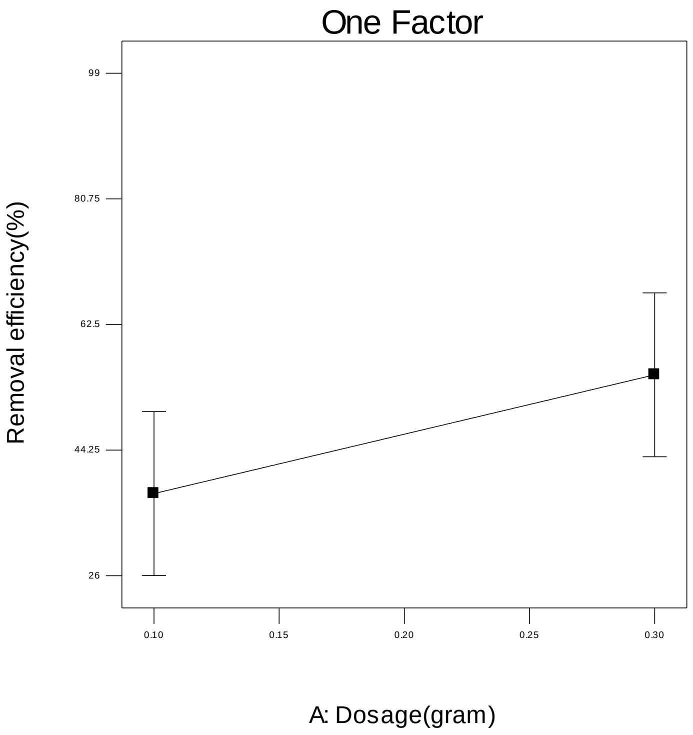

Figure 15: Effect of catalyst amount on photodegradation of dye

We observe that initially with increasing catalyst amount the reaction was found to occur slower due to small in the number of active surfaces on the catalyst required for the dye adsorption. However, beyond 0.2 gram the reaction rate increased, which could be due to the increase in the number of the active surfaces on the catalyst.

4.6.2. Pollutant Concentration (MB)

Keeping the catalyst loading concentration constant at (0.1 gram) per 100 ml of the dye solution, the effect of varying amounts of the dye was studied on its rate of degradation from 10 ppm to 30 ppm. As the concentration of MB increases, the rate of degradation was found to be decrease. This is because as the number of dye molecules increase, so that, the amount of light (quantum of photons) penetrating the dye solution to reach the catalyst surface is reduced due to the hindrance in the path of light. Thus, the formation of the reactive hydroxyl and superoxide radicals is also simultaneously reduced. As the result, there should be an optimum value maintained for the catalyst and the dye concentration, wherein maximum efficiency of degradation can be achieved.

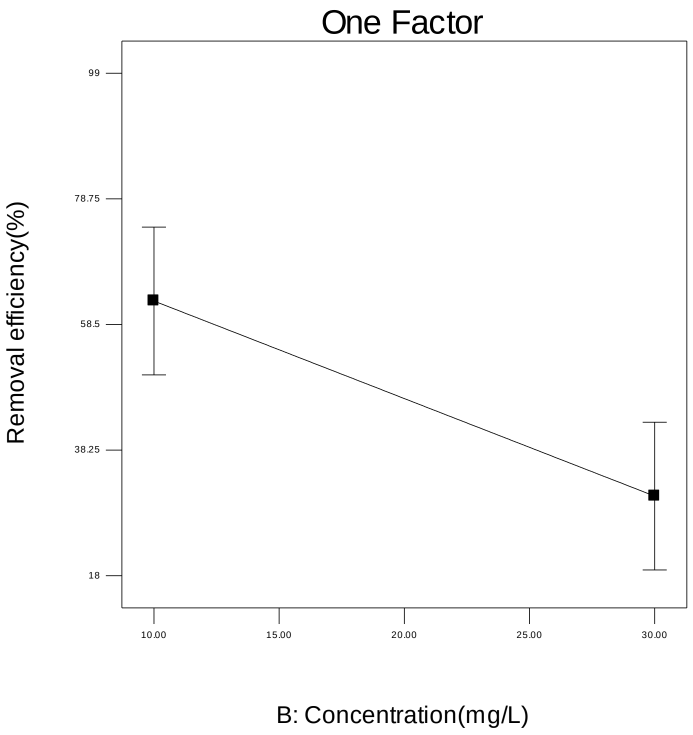

Figure 16: Effect of dye concentration on MB decolorization

4.6.3. UV irradiation time

The effect of irradiation time on photodegradation of MB dye was investigated under UV light. As shown from the figure 17, the percentage of photodegradation increase as time increase, this is due to the fact that as time increase the bond between molecules of MB dye becomes weaker and the chromophore part of the molecules breaks down, thus indicating the change in colour of the MB dye solution. The maximum degradation efficiency occurred at 180 min.

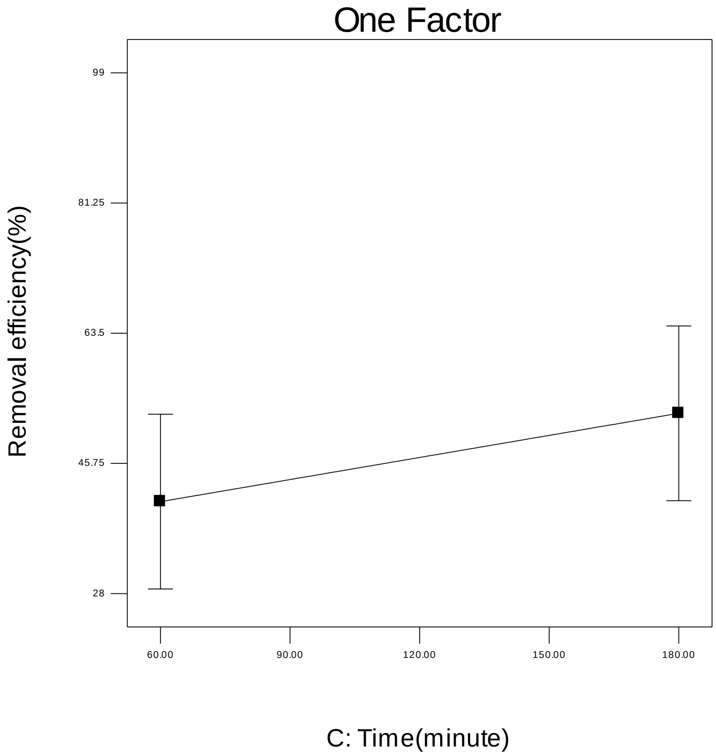

Figure 17: Effect of UV irradiation time on MB decolorization

3D- plot Interaction effects

The interaction effects of dye concentration, and dosage of catalyst at a time as seen from Figure 18, shows as the mount of dose of catalyst increase percentage removal increases, whereas an increase in dye concentration the removal efficiency decreases. This is due to the fact that the amount of photocatalyst active site available is high to absorb the dye at high dose of catalyst and results maximum in removal efficiency at maximum dosage, and minimum Removal efficiency at maximum dye concentration due to less in number of active site to adsorb the dye concentration.

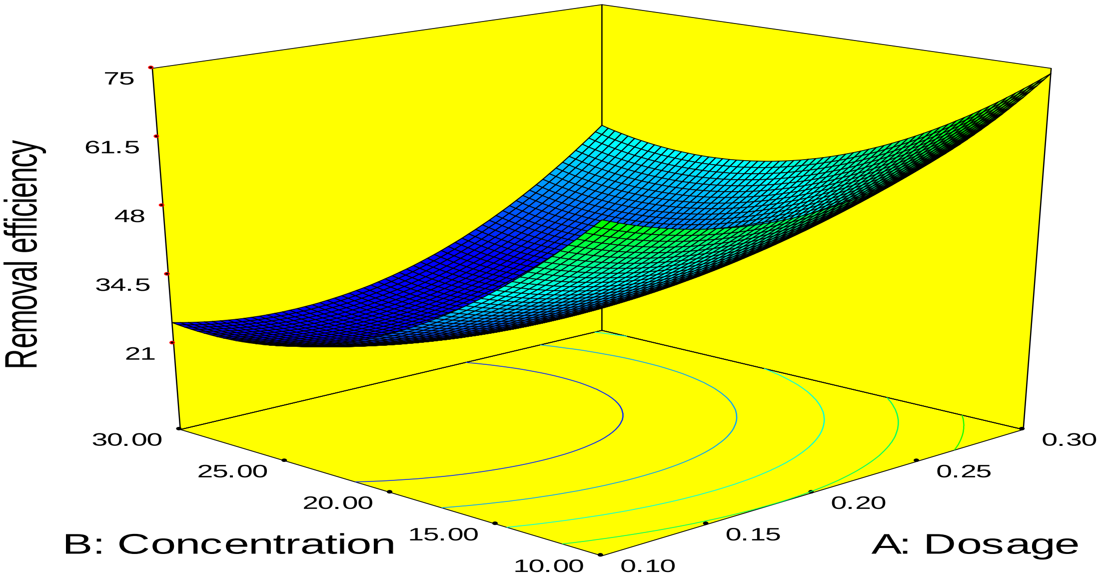

Figure 18: 3D plot showing the interaction effect of dosage of catalyst and pollutant concentration

On the other hand, from Figure 19, an increase in UV irradiation time and dosage of catalyst at a time will results maximum removal efficiency, this because of the longer in the duration of UV irradiation time results to break the molecules of dye and the reason from figure 18 and the maximum is found at their minimum interaction values. The interaction effect of concentration of pollutant and UV irradiation time is as a result the reasons described in Figure 18, for the dye concentration and Figure 19, for UV irradiation time.

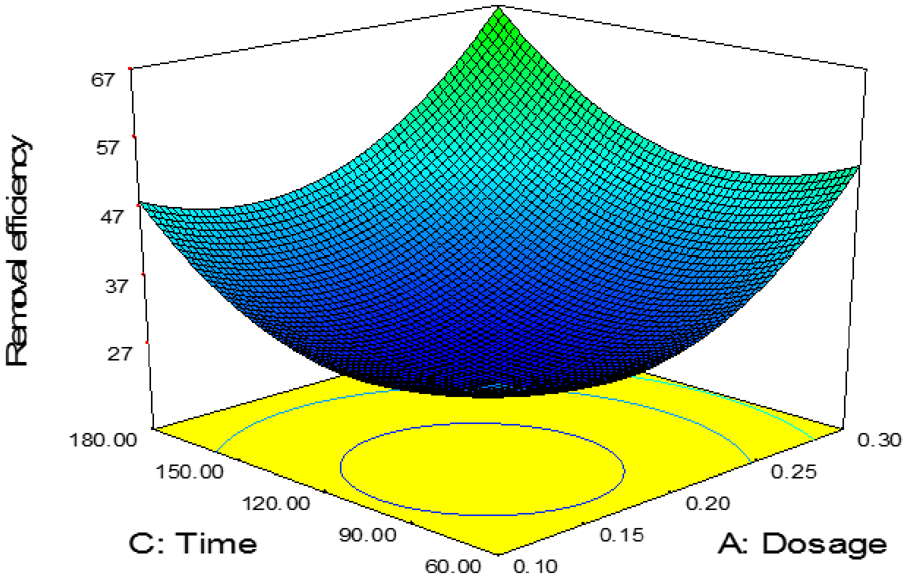

Figure 19 : Three-dimensional response plot showing the interaction effect of dosage of catalyst and UV irradiation time on removal eff

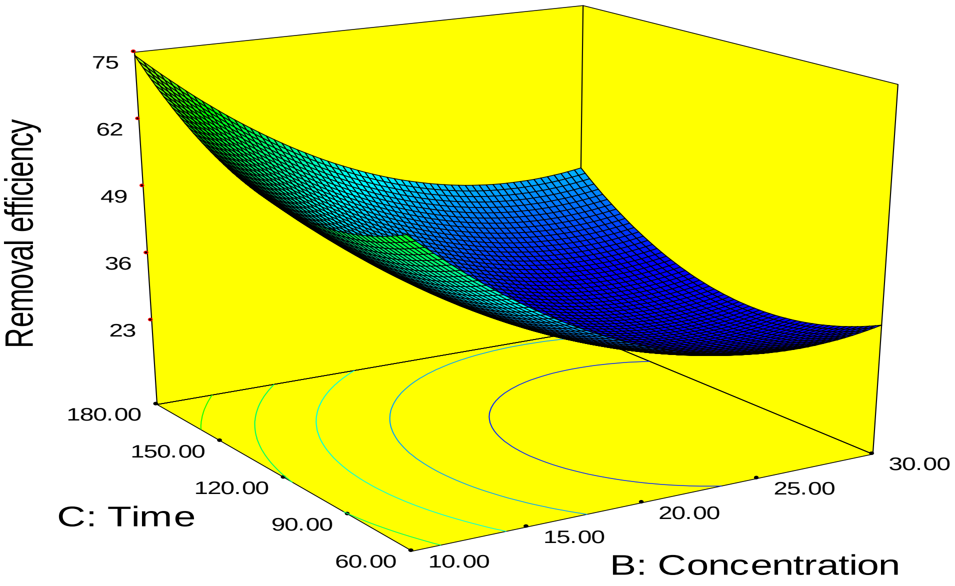

Figure 20 : Three-dimensional response plots showing interaction effect of the concentration and Uv irradiation time on removal efficiency of methylene blue

4.7. Optimization of the Model

The decolorization efficiency of MB can be optimized by manipulating the process parameters like dosage of catalyst, concentration of pollutant and UV irradiation time which have an effect on the degradation of dye. Though, it is difficult to find the optimum point for the response, due to the interaction and imprecise effect of the parameters, a function of desirability was applied using design expert software version 7 numerical optimization. Numerical optimization presents a complete advanced explanation of the most effective mothed in process optimization. The upper and lower limit values of each parameter and its response are predicted by the model depending on the choice of goal. The ultimate goal of this optimization was to obtain the maximum response (decolorization efficiency) that simultaneously satisfies all the variables at their desired levels or values. Thus, based on the values and constraints of parameters in the Table 11, a maximum removal efficiency of 94.89% was obtained with desirability of 0.94.

Table 11: Numerical optimization criteria for decolorization efficiency of MB

Constraint	Goal	Lower value	Upper value
Dosage	In range	0.1	0.3
Concentration	In range	10	30
Time	In range	60	180

4.8. Kinetics

The control experiments were carried out to show that the photocatalysis has took place in the presence of both light and catalyst. Thus, the effect of the presence of light and Titanium dioxide photocatalysts on the photocatalytic degradation of methylene blue was carried out with initial MB concentration of 10 mg/L and catalyst loading of 0.1 gram. The dark run was also carried out with the presence of catalyst but without light irradiation to determine adsorption desorption equilibrium point.

In this experimental condition, the photodegradation rate and rate constant of the degradation of MB using TiO_2 nanoparticles were investigated. As shown from Figure 21, the relationship between time and ln (co/c) is of good linearity, so the degradation of MB exhibits first order kinetics, fitting well with the classic Langmuir-Hinshelwood (LH) model. In this model, the reaction of degradation follows a rate determining step where an adsorbed molecule reacts with a reactive transient such as a hydroxyl radical formed on the surface by oxidation of H_2O or a surface OH group.

Thus, applying the Hinshelwood (LH) model:

$$\ln\left(\frac{Co}{C}\right) = Kapp\ x\ t \qquad (4.8)$$

The following graph is generated at every instant of time for the photodegradation.

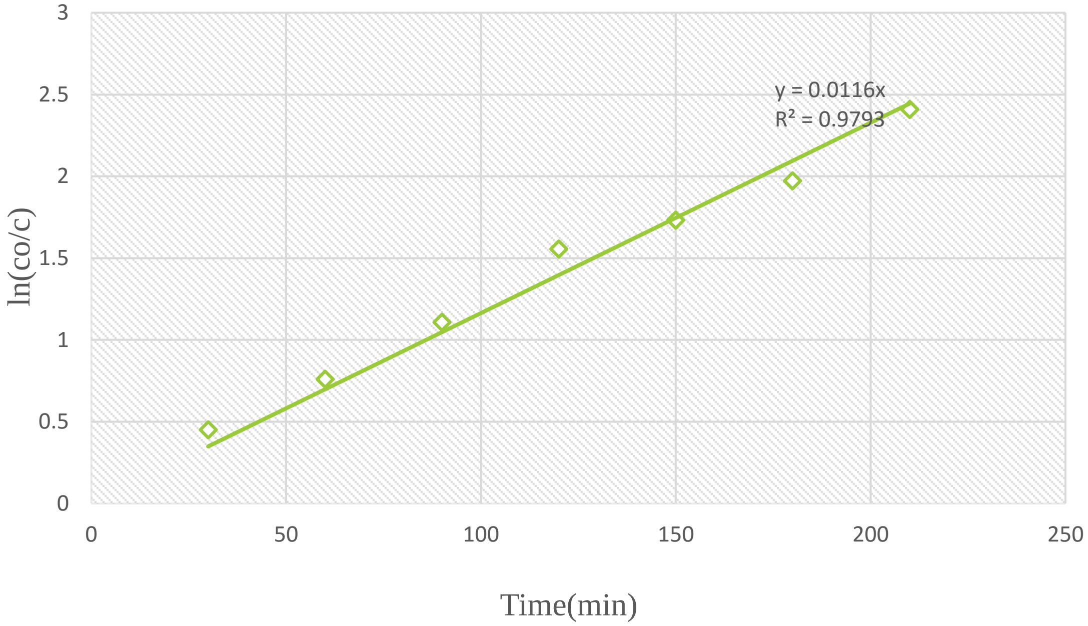

Figure 21: Pseudo-first order of the reaction rate in photocatalytic reaction, Co at 10 ppm

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Photocatalysis by using nanoparticles of titanium dioxide in conjunction with UV-light has been widely studied on lab scale by the researchers for decontamination of drinking water. In this study photodegradetion of methylene blue using titanium dioxide photocatalyst was investigated and optimized by applying surface response methodology. One of the major advantages of this technology (AOP) lies in its capability almost completely mineralize the pollutants into harmless compounds (carbon dioxide and water) without producing any other waste streams to the environment. The optimization of operational parameters for photodegradation of MB dye were investigated using CCD Response surface methodology. Under optimized process conditions MB decolorization efficiency of 94.89% where predicted.

Furthermore, the physiochemical characteristics of the catalyst was investigated, and the result indicates that the photocatalyst have the specific surface area 55.6 m^2/g and pore size of 9.78 nm based on BET and BJH methods respectively. The XRD analysis indicates that 100% anatase composition and crystallite size of 39.3 nm. In addition to this, the effect of different process parameters were studied, the result indicates that the photodegradation of MB is highly affected by three selected parameters, i.e., dosage of catalyst, concentration of pollutant and UV irradiation time.

5.2. Recommendations

Ultra violet light activated titanium dioxide for decolorization of MB is an important research issue. Considering the results obtained in this thesis work, the following recommendations are suggested for future investigation(study).

- In this study, heterogeneous photocatalyst (commercial Titanium dioxide nanoparticles) with specific surface area and crystallite size (55.64 m^2/g and 39.3 nm) has been shown an effective method to degrade organic dyes (MB). Thus, for future investigation, synthesized titanium dioxide instead of UV light activated commercial titanium dioxide Nano photocatalysts should be consider to study their effect on photodegradation.
- The Current study focuses on the effects of operating parameters such as initial substrate(dye) concentration, catalyst loading and UV irradiation time has been shown significantly affected the photocatalytic degradation. However, the effects of light intensity, PH, the existence of oxidizing agents and air flow rate were not yet evaluated on this aspect. Thus, a systematic study should be carried out to study these effects on degradation of dye.
- Total organic carbon concentration of degraded dye pollutants should also be examined to study the mineralization efficiency of the photocatalyst.
- The economic feasibility and practical application of the photocatalyst needs further investigation.

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ANNEXES

The beer Lamber law for determination of concentration of A given pollutant whose abs is known:

$$C = \frac{A - intercept}{Slope} \qquad (3)$$

Where A is the intercept for standard calibration plot of MB.

C is the concentration of unknown pollutant(MB)

Slope and intercepts are from standard calibration plot as shown from the fig below.