TREATMENT OF METHYLENE BLUE WASTE WATER USING SILVER-DOPED TITANIUMDIOXIDE ILLUMINATED BY FLOURESCENT LIGHT

BY

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DECLARATION

This is my original work and has not been presented for a degree in any other University.

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DEDICATION

To my parents Mr. and Mrs. Eliaph Chemai, my wife Winny Soy, my sons; Renny,

Roy and Ryan. To all my brothers and sisters. Your support has been priceless.

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ABSTRACT

Textile industries produce large amounts of wastewater due to high consumption of water in the dyeing and finishing operations. At the present time, great efforts are being expended to minimize the quantity and toxicity of industrial effluents. Methylene blue is the most common among all other dyes in its category. Apart from being a textile dye, it is also used in the lab as an indicator, for staining in bacteriology and as an antiseptic. The color that remain in the unexhausted dye effluent cause disturbance to the ecological system. It can also cause health problems to humans when ingested including diarrhea, gastritis, mental confusion, increased heart rate among others. Thus removal of methylene blue from waste water has become a major environmental concern. The objective of this study was to investigate the use of silver-doped titanium dioxide catalyst in the photo-degradation of methylene blue waste water using fluorescent light. The effect of initial pH and catalyst dosage were investigated at the optimum conditions. It was found that alkaline medium favored the adsorption of the dye onto the catalyst surface. Increase in catalyst dosage led to an increase in degradation rate but dropped when the optimum catalyst dosage was exceeded. Minitab statistical tool was used to design the experiments based on the central composite design. Sol-gel acid catalyzed method was used to prepare the catalyst. The absorbance of the samples was measured using a UV spectrophotometer and percentage degradation determined. A fully quadratic regression equation that related the variables and the response was developed. The two way variable interactions of the regression model were discussed. At these conditions, the percentage degradation was found to be 90% with the chemical oxygen demand (COD) reduction of 95.5% indicating complete mineralization of the dye. The colour index was found to be 37 platinum cobalt units after degradation which is within the required Environmental water discharge standards. When pure (undoped) catalyst was used under the same light intensity, the percentage degradation was found to be 16% indicating that doping the catalyst with silver enhanced its excitation by fluorescent light. Kinetic studies indicate that the reaction process is a first order and follow Langmuir-Hinshelwood adsorption kinetics which means that the rate of reaction is controlled by the reaction of adsorbed molecules on the catalyst surface. The catalyst was reused three times without appreciable loss of its catalytic activity. More research need to be done on doped titanium dioxide catalyst immobilized on a surface used in the treatment of textile dyes because it can be more economical in terms of catalyst recovery. Pilot plant design and process development should be done before actual full scale implementation.

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CHAPTER ONE

1.0 INTRODUCTION

Textile dyes are potentially toxic because of their low removal rate and if untreated would cause long-term health concerns (Gomes and Cfaria, 2003). As the worlds population continues to grow, demand for clean and safe water has risen simultaneously. Therefore a lot of efforts has been made to meet this ever rising demand. This means that waste waters from industry and domestic sources requires recycling and treatment. Wastewaters emitted from industry (textile dyes and other industrial dye stuffs) represent a fraction of an increasing enviromental danger. Estimates indicate that approximately 15–20% of the synthetic textile dyes used is lost in wastewater streams during manufacturing or processing operations (Harikumar et al., 2013). For this reason, a lot of effort is being put in removing these dyes and other commercial colorants.

The clean-up of these chemicals from water has been a complex problem because of the non-biodegradable nature of some of the dyes as well as due to the presence of toxic chemical elements, heavy metals and carcinogenic aromatic amines in the dye effluent. In addition to the effluent, gaseous emissions such as sulfur dioxide, nitrogenous gases and ammonia are emitted. Solid wastes in the form of sludge, gypsum and sludge from treatment facilities are also generated. Dye stuffs are highly structured compounds and are difficult to break down biologically (Faisal et al., 2007 and Shibata et al., 2006).

Since textile waste water has posed environmental and health concerns, it has received increased attention in terms of removal of its dye pollutants. Physical

techniques such as adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents amongst others, can be used efficiently (Karthik et al., 2014). Most of these conventional methods are either not very effective or not environmentally compatible. Titanium dioxide semiconductor photo catalytic system is one of the most attractive means of treating dye waste water than many other conventional chemical oxidation methods. Titanium dioxide in anatase form is the most practical for photo-catalytic enviroment applications such as water purification, wastewater treatment and water disinfections. It is biologically inert and chemically stable with respect to photocorrosion and chemical corrosion and it is also inexpensive. Its disadvantage however, is that it has too high band gap energy of about 3.2 eV that enables it to absorb only UV light with wavelength lower that 388 nm thus reducing the solar harvesting efficiency down to 5 % (Giuseppe et al., 2017).

Modification of Titanium dioxide photo catalysts is therefore necessary to improve on the pollutant degradation using visible light. Doping of titanium dioxide helps to extend the range of its excitation energy to the visible region. Using titanium dioxide catalyst in powder form give increased photocatalytic activity due to increased surface area. This study investigated the use of silver-doped titanium dioxide catalyst in the photo degradation process of methylene blue textile waste water.

1.1 PROBLEM STATEMENT

Textile effluents are considered very complex since they contain salt, surfactants, metal ions and their metal complexes, toxic organic chemicals, biocides and toxic anions. Dyes and their precursors are well-known for high toxicity and suspected to be human carcinogens as they form toxic aromatic amines (Gomes and Cfaria, 2003).

These dyes are difficult to break down biologically due to the complex nature of their chemical structures. Photo catalytic treatment of waste water using titanium dioxide catalyst therefore can provide a viable solution to this problem. The limitation of titanium dioxide lies in the fact that it can only absorb UV light due to its high band gap energy and therefore cannot be sensitized by visible light.

1.2 JUSTIFICATION OF THE STUDY

As the world population continues to grow, demand for clean and safe water has risen simultaneously. Waste water released from textile industries pollute water bodies and pose health concerns to the living organisms. Methylene blue is the most commonly used dye in its category (Meena et al., 2012). It can cause eye injury for both human and animals. On inhalation, it can cause rise to short periods of rapid and difficult breathing. Ingestion can cause nausea, vomiting, diarrhea, gastritis and mental confusion. Therefore it is important to remove methylene blue from waste water before discharge to the water bodies.

The catalysts characterized by semiconductor usually are oxides that can be more appealing than the more conventional chemical oxidation methods because semiconductors are inexpensive, nontoxic, and capable of extended use without substantial loss of photo catalytic activity. Furthermore, semiconductor particles can be recovered by filtration or centrifugation or can be immobilized in a fluidized bed reactor.

The catalyst was doped with silver because it positively influences the photo-catalytic activity by facilitating electron-hole separation. It also possesses strong electron trapping ability (Yang et al., 2008). Doping the catalyst helps to extend its range of

excitation energies to the visible region in order to avoid the use of UV light which is more expensive source of energy. In this study silver was used to dope titanium dioxide so that the catalyst could be illuminated by fluorescent light during the degradation process. The photo catalysts have been much studied because they are largely available, inexpensive, non-toxic, show relatively high chemical stability and may lead to total mineralization of the dye to CO_2, water and mineral acids.

1.3 OBJECTIVES

1.3.1 Overall Objective

The overall objective of the study was to degrade methylene blue waste water using silver-doped titanium dioxide catalyst illuminated by fluorescent light.

1.3.2 Specific Objectives

The study was done to meet the following specific objectives;

i. To develop a mathematical model that depicts the photo degradation of methylene blue waste water catalyzed by silver-doped titanium dioxide catalyst.

ii. To determine the optimum reaction conditions and investigate the effect of initial pH and catalyst dosage on the photo degradation of methylene blue waste water.

iii. To determine the extent with which silver-doped titanium dioxide catalyst can be re-used in the treatment of methylene blue waste water.

iv. To study the parametric and kinetic models depicted by the photo degradation process.

1.4 SCOPE OF THE STUDY

The study will be confined to the following areas;

i) Treatment of simulated methylene blue waste water using silver-doped titanium dioxide catalyst.

ii) Formulation of parameters that enable for optimum conditions for methylene blue waste water treatment using the silver doped titanium dioxide catalyst.

1.5 LIMITATIONS OF THE STUDY

i) Laboratory experiments may not predict the actual large scale situation.

ii) Equipment unavailability limited the scope of the study.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Dyes are extensively used in the textile industry. Decolourization of effluent from textile dyeing and printing industry was regarded important, because of aesthetic and environmental concerns (Sarayu and Kanmani, 2003). The removal of colour from wastewater is often more important than the removal of other organic colorless chemicals (Grzechulska and Morawski, 2002). Due to high concentration of organics in the effluents and higher stability of modern synthetic dyes, their discharges into rivers are harmful to aquatic life (Acosta et al., 2005). Thus there is an urgency of finding a potential advanced treatment process, which could be an economic and effective process of treating colored wastewater completely.

Methylene blue is one of the most commonly used dye in the industry. It can be used for the following purposes:

- Dyeing of fabric

- Staining in bacteriology

- Oxidation-reduction indicator

- Antidote to cyanide poisoning

- Antiseptic

It has the chemical formula, $C_{16}H_{18}ClN_3S$ with a molecular weight of 319.85. 1g dissolve in 25ml of water and its peak absorption is at wavelength of about 609nm and 668nm.

2.2 TREATMENT OF TEXTILE WASTE WATER

Semiconductor photo-catalysis is an attractive treatment for industrial wastewater. It can be defined as the reaction in which the decomposition of organic substances in an aqueous solution takes place by means of a semiconductor in the presence of light. Semiconductors are used to degrade the organic pollutant in water to less harmful materials (Fang et al., 2005). TiO_2 and ZnO have photo-catalytic properties to be promising substrate for photo-degradation of water pollutants and show appropriate activity in the range of solar radiation (Hussein and Alkhateeb, 2007). The overall benefit treating of industrial textile wastewater include saving huge amount of water because textile dyeing are regarded as chemical and water intensive.

Textile dyes can be degraded using either of the following methods;

- Photo degradation using semiconductor photo catalysts.

- Treatment using oxidation processes.

- Treatment using electrochemical techniques.

- Treatment based on biological processes.

- Treatment by adsorption processes.

2.2.1 Photo-Degradation of Dyes Using Titanium Dioxide

Titanium dioxide as a semi-conductor has been successfully used as a photo-catalyst for oxidative degradation of organic compounds including dyes. Pure titanium dioxide is not common in nature and it is derived from illmenite or leucoxene ores. These ores are the principal raw materials used in the manufacture of titanium dioxide pigment. The pigment is produced either by the sulphate process, which uses sulfuric acid or

the chloride process, which uses chlorine. Figure 2.1 shows different crystalline forms of titanium dioxide
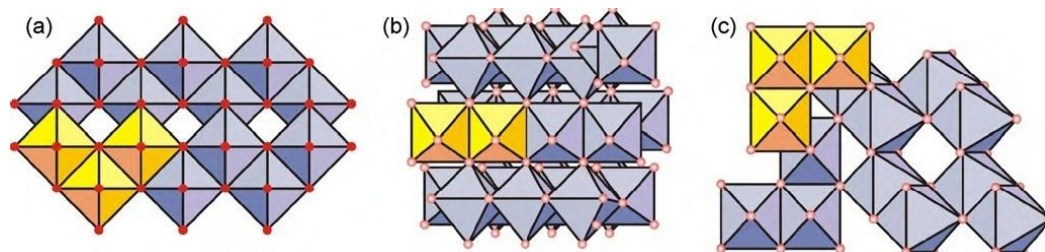
(a) Anatase, (b) Brookite and (c) Rutile (Khataee and Kasiri 2010).

Figure 2.1: Crystalline structures of titanium dioxide

TiO_2 has many properties, such as transparency to visible light, high refractive index and a low absorption coefficient. Anatase and rutile are the two principle polymorphs of TiO_2 associated with energy band gap energies of 3.2 and 3.1 eV, respectively. Comparatively, the photo-degradation reaction rate is more rapid on anatase than any other form. The reaction rate is affected by the crystalline state and textural properties such as surface area and particle size of TiO_2 powder. Some of these factors are correlated. For instance high degree of crystallinity is achieved through a high-temperature thermal treatment leading to a reduction in the surface area (Khataee A.R and Kasiri M. B, 2010).

Photo-catalytic activity of TiO_2 is affected by its crystal structure. Amorphous TiO_2 for instance displays little photo-catalytic activity because of the presence of non-bridging oxygen atoms in the bulk of TiO_2. The defective Ti–O atomic arrangement act as recombination centers of the generated electron–hole pairs and inhibit the photo-degradation rate (Khataee and Kasiri, 2010). The photo-catalytic performance

of TiO₂ also depends on its surface properties. The larger the surface area per unit mass, the higher the photo-catalytic activity.

Figure 2.2 illustrates that, when TiO₂ is illuminated with UV light (frequency< 390 nm), an electron excites out of its energy level in the valence band and leaves a hole. If there are defects on the catalyst structure, recombination (electrons attaching back to valence band) occur. Recombination can also occur if the irradiation source lacks sufficient energy to maintain the electrons at the conduction band.

UV irradiation
Frequency < 390nm
Conduction band (e⁻)
Hydroxyl radicals
Recombination
Valence band (h⁺)
Hydroxyl radicals
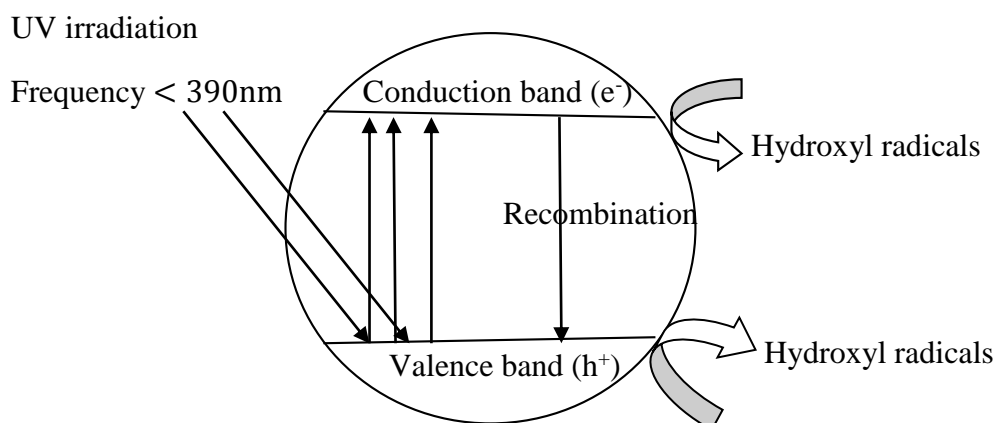
Figure 2.2: General mechanism of photo-catalysis on TiO₂

Electrons are promoted from the valence band to the conduction band of TiO₂ to give electron–hole pairs as shown by equation 2.1:

$$TiO_2 + hv(\lambda < 390nm) \rightarrow e^- + h^+ \ldots\ldots. \text{equation } 2.1$$
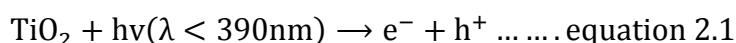
The valence band (h+) potential is positive enough to generate hydroxyl radicals (•OH) at the surface of TiO₂ and the conduction band (e−) potential is negative enough to reduce molecular oxygen as shown in the following equations:

$$e^- + O_{2(ads)}{}^+ \rightarrow{}^\bullet O_{2(ads)}{}^- \ldots\ldots.. \text{equation } 2.2$$

$$e^- + H_{(ads)}{}^+ \rightarrow {}^*H_{(ads)} \ldots \ldots \text{equation 2.3}$$

$$h^+ + OH_{(ads)}{}^- \rightarrow {}^\bullet OH_{(ads)} (\text{ in alkaline solutions}) \ldots \ldots . \text{equation 2.4}$$

$$h_V{}^+ + H_2O_{(ads)} \rightarrow H^+ + {}^\bullet OH_{(ads)} (\text{ in neutral solutions}) \ldots \ldots \ldots \text{equation 2.5}$$
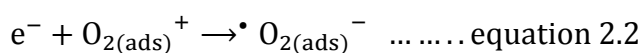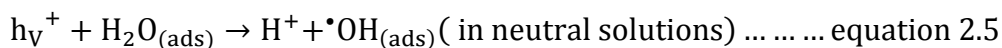
The hydroxyl radical is an oxidizing agent which reacts with the organic matters present at the surface of the catalyst to produce harmless chemical species like CO_2, H_2O and mineral acids (Khataee and Kasiri, 2010). The decomposition can be explained through the following reactions (Daneshvar et al., 2003);

$$h_{VB}{}^+ + \text{Organic Matter} \rightarrow \text{Organic Matter}^{\bullet+} \rightarrow (\text{ oxidation of Organic matter})$$

$${}^*OH_{(ads)} + \text{Organic Matter} \longrightarrow CO_2 + H_2O + \text{Mineral acids}$$
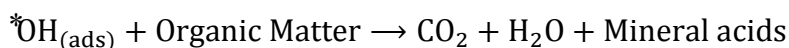
TiO_2 in anatase form is the most practical for photo-catalytic environment applications such as water purification, wastewater treatment and water disinfections. It is biologically inert and chemically, stable with respect to photocorrosion and chemical corrosion and it is also inexpensive. Its disadvantage however, is that it has too high band gap energy (about 3.2 eV) that enables it only to absorb UV light with wavelength lower than 388 nm thus reducing the solar harvesting efficiency down to 5 % (Giuseppe et al., 2017). There have been many efforts to make a TiO_2 photo catalyst that would be sensitive to visible light illumination.

Dye sensitization

Dye sensitization is one of the techniques used to make the catalyst respond to visible light. The mechanism of dye sensitization and mineralization of the dye is described by the following equations (Anila et al., 2014):

$$\text{Dye} + h_V \rightarrow \text{Dye}^\star \ldots \ldots \ldots \ldots . \text{equation 2.6}$$

$$Dye + TiO_2 \rightarrow Dye^* + TiO_2(e) \ldots \ldots \ldots. \text{ equation 2.7}$$

$$TiO_2(e) + O_2{}^{*-} + 2H^+ \rightarrow H_2O_2 \ldots \ldots \ldots \ldots \text{ equation 2.8}$$

$$H_2O_2 + TiO_2(e) \rightarrow {}^*OH + OH^- \ldots \ldots \ldots \ldots.. \text{ equation 2.9}$$

$$Dye^{*+} + O_2\left(or\ O_2{}^{*-}or\ {}^*OH\right) \rightarrow \text{peroxylated or hydroxylated intermediates}$$
$$\rightarrow \text{mineralized products} \ldots \ldots \ldots \ldots. \text{ equation 2.10}$$
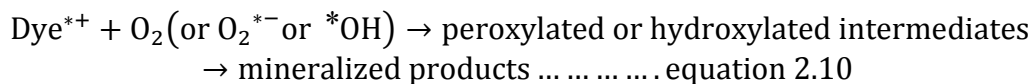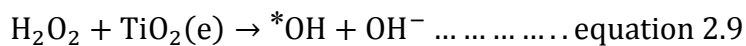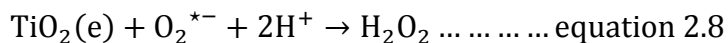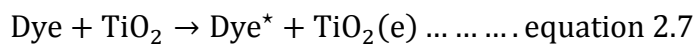
The dye is excited by visible light from the ground state (dye) to form an oxidized dye radical (dye*). This oxidized dye radical is also produced when the dye comes into contact with the catalyst forming catalyst anion. It forms hydrogen peroxide when it comes into contact with superoxide radical anions $(O_2{}^{*-})$. Superoxide radical anions are form from the reaction of dissolved oxygen with trapped electrons which eventually form hydroxyl radicals (*OH). The excited state of the dye is further converted into semi-oxidized radical cation (Dye^{*+}) by electron injection into the conduction band of the catalyst. The dye in this state then reacts with dissolved oxygen or superoxide radical ions or hydroxyl radicals to form mineralized products.

Ashraful et al., (2017) studied photocatalytic degradation of orange II and methyl orange dyes using dye sensitization technique. TiO_2 and ZnO were used as catalysts under fluorescent light irradiation. Degradation of Orange II and Methyl orange was 61% and 24% respectively on TiO_2 and 57% and 28% respectively on ZnO. They found that degradation of the dyes increased significantly when fluorescent irradiation was used. The challenge though with dye sensitization technique is that the reacting mixture must be freed from oxygen as far as possible because oxygen superoxide radical formed eventually degrade the sensitizing dyes causing inactivation of the catalytic system (Debabratar et al., 2008).

Coupling of titanium dioxide

Coupling TiO_2 with another material with lower band gap can help bring the catalyst's excitation energy to the visible region. Haimei et al., (2006) developed a photo-assisted sol-gel method to prepare a binary TiO_2-Ti_2O_3 photo-catalyst which exhibits a photo-catalyst activity under visible light illumination. They used it in the decomposition of organic dye pollutants and small molecules. Titanium III oxide (Ti_2O_3) has a narrow band gap and its energy level is located between the conduction band and valence band of TiO_2. An electron may be excited to the energy level of Ti_2O_3 from the valence band of TiO_2 or to the conduction band of TiO_2 from the energy level of Ti_2O_3 when excited by visible light. From the study, the prepared photo-catalyst showed extended response to visible light in the degradation of organic pollutants and environmental wastewaters under sunlight irradiation.

Doping of titanium dioxide

Doping is a process of introducing an element into the crystal lattice of a semiconductor in order to modify its electronic properties altering the absorption spectra of the catalyst into the visible region. Doping the catalyst decreases the energy required for electron transition from the valence band to the conduction band causing more photo-generated carriers to participate in dye degradation reactions (Xia et al., 2010). Doping can be done using alkaline metals, transition metals, earth alkaline metals, rare earth metals and noble metals. A lot of research has been done to investigate the effect of some elements used as dopants on photocatalytic activity of TiO_2.

Ayebe et al., (2017) investigated photo catalysis of basic black II dye using titanium dioxide doped with Zinc. Results obtained indicated that 99.92% of the dye was degraded under visible light irradiation when 1% $Zn-TiO_2$ was used. Avasarala et al., (2016) researched on degradation of methyl orange dye using TiO_2 doped with magnesium under visible light. It was concluded that doped catalyst exhibited better photocatalytic properties compared to undoped catalyst.

The methods used to dope the catalyst can affect their performance when excited using visible light. The methods used to prepare the catalyst include oxidation, vapor deposition, hydrolysis, hydrothermal oxidation, Mechanical alloying, co-precipitation, impregnation and sol-gel. For instance, Saepurahman et al., (2010) investigated photo-catalytic activity of TiO_2 doped with Tungsten trioxide (WO_3) prepared using impregnation method for degradation of methylene blue waste water. It was found that preparing the catalyst using this method did not shift the absorption spectrum of TiO_2 into the visible region.

Wen et al., (2006) prepared the TiO_2 catalyst doped with Lanthanum (La) using the sol-gel method and calcined it at different temperatures. For comparison, pure TiO_2 was prepared without doping using the same procedure. It was shown that the La-doped TiO_2 particles have higher photo-catalytic activity for the degradation of dyes than pure TiO_2. It was found that the La-doping suppresses the formation of any impurity phase and prevents phase transition of anatase to rutile. It was also noted that inappropriate amount of La doping may slow the radiative recombination process of photo-generated electrons and holes in TiO_2. This was attributed to the introduction of new defect sites (recombination centers) that enhance the recombination of photo-

generated electrons and holes. The amount of dopant used must therefore be carefully optimized in order to avoid forming stable insulators (Luminita et al., 2009). Another setback in doping technique is that some dopants have limited long term instability, low reactivity and low quantum efficiency. To address this, two elements can be co-doped into the catalyst crystal structure. Tao et al., (2010) studied the kinetics of photo-catalytic activity of cerium and nitrogen co-doped TiO_2 nanoparticles. It was found that the synergistic effect of co-doping effectively inhibited the recombination of photo-generated electrons and holes compared to when it was doped with nitrogen alone.

Catalyst Immobilization

The use of TiO_2 powder has been widely accepted because of its large surface area of contact. A lot of energy is however used to keep the catalyst in suspension and separation of the catalyst after effluent treatment is difficult. Many researchers have devoted their efforts to investigate the possibility of immobilizing the catalyst on a support for ease of separation. Zulkarnain et al., (2005) investigated the removal of Methyl Orange dye using immobilized titanium dioxide illuminated by fluorescent lamps. The catalyst was prepared by the sol-gel method and immobilized on glass plates. It was found that when photo-degradation experiments were carried out under illumination of light, total removal of pollutants was enhanced significantly. Immobilizing the catalyst helped reduce catalyst loss. However, it was found that many intermediates were produced during the course of the photo-degradation process which required prolonged reaction time.

Boualem et al., (2009) noted that the photo-activity of supported materials is not as observed with TiO_2 powder dispersion mainly because of saturation of active sites on TiO_2 particles. In order to solve this problem, photo-catalytic degradation of solophenyl red dye using TiO_2-Pillared montmorillonite as a photo-catalyst was studied. They noted that the main primary step is the adsorption of organic substrate on the support during the equilibrium step followed by an electronic transfer of electrons from the conduction band of TiO_2 toward the substrate to the holes of the valence band of TiO_2 occurring during the illumination step. TiO_2 pillars within the montmorillonite are easily accessible by dye molecules because they are at the photo-catalyst surface. It was found that for the same amount of TiO_2, apparent rate constants were higher with pure TiO_2 than with TiO_2 on montmorillonite. It was noted that the higher the content of the catalyst in dispersion, the bigger the gap between the degradation rate constants of the dye. This was attributed to competitive adsorption of the dye between TiO_2 pillars and montmorillonite, which decreased the probability for dye molecules to be close to the active sites of hydroxyl radicals production. It was concluded that TiO_2-pillared montmorillonite was more convenient for recovery than TiO_2 powder. Immobilizing the catalyst on montmorillonite improved the catalyst activity by increasing the active sites available for adsorption of the dye.

It has been observed that the immobilized TiO_2 is easily separable but suffers from very low surface areas and difficult distribution inside a photo-reactor which limits its activity. In order to remedy this shortcoming, some group of researchers developed TiO_2 supported on magnetic powder because of its sufficient surface area along with magnetic core which facilitates separation after the treatment using a magnetic separator. Tarek et al., (2009) studied the treatment of synthetic dyes waste water

utilizing a magnetically separable photo-catalyst $TiO_2/SiO_2/Fe_3O_4$ (TSF). Three commercial dyes, Remazole golden yellow G, Remazole brilliant blue R and reactive orange 16 were mixed and treated with the catalyst. Parametric and kinetic models governing the photo-catalyst activity were studied. Photo-catalytic reaction rate was seen to be described by the Langmuir-Hinshelwood (L-H) kinetic model modified to accommodate reactions occurring at a solid-liquid interface. It was found though that the L-H model could not be applied at very high dye concentration and low pH value because of limited light transmittance inside the photo-reactor. Acidic conditions favored adsorption of the anionic dyes on catalyst surface attributed to high electron density of benzene rings present in the dyes. It was concluded that the TSF photo-catalyst could be used several times with nearly the same efficiency and helped tremendously in catalyst recovery through magnetic means.

Another group of researchers, (Feng et al., 2000) compared the catalytic activity of pure TiO_2 (T), TiO_2 and Fe_2O_3 (T+F), TiO_2-SiO_2-Fe_2O_3 (TSF), TiO_2-Fe_2O_3 (TF) and pure Fe_2O_3 (F) under visible and UV irradiation. Photo-degradation rates on the photo-catalysts followed the order; T> T+F>TSF> TF>F. It was reported that the photo-catalytic activity of TF catalyst decreased because electrons and the holes were seized by the Fe_2O_3 conglomeration. As for the TSF photo-catalyst, it was found that SiO_2 membrane decreases the Fe_2O_3 conglomeration influence because SiO_2 membrane prevents the injection of charges from TiO_2 particles to Fe_2O_3 conglomeration to some extent. No particles were detected in the degraded solution after the TSF photo-catalyst had been separated by a magnetic field. When the

catalyst was reused, it was found to be effective and the reproducibility of photo-catalytic activity was good.

2.2.2 Factors Affecting Photocatalytic Degradation of Textile Waste Water

Effect of pH

The pH of textile waste water is very important in the process of photo-catalysis. It influences the adsorption of the organic molecules onto the catalyst and its surface charge. The TiO_2 surface is positively charged in acidic media whereas it is negatively charged under alkaline conditions (Gnanaprakasam et al., 2015). It is therefore expected that there will be increased adsorption of cationic dyes at alkaline conditions and anionic dyes at acidic conditions. The positive holes are considered as the major oxidation species at acidic conditions whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels. In alkaline solutions hydroxyl radicals are generated by oxidizing more hydroxide ions available on TiO_2 surfaces (Faisal et al., 2007). TiO_2 particles tend to agglomerate at low pH which leads to a decrease in the surface area available for dye adsorption and photon absorption (Attia et al., 2008). Therefore pH plays an important role both in characteristics of textile waters and in the reaction mechanisms and has to be taken into consideration in photocatalytic degradation of textile waste water.

Effect of mass of catalyst

Photo-catalysts dosage added to the reaction vessel is a major parameter affecting the photo-catalytic degradation efficiency (Dong et al., 2010). Photo-catalytic degradation efficiency increases with an increase in catalysts mass. This is brought by an increase

in the amount of active sites available on the catalyst surface. This result in an increase in the number of dye molecule adsorbed on to the catalyst surface leading to an increase in the degradation rate (Kim and Lee, 2010).

Increasing the mass of the catalysts increases the amount of hydroxyl radicals produced from light irradiation. At low catalyst loading, more light is transmitted into the reactor and little of this light is utilized for the reaction process. Beyond an optimum catalyst loading, degradation rate reduces due to increased opacity of the catalyst suspension inside the reactor thereby affecting efficient utilization of light. Infiltration depth of the photons produced diminishes and reduces the amount the catalyst being activated (Gnanaprakasam et al., 2015). Deactivation of activated photo-catalyst molecules colliding with ground state molecules due to increased catalyst load may also reduce photo-catalyst activity (Kim and Lee, 2010).

Effect of Temperature

Photo-catalytic reactions are not affected by temperature change. Temperature dependent steps in photo-catalytic reaction are adsorption and desorption of reactants and products on the surface of the catalyst. These steps are not rate determining in photocatalytic reactions. Attia et al., (2008) found that the activation energy of photocatalytic reactions of real textile industrial wastewater is about 21 ± 1 kJ/mol on TiO_2 and 24 ± 1 kJ/mol on ZnO. Kim and Lee, (2010) found that the apparent activation energy in photocatalytic reactions is minimal and that the true activation energy is nil. They concluded that these types of reactions can be operated at room temperature. Palmer et al., (2002) observed that the effect of temperature on the photo-catalytic degradation is insignificant in the temperature range of 10^oC to 68^oC.

They observed that high temperatures may have a negative impact on the concentration of dissolved oxygen in the solution and can cause recombination of holes and electrons at the surface of the photo-catalyst. Photocatalytic degradation of textile dyes can be carried out by keeping the temperature range at room conditions.

2.2.3 Treatment of Waste Water Using Oxidation Process

Advanced Oxidation Processes (AOPs) are chemical oxidation processes based on the use of hydroxyl radicals ($\overset{*}{O}H$), powerful oxidizing species. Vilar et al., (2011) investigated the efficiency of real textile waste water by using different systems. These systems includes; Ultra Violet light (UV)/hydrogen peroxide (H_2O_2), UV/TiO_2, UV/TiO_2/H_2O_2, Fenton and solar-photo-Fenton. The use of sunlight irradiation together with H_2O_2 gave the highest degradation efficiency of up to 93% compared to using TiO_2/UV system (36%) although similar mineralization was obtained. It was observed that by using TiO_2/H_2O_2/UV system, an initial reaction rate of more than 10 times was attained compared to UV/H_2O_2 system leading to a faster decolorization and mineralization. It was pointed out that the degradation of dyes in textile wastewaters by UV/H_2O_2 system occur by the generation of hydroxyl radicals through the photolysis of hydrogen peroxide under solar irradiation (Muruganandham and Swaminathan, 2007). It was found that hydrogen peroxide is an effective agent for decolorization because it is able to degrade the dyes' structure into intermediate compounds. The only limitation is that it cannot degrade further the intermediate products into less harmful species like CO_2 and other more oxidized products. Finally, the combination of iron with H_2O_2 and solar radiation (solar-photo-Fenton) was tested. It was observed that combination of catalysts and hydrogen peroxide as an

oxidant (UV/TiO₂/H₂O₂ and photo-Fenton) proved to be more efficient than TiO₂ or H₂O₂ alone with solar irradiation. Solar-photo-Fenton system was found to be the most efficient of all solar AOPs studied, enhancing the biodegradability of the leachate and making possible its combination with biological oxidation processes.

Francisco et al., (2004) studied the combination of hydrogen peroxide as a bleaching agent, and solar or ultraviolet radiation for photochemical degradation of textile dyes without using solid catalyst like titanium, iron or manganese oxides. The photo-degradation mechanisms using H₂O₂ as a bleaching reagent may be quite different from the proposed mechanisms with a solid catalyst like TiO₂. The use of H₂O₂ for inhibiting electron-hole recombination has been useful because they trap the photo-generated electrons more efficiently than oxygen (Cisneros et al., 2002). The proposed mechanism is shown by the following reaction equations:

$$H_2O_2(ads) + 2e^- \rightarrow 2OH \qquad \dots \text{equation 2.11.}$$

$$H_2O_2(ads) + 2h^+ \rightarrow O_2 + 2H^+ \qquad \dots \text{equation 2.12}$$

$$H_2O_2(ads) + h^+ \rightarrow HO_2{}^* + H^+ \qquad \dots \text{equation 2.13}$$

$$H_2O_2(ads) + e^- \rightarrow OH^* + OH^- \qquad \dots \text{equation 2.14}$$
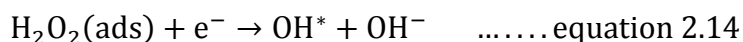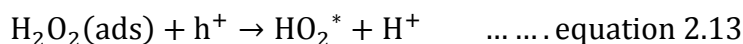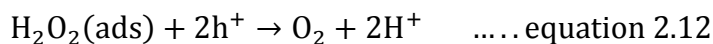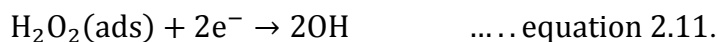
Under short UV light, hydrogen peroxide is rapidly dissociated, producing hydroxyl radicals responsible of breaking down complex dyes structure into intermediate compounds. This is illustrated by the following equations:

$$HO - OH + hv \rightarrow OH^* + OH^- \qquad \dots \dots \dots \text{equation 2.15}$$

$$\text{and } R_1 - N = N - R_2 + OH^* \rightarrow \text{degradation products} \quad \dots \dots \text{equation 2.16}$$
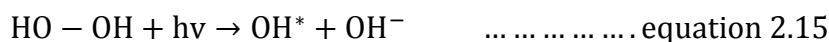
Where the degradation products are: CO_2, NO_3^-, SO_4^{2-} Cl^-, H_2O, and small molecules of aliphatic organic acids (Salem et al., 2014)

This method gave high mineralization and degradation rates on textile waste water. Although less efficient than UV radiation, solar radiation was capable to completely remove the color of the dyes.

Rahman et al., (2009) studied the degradation of Malachite Green dye by Fenton's reagent under xenon beam. The Fenton process uses Fe_2^+ to react with H_2O_2 to generate hydroxyl radicals with powerful oxidizing ability. It was found that Fenton degradation of Malachite Green (MG) dye under xenon beam irradiation was initiated by the photolysis of Fe (III)-hydroxyl species, other than through the electron transfer from the excited dye into ferric species. The mechanism of hydroxyl free radical generation follows the following equations (Nese and Filiz, 2013):

- In the presence of ferrous iron;

$$H_2O_2 + Fe(II) \rightarrow OH^* + OH^- + Fe(III) \qquad \ldots\ldots \text{equation 2.17}$$
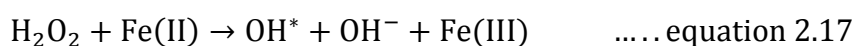
- In the presence of ferric iron;

$$H_2O_2 + Fe(III) \rightarrow HOO^* + H^+ + Fe(II) \qquad \ldots\ldots\ldots \text{equation 2.18}$$

$$2HOO^* \rightarrow 2OH^* + O_2 \qquad \ldots\ldots\ldots\ldots \text{equation 2.19}$$
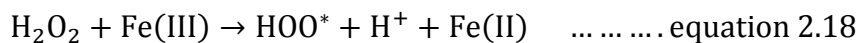
The hydroxyl radicals produced attacks the dye molecules in a similar manner shown by equation 2.16 to produce smaller molecular products. Although hydroxyl radicals are powerful species, Fenton reagent do not reach deep mineralization of organic

pollutants (Ma et al., 2006). Fenton reaction is powerful at initial stages and gradually loses its capability for pollutant degradation with reaction time (Nese and Filiz, 2013).

2.2.4 Chemical and Electrochemical Techniques

Chemical and electrochemical techniques use an electrochemical cell to degrade industrial waste water. The most common technologies are electro-coagulation, electro-oxidation and electro-reduction. Electro-coagulation method is mainly used in removing heavy metals, organic and inorganic pollutants. It involves electrocoagulation processes to produce a coagulated residue which can be separated from the water. The most popular and widely used technology is based on electro-oxidation.

In electro-oxidation processes, anodic oxidation occurs directly or indirectly. Direct oxidation involves transfer of electrons from the organic matter to the electrode while indirect oxidation involves generation of hydroxyl radicals for dye degradation. The reaction mechanism involved in direct oxidation is described as follows (Mireia and Carmen, 2012):

- Water is discharged at the anode to produce adsorbed hydroxyl radicals as shown by the following equation:

$$M + H_2O \rightarrow M(OH^*) + H^+ + e^- \dots\dots\dots\dots. \text{equation } 2.19$$
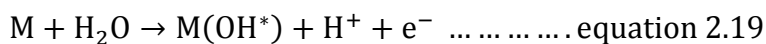
- The adsorbed hydroxyl radicals react with dye molecules (R) in the waste water and break it down to less harmful compounds.

$$R + M(OH^*) \rightarrow M + RO + H^+ + e^- \dots\dots\dots\dots \text{equation } 2.20$$
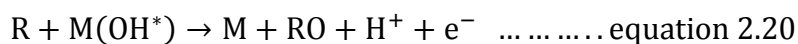
The efficiency of mineralization depends on the material used to make the anode (Mireia and Carmen, 2012).

In indirect electro-oxidation, oxidants are generated during electrolysis and reacts with the dyes. In chloride media, chlorine or chlorine-oxygen species are generated and take part in degradation of the dyes. This can be illustrated by the following equations:

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad \text{equation 2.21}$$

$$Cl_{2(aq)} + H_2O \rightarrow ClO^- + Cl^- + H^+ \quad \ldots \ldots \ldots .. \text{equation 2.22}$$

$$Dye + ClO^- \rightarrow dye\ intermediates \rightarrow CO_2 + H_2O + Cl^- \quad \ldots \ldots .. \text{equation 2.23}$$
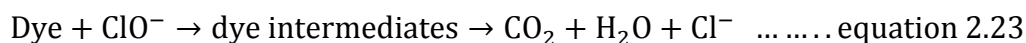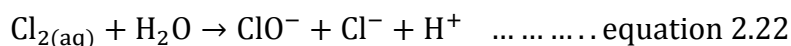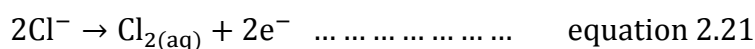
Indirect oxidation may also occur based on electro-Fenton process where hydroxyl radicals are generated from Fenton's reaction. Hydrogen peroxide is also electrogenerated from the solution. The hydrogen peroxide and hydroxyl radicals produced are responsible for dye degradation and are generated as per the following reactions:

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \ldots \ldots \ldots .. \text{equation 2.24}$$

$$O_{2(g)} + Fe^{2+} \rightarrow Fe^{3+} + OH^* + OH^- \ldots \ldots \ldots .. \text{equation 2.25}$$
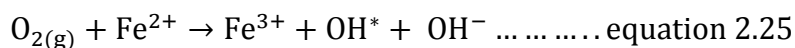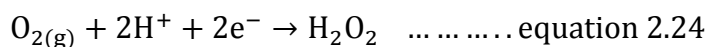
Electrochemical technology has attracted a lot of interests because of its simplicity, ease of control of reaction conditions and its high efficiency in degradation of textile pollutants. Its limitation however is in its high power consumption (Najafpoor et al., 2017).

2.2.5 Biological Systems

Lourenc et al., (2001) noted that waste water containing azo dyes are difficult to remove by using the conventional waste water treatment systems based on aerobic processes as a stand-alone process. Eltaief et al., (2007) studied the aerobic biodegradability of textile dye (indigo) by a combination of two aerobic bioreactors; Continuous Stirred Tank Reactor (CSTR) and Fixed Film Bioreactor (FFB). It was found that there was high organic loading attributed to the presence of grease, dirt, sizing agents, nutrients from dye bath additives and residual dyes. 95% of the color was removed in the process. COD and color removal efficiencies were found to be higher than those obtained from CSTR and FFB reactors as stand-alone processes. Popli and Upendra, (2015) studied anaerobic-aerobic sequential treatment of azo dyes. They concluded that anaerobic digestion is positively affected by higher retention time, higher concentration of biomass and primary substrate. It is negatively affected by complexity of dye structure, presence of alternative electron acceptor and high initial dye concentration. Aromatic amines were generated in the process and it was not possible to determine the extent of mineralization.

Mustafa and Delia, (2007) studied aerobic and anaerobic treatment of simulated textile waste water using anaerobic sequential up-flow anaerobic sludge blanket reactor (UASB) and aerobic CSTR reactor system to degrade azo dyes including Reactive Black 5, Direct Red 28, Direct Black 38, Direct Brown 2 and Direct Yellow 12. The results showed that there was a complete biodegradation and decolorization of the dye by using the system. However, the breakdown products such as aromatic amines were not ultimately metabolized, and accumulated under anaerobic conditions.

These aromatic amines resisted and inhibited further the anaerobic degradation. Aromatic amines were mainly degraded under sequential aerobic stage even at low high retention times while significant amount of color was removed under anaerobic stage. It was concluded that aerobic post-treatment step would be required for the mineralization of simulated textile or dye effluents containing azo dyes.

Biological treatment processes is an attractive option in the treatment of textile waste water but the challenge lies in the fact that aromatic amines are generated in the process. Using biological processes as a standalone is not effective and requires other treatment processes for it to yield desirable results.

2.2.6 Adsorption Processes

Adsorption is a process of transferring a substance into an active site of an adsorbent. It is a process mainly used to remove heavy metals from an industrial waste water stream. Kaushik et al., (2009) carried out a research to minimize the organic chemical load (unexhausted dye contents) in direct dyes effluent using low cost adsorbents. In the research, it was pointed out that activated carbon is reasonably effective in the decolorization of dyeing effluent though it needs regeneration or disposal once it is fully loaded and also has a limitation of high cost. It was from this limitation that the researchers developed low cost adsorbents to treat textile waste water. Waste materials including sugarcane bagasse pith, saw dust and brick powder were used as adsorbents in the direct dyes effluent on laboratory scale for the minimization of harmful unexhausted organic dye contents, before its discharge to the environment. From the study, it was found that in comparison with other adsorbents, activated carbon show good adsorption capability. This is attributed to its orxganophillic

character and the presence of matrix of micropores which yields greater active surface area enhancing adsorption. It was noted that sugarcane bagasse pith show good removal of organic pollutant compared to sawdust and brick powder.

The presence of a number of hydroxyl groups in cellulose, hemicellose and lignin part of the adsorbent form hydrogen bonds with the dye molecules help in the removal of unexhausted dye molecules (Kaushik et al., 2009). The factors that affect adsorption include adsorbent surface charge and physical and chemical nature of the adsorbent and adsorbate. Adsorption process is an attractive treatment option as long as a solution is provided for disposal of spent adsorbents.

2.2.7 Comparison of the Treatment Methods

The following table summarizes the various treatment methods used to treat textile waste water.

Table 2.1: Summary of textile waste water treatment methods

Treatment method	Advantage	Disadvantage
Physical Methods		
Adsorption using activated Carbon	-Economically attractive -Good removal efficiency	-high icost intensive -regenerative process
Adsorption using peat	-Effective adsorbent -No activation required	-low active Surface area
Adsorption using wood chips	-Good sorption for specific colorant	-Larger contact times and huge quantities required
Ion exchange	-Regeneration with low loss of adsorbents	Specific in application
Chemical Methods		
Oxidation	-Effective for both soluble & insoluble colorants	Problem with sludge disposal
Fenton's	-Capable of decolorizing wide variety of wastes. -No alternation in volume	Prohibitively expensive
Ozonation	-Effective for azo dye removal	-Not suitable for dispersed dyes -Release aromatic amines
Coagulation and precipitation	Short retention time & low capital costs. Good removal efficiencies	-High cost of pH adjustment -high cost of dewatering and sludge handling
Biological Methods		
Aerobic process	Color removal is facilitated along with COD removal	-Longer retention times -Less resistant to recalcitrant
Single cell	-Good removal efficiency for low volumes and concentrations. -Very effective for specific colorant removal	-Culture maintenance is cost intensive -Cannot cope up with large volumes of colored effluents
Emerging technologies		
Advanced oxidation	-Complete mineralization ensured -Growing number of commercial application -Effective pretreatment in integrated systems enhances biodegradability	-Cost intensive process
Photo-catalytic degradation	Cheap and very effective with azo dyes Less investment involved	Still under research awaiting full implementation.

Table from Byberg and Cobb, (2012).

Photo-catalytic degradation is attracting a lot of research currently because of its cost effectiveness. Doping especially has attracted a lot of interest because it offers a solution of a cheaper alternative of using visible light to degrade textile dyes. It is from this motivation that this research seeks to fill the gap of finding the optimum condition for degradation of methylene blue waste water using titanium dioxide doped with silver.

CHAPTER THREE

MATERIALS AND METHODS

3.1 MODELING AND OPTIMIZATION OF REACTION CONDITIONS

The variables investigated in this study were initial pH, initial dye concentration, catalyst dosage and the reaction time. The goal was to find the optimal conditions required to maximize the percentage degradation (response) of methylene blue waste water. The steps that were used to arrive at the optimum took the general layout outlined in Figure 3.1.

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┌─────────────────────────────────────┐
│      Design of Experiments          │
└─────────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────┐
│   Preparation of catalyst and reagents │
└─────────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────┐
│        Experimental Runs            │
└─────────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────┐
│        Analysis of Results          │
└─────────────────────────────────────┘
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│     Optimization of parameters      │
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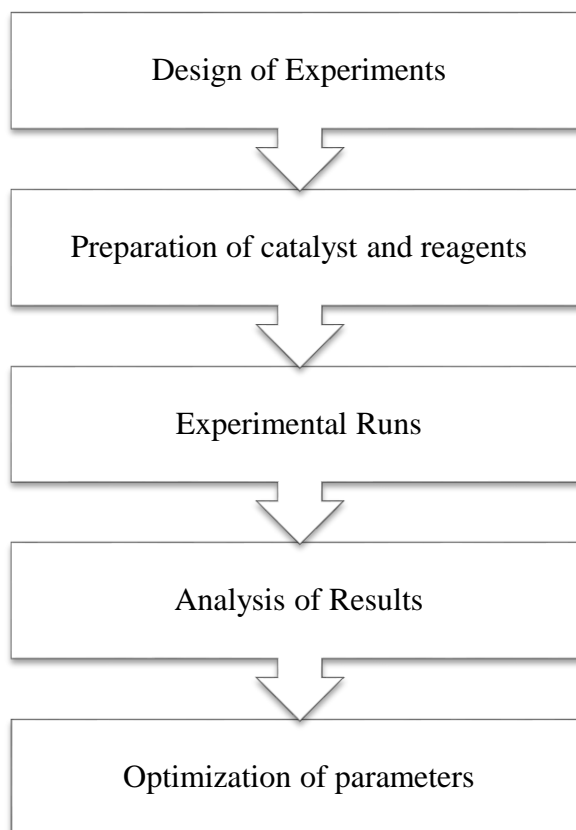
Figure 3.1: General layout of experimental design

3.1.1 Design of Experiments

Minitab was used to design the experiments and the worksheet Table A1 shown in the appendix was generated. All the actual and coded factor values were varied on five levels as shown in Table 3.1.

Table 3.1: Factor levels

Variables	Factor levels				
Coded factor values	-2	-1	0	1	2
Initial pH	3	5	7	9	11
Catalyst dosage, g/l	1	2	3	4	5
Initial dye concentration, ppm	10	20	30	40	50
Reaction time, min	24	48	72	96	120

A two level, full factorial central composite design was chosen because it allows for efficient estimation of quadratic terms in the regression model. There were a set of 30 experiments with three replicas done for the four factors. This amounted to a total of 90 experimental runs. The experiments were randomized into six blocks to rid nuisance variables. Each block represented the day in which the particular number of runs were conducted. The experimental runs were conducted based on the worksheet and the absorbance for each run measured using a UV spectrophotometer and recorded.

3.1.2 Generation of Regression Equation and Analysis of Variance

The analysis of variance (ANOVA) table, model summary, coded coefficient table and the regression equation based on the Percentage degradation (response) of each run was generated. The terms in the regression equation were checked to determine their significance.

The ANOVA table gives statistical indicators for each regression model that indicates the best model that can be used. The p-value for lack-of-fit statistic was used to choose the best regression model for the experimental data.

3.1.3 Optimization of Reaction Conditions

The reaction condition for the photo degradation of the methylene blue waste water was optimized with the objective of maximizing degradation efficiency. Using the experimental data from the design of experiments, optimization plots and the optimum conditions that maximize the degradation of the dye were generated. The plots were used to study the optimum reaction conditions.

3.1.4 Effect of Interactive Variables

The interactive effect between two parameters was investigated by keeping the other variables constant. Three dimensional surface plots and their contours were generated and analyzed. The 3D surface plots are the representations of the regression equation. The analysis was done based on the following interactions:

- pH and initial dye concentration

- pH and catalyst dosage

- pH and reaction time

- Initial dye concentration and catalyst dosage

- Initial dye concentration and reaction time

- Catalyst dosage and reaction time

3.1.5 Photo-Catalytic Reactor Vessel

Experiments were carried out in a custom made photo catalytic reactor. The cylindrical reactor enclosure with a height of 44cm and a diameter of 30cm was made from a cardboard material. It was lined with aluminum foil on its walls to ensure maximum light reflection on its interior. Fluorescent bulbs were installed on the upper part of the enclosure and a sampling point. Air was bubbled continuously into the solution reservoir by use of a pump to ensure a constant supply of oxygen and to give agitation effect to the solution. The solution was continuously stirred using a magnetic stirrer so as to keep the catalyst evenly dispersed. Three 20W fluorescent lamps were lit throughout the experiments. 10 ml sample aliquots were taken out from the sampling point using a syringe while the process was going on to ensure minimal disturbance.

The photo-degradation process was carried out to compare different conditions that the waste water was subjected to. The process was carried out to compare the following;

- Silver doped titanium dioxide catalyst with fluorescent light illumination
- Pure titanium dioxide with fluorescent light illumination
- Silver doped titanium dioxide catalyst without fluorescent light illumination

Three experimental runs were conducted for each condition and the percentage degradation evaluated. The experimental set up is shown in Figure 3.2.
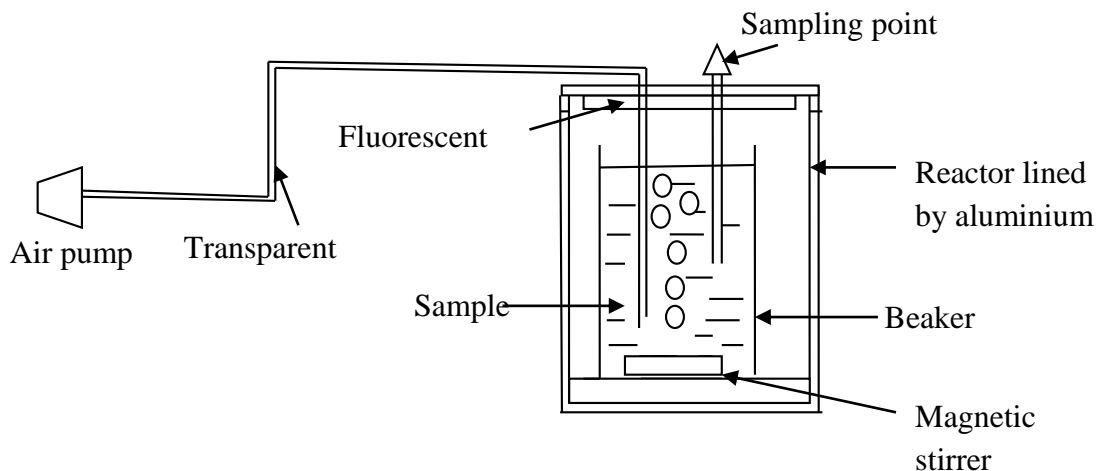
Figure 3.2: Experimental apparatus set up

3.1.6 Preparation of the Catalyst

The following reagents were used to prepare the catalyst:

i)   Titanium isopropoxide solution

This is a titanium precursor used to synthesize titanium dioxide based particles. It has a chemical formula; $C_{12}H_{28}O_4Ti$ with a molecular weight of 282.22 g/mol, melting point of $14\,^{\circ}C$ -$17^{\circ}C$ and boiling point of $232^{\circ}C$. The one used in this study was sourced from Sigma Aldrich Company, with a concentration of 97%.

ii)   Silver nitrate

iii)   Absolute Ethanol solution (99%)

iv)   2M Acetic acid

Silver-doped Titanium dioxide catalyst was synthesized by the sol-gel acid-catalyzed formation method. The following procedure was used (Zulkarnain et al., 2005);

- 20 ml absolute ethanol solution and 12 ml of titanium isopropoxide solution was dissolved in 200ml of deionized water in a 250ml beaker and stirred for 30 minutes.

- A mixture of 2ml silver nitrate solution and 2ml, 2M acetic acid was added drop wise under vigorous stirring.

- The white precipitate formed was separated from the solution and dried in an oven at 60°c for 30 minutes.

- The catalyst was then calcined in an electric furnace at 450°c for 2 hours.

- It was then stored in the dark awaiting its usage.

- The catalyst without doping was prepared using the same procedure.

3.1.7 Equipment used for Degradation Studies

i)   UV Spectrophotometer

A UV-VIS spectrophotometer, type UVM, ini-1240, 220-240V, 50/60Hz from Shimadzu was used to measure the absorbance of the samples after the reaction was carried out. A standard curve showing maximum wavelength peaks for methylene blue was obtained by running a blank solution containing distilled water and then a solution containing methylene blue. A standard graph for estimating the concentration of the dye was obtained by reading the absorbance of the dye at known initial concentration.

At low concentrations, the absorbance of the samples is directly proportional to the concentration. The percentage degradation, R can therefore be calculated from equation 3.1.

$$R = \frac{A_0 - A}{A_0} \times 100\% \ldots \ldots \ldots \text{equation } 3.1$$

ii)   pH meter

The pH meter with digital display, model NHB-150, Power rating 12V, 500mA was used to measure the pH of the waste water before degradation was carried out. Concentrated hydrochloric acid and sodium hydroxide were used to adjust the pH of the solution.

iii)   Magnetic stirrer

A magnetic stirrer Model, Heldolph MR200 with a maximum speed of 1500 revolutions per minute was used to agitate the waste water while it was being degraded. This was done in order to make sure that the catalyst was available and evenly distributed in the reaction media. The magnetic stirrer was also used for mixing of reagents required for running the experiments.

iv)   Air pump

An air pump, Model type, Elite 802, Power rating 3.5W with a maximum air pump rate of 1500 cc/min was used to bubble air into the reaction media. This was to ensure that oxygen is available at the catalyst surface for production of oxygen radicals required to break down the dye molecule. It also helps to keep the catalyst evenly dispersed in the solution and to provide turbulence necessary for reaction to proceed effectively.

v) Centrifuge

A centrifuge type D-7200 Tuttlingen with frequency 50/60Hz, Power 50W and a maximum speed of 600 revolutions per minute was used to separate the catalyst from the reaction media. The products were poured into the centrifuge tubes and spun at 600 revolutions per minute for 10 minutes. The centrifugal forces generated separates the solid catalyst from the liquid and the supernatant was sucked out immediately using a syringe into a sampling bottle to await further analysis.

vi) Muffle furnace

An electric muffle furnace, model N41-400 from Nobertherm Grabtt Company, Germany with power rating 18.8A, 13KW with maximum operation temperature of 1200°C was used to calcine the catalyst. It contains a control device used to set temperature that is to be achieved in a desired amount of time and to keep it constant for set time duration. The catalyst powder was placed in ceramic crucibles and put into the furnace chamber where it was calcined at 450°C for 2 hours.

vii) Drying Oven

A drying oven, model type, UE 200-800 from Memmert Company, Germany was used to dry the catalyst. It has a capacity of 32L, current of 4.8A and a power rating of 1100W. It has a built in time control to set the drying time to a desired duration. It was used to dry the catalyst after it had been synthesized before taking it for calcination.

viii)   Weighing scale

A weighing scale model HI 2211, power 12V dc from Hanna instruments was used for weighing purposes.

3.1.8 Measurement of Chemical Oxygen Demand

Measurement of Chemical Oxygen demand (COD) was done in order to determine the degree of mineralization of the dye. This was done before and after the degradation had been carried at the optimum condition. The procedure used for determination of COD was as per American Public Health (APHA) standard procedure (APHA, 2005). The closed reflux titrimetric method was used.

The reagents used for the analysis were as follows:

    i)   0.01667M standard potassium dichromate ($K_2Cr_2O_7$) digestion solution

This was prepared by adding 4.903g of $K_2Cr_2O_7$ previously dried at 150°C, 167 mL of concentrated H_2SO_4 and 33.3g mercuric sulphate ($HgSO_4$) to 500 mL of distilled water. The solution was allowed to cool and then diluted to 1000 mL.

    ii)   Sulfuric acid reagent

This was prepared by adding 5.5g of silver sulphate (Ag_2SO_4) to concentrated H_2SO_4 sulphuric acid. It is then left to stand for one day to dissolve and mix.

    iii)   Ferroin Indicator solution

    iv)   0.10M Standard Ferrous Ammonium Sulfate (FAS) titrant

This was prepared by dissolving 39.2g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. 20 mL of conc. H_2SO_4 was then added, cooled and diluted to 1000 mL. The solution was then standardized using standard $K_2Cr_2O_7$ digestion solution as follows:

- 5.0 mL of digestion solution was pipetted into a beaker.

- 10 mL reagent water was added to substitute for sample.

- 2 drops of the diluted Ferroin indicator added and titrated with the FAS titrant.

The molarity of the FAS solution was calculated using equation 3.2 (APHA, 2005):

$$\text{Molarity of FAS solution} = \frac{\text{Volume of 0.01667M } K_2Cr_2O_7 \text{ solution titrated, mL}}{\text{Volume of FAS solution used in titrated, mL}} \times 0.10$$

……….equation 3.2

The following procedure was used to determine the COD:

- Culture tubes and caps were washed with 20% H_2SO_4

- 2.5 mL of the sample was placed in the culture tube and 1.5 mL $K_2Cr_2O_7$ digestion solution added.

- 3.5 mL sulphuric acid reagent was poured on the inside walls of the vessel to form an acid layer under the sample-digestion solution layer.

- The tubes were tightly capped and inverted for proper mixing.

- The tubes were then placed in the block digester, preheated to 150°C and refluxed for 2 hours.

- The tubes were allowed to cool to room temperature and placed in the test tube rack.

- 2 drops of Ferroin indicator was added and stirred using a magnetic stirrer while titrating with standardized 0.10 M FAS to the end point.

- A blank containing the reagents and distilled water with a volume equal to that of the sample was also refluxed and titrated.

Equation 3.3 was used to determine the COD (APHA, 2005):

$$\text{COD in mg } O_2/L = \frac{(A - B) \times M \times 8000}{\text{mL sample}} \dots. \text{equation 3.3}$$

Where,

A = mL FAS used for blank,

B = mL FAS used for sample,

M = molarity of FAS

3.1.9 Dyeing of Acrylic Fiber.

2g acrylic fiber was weighed and put in a dyeing cylinder containing 200mL of water. 0.04g of methylene blue was then weighed and put into the cylinder containing the fiber. A retarding agent was then mixed into the contents and heated for 1 hour. The waste water generated was collected and stored awaiting its treatment.

3.1.10 Measurement of color units

Color was measured as per the standard procedure provided by the operation manual of the DR2800 UV spectrophotometer. The color index was read in platinum-cobalt units.

3.2 PARAMETRIC EFFECTS

3.2.1 Effect of Initial pH

At optimum initial dye concentration and catalyst dosage as determined in section 3.1.3, the photo degradation process was done for a reaction time of 102.5 minutes. The pH was set at 2, 4, 6, 8, 10, 12 and 14. Samples were taken after reaction time and absorbance values read and percentage degradation determined.

3.2.2 Effect of Catalyst Dosage

At the optimum pH value and optimum initial dye concentration, the process was carried out while varying the catalyst dosed into the reactor. The catalyst dosage was varied at 1g/L, 2g/L, 3g/L, 4g/L and 5g/L. After 102.5 minutes of reaction time, the samples were taken and their absorbance read off using UV spectrophotometer and percentage degradation determined. The results were then plotted on a graph so as to analyze its effect.

3.3 CATALYST RE-USE

The aim of catalyst re-use is to investigate whether the same catalyst can be re-used several times without loss of its catalytic activity. The catalyst that was used for the reaction process was regenerated and used for a second and a third run.

To regenerate the catalyst for the experimental runs, the following procedure was used (Zulkarnain et al., 2005):

- The catalyst was recovered from the solution after degradation by use of a centrifuge and by filtering.

- The catalyst was boiled in distilled water till a colorless wash liquid was obtained.

- It was then dried in a hot air oven at 90°c for 30 minutes

- Calcined at 450°c in a furnace for 2 hours.

- Stored in the in the dark to await usage in the next run.

The catalyst dosage was kept at the optimum during the experimental runs. The percentage degradation was evaluated and a comparison made.

3.4 TEST FOR PARAMETRIC REACTION KINETICS

A reaction process that follows first order kinetics is described by the following equation;

$$\ln\frac{C}{C_0} = -K_1 t \ldots \ldots \text{equation 3.4}$$

Where;

C = concentration of the dye at a time, t

C_o = initial concentration of the dye at time, t = 0

K_1 = Pseudo-first order reaction constant

t = reaction time

Since concentration is directly proportional to absorbance, then the ratio of concentration is equal to the ratio of the absorbance. Therefore;

$$\ln \frac{A}{A_0} = -K_1 t \ldots \ldots \text{equation 3.5}$$

For data to fit equation 3.5 shown, a plot of $\ln \frac{A}{A_0}$ against time must give a straight line with K_1 being the slope. The condition of reaction was kept at the optimum pH, optimum catalyst dosage, optimum initial dye concentration and optimum reaction time. The values of ln (A/Ao) were then evaluated and plotted on a graph with time, t. The samples were withdrawn at 20 minute time interval and absorbance read.

In order to study the kinetics of the photo-catalytic process, the Langmuir-Hinshelwood (L-H) model was used. The Langmuir-Hinshelwood kinetic model is given by the following equation (Kumar et al., 2008);

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1 + KC} \ldots \ldots \text{equation 3.6}$$

Where r represents the rate of reaction that changes with time in mg/Lmin

k_r = rate constant for photolysis in mg/Lmin

K = rate constant for adsorption in L/mg

C = concentration of the dye in the bulk solution at any time, t (minutes)

Linearizing the L-H model yields the following equation;

$$\frac{1}{r} = \frac{1}{k_r} + \frac{1}{k_r KC} \ldots \ldots \text{equation 3.7}$$

Equation 3.7 can be written in terms of initial rate, r_0 and initial concentration of the dye, C_0 as follows:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r KC_0} \ldots \ldots \text{equation 3.8}$$

If the photo-catalytic degradation process follows this model, then a plot of $\frac{1}{r_0}$ Vs $\frac{1}{C_0}$ generates a straight line.

The initial rate of reaction was determined by computing the slope of the tangent of the concentration-time graph at the start of the reaction process. All other conditions were kept constant at the optimum. The following procedure was used (Tarek et al., 2009):

- A series of experiments with initial concentrations of the dye of 10ppm, 20ppm, 30ppm, 40ppm and 50ppm were carried out while keeping the pH at 10.9, catalyst dosage at 3.75g/l and reaction time at 102.5 minutes.

- Samples were taken out at 10 minutes time interval and absorbance read in a UV spectrophotometer.

- Concentration was obtained by interpolating from a standard absorbance-concentration graph.

- Concentration- time graphs were then plotted of each initial dye concentration.

- The initial rate (slope of the curve at the start of each run) was then calculated.

- The initial rate was then plotted against the concentration to determine the reaction model.

CHAPTER FOUR

RESULTS AND DISCUSSION

A standard calibration curve obtained from the UV spectrophotometer used to measure the   absorbance of methylene blue is shown in Figure 4.1. The initial concentration of the dye was kept at 50 ppm.
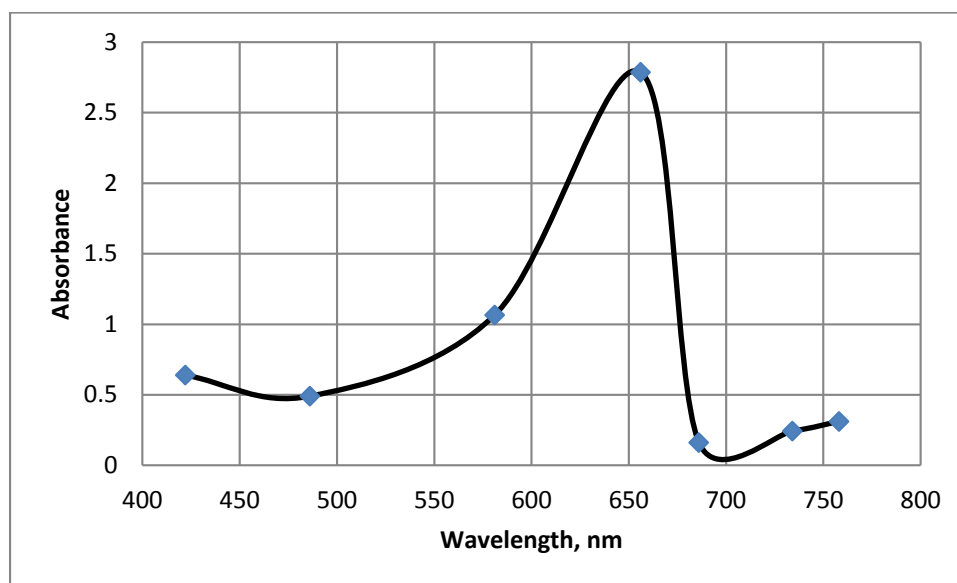
Figure 4.1: Standard calibration curve for methylene blue

From the curve, it can be seen that the maximum peak wavelength for methylene blue is at 656 nm. The absorbance of the samples was therefore read from this wavelength. A standard graph relating the absorbance of the dyes at different dye concentration is presented in Figure 4.2. The concentration of the dye can be read from its known absorbance by interpolation technique.
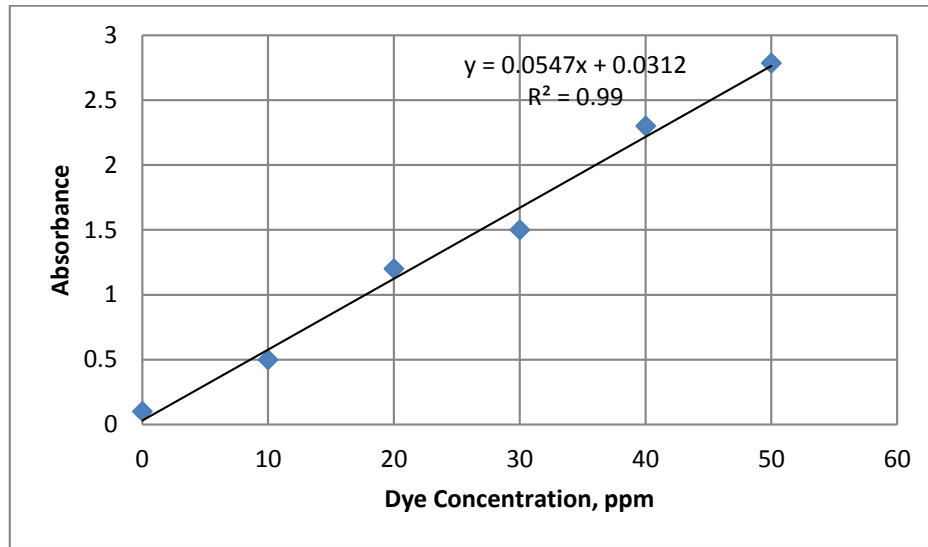
Figure 4.1: Standard absorbance-concentration graph.

4.1 PHOTO-DEGRADATION REGRESSION MODEL

As explained in section 3.1, the regression model that predicts the photo-degradation of the methylene blue waste water using silver-doped titanium dioxide catalyst was generated. The full quadratic regression equation shown by equation 4.1 was obtained.

$$y = -111.22 + 26.49X_1 + 0.9758X_2 + 13.297X_3 + 0.3174X_4 - 1.5566X_1^2$$
$$- 0.021472X_2^2 - 2.5889X_3^2 - 0.005927X_4^2 + 0.03521X_1X_2$$
$$+ 0.1708X_1X_3 + 0.05417X_1X_4 - 0.01333X_2X_3 + 0.003438X_2X_4$$
$$+ 0.04601X_3X_4$$

……. equation 4.1

Where;

y = percentage degradation

X_1 = Initial pH

X_2 = Initial dye concentration

X_3 = catalyst dosage

X_4 = Reaction time

Table 4.1: Analysis of Variance

Source	Df	Sum of square	Mean Squares	F-Value	P-value	Effect	VIF	Remark
Model	19	34865.2	1835.0	9706.94	0.000			Significant
Blocks	5	18.1	3.6	19.13	0.000			Significant
Linear	4	30458.7	7614.7	40280.55	0.000			Significant
Initial pH, X_1	1	29768.0	29768.0	157468.26	0.000	40.6667	1.00	Significant
Initial Dye concentration, X_2	1	143.9	143.9	761.39	0.000	2.8278	1.00	Significant
catalyst dosage, X_3	1	252.4	252.4	1335.03	0.000	3.7444	1.00	Significant
Reaction time, X_4	1	294.4	294.4	1557.52	0.000	4.0444	1.00	Significant
Square	4	3942.5	985.6	5213.77	0.000			Significant
X_1^2	1	3190.0	3190.0	16874.86	0.000	-12.453	1.05	Significant
X_2^2	1	379.4	379.4	2006.88	0.000	-4.2944	1.05	Significant
X_3^2	1	551.5	551.5	2917.39	0.000	-5.1778	1.05	Significant
X_4^2	1	959.0	959.0	5073.02	0.000	-6.8278	1.05	Significant
2-Way Interaction	6	445.9	74.3	393.15	0.000			Significant
X_1X_2	1	23.8	23.8	125.90	0.000	1.4083	1.00	Significant
X_1X_3	1	5.6	5.6	29.64	0.000	0.6833	1.00	Significant
X_1X_4	1	324.5	324.5	1716.45	0.000	5.2000	1.00	Significant
X_2X_3	1	0.9	0.9	4.51	0.037	-0.2667	1.00	Significant
X_2X_4	1	32.7	32.7	172.82	0.000	1.6500	1.00	Significant
X_3X_4	1	58.5	58.5	309.57	0.000	2.2083	1.00	Significant
Error	70	13.2	0.2					
Lack-of-Fit	58	12.6	0.2	3.93	0.060			Not Significant
Pure Error	12	0.7	0.1					
Total	89	34878.5						

As shown in table 4.1, the P-value on lack-of-fit is 0.06 which is greater than 0.05 (confidence level) indicating that the full quadratic model is a good representative of the data generated. The other P-values in the table are all significant because they are less than 0.05 indicating that all the terms in the mathematical model are significant in predicting the response (percentage degradation). All the squared terms in the quadratic model are all significant implying that that there is curvature in the response surface. The initial pH has the greatest effect of 40.6667 on the degradation process compared to the other variables. It must therefore be taken carefully optimized in the reaction process. Variance Inflation Factor, VIF measure how much the variance of the estimated regression coefficients are inflated as compared to when the predictor variables are not linearly related. It indicates the extent to which multicollinearity (correlation among predictors) is present in a regression analysis. In the analysis, it can be seen that, VIF are all close to 1 meaning the predictors are not correlated and that the variance of regression coefficients is minimal and stable. The coefficients in the regression equation are therefore reliable in predicting the response and can be used to analyze the reaction system.

Table 4.2: Model summary

Parameter	
S	0.434789
R^2	99.96
R^2 Adjusted	99.95
R^2 Predicted	99.95
Unusual Observations	
43th Run	0.94 Residual
57th Run	0.93 Residual
85th Run	0.95 Residual

In the model summary, shown in Table 4.2, the statistical value of S was found to be 0.434789, meaning that the model predicts the response well. The value of R^2, R^2 adjusted and R^2 predicted are 99.96%, 99.95% and 99.94% respectively. Since the value of R^2 predicted is close to R^2 adjusted and R^2, it means that the mathematical model can predict new observations accurately and can be used to fit new data under the same operating conditions as those done in this study.

The analysis showed unusual observation on 43th, 57th and 85th experimental runs showing residual values of 0.94, 0.93 and 0.95 respectively. The residual values show a possible small error during the experimental run or there could be other extraneous factors that affected the reaction process. Owing to the fact that there are only 3 unusual observation out of a total of 90 experimental runs representing only 3.3% and that the residual values are low, it can be concluded that the model is a good fit for the predicted response.

From the statistical analysis of the regression model, it was concluded that the full quadratic equation represented by equation 4.1 is a good representative of the percentage degradation from the experimental data generated.

4.2 EFFECT OF INTERACTIVE VARIABLES

In order to investigate the interaction between two variables, the other two variables were kept at their optimum values and their 3-D surface and contour plots analyzed. The main aim is to mark efficiently the points that give maximum percentage degradation of the dye.

4.2.1 Interaction Effect of Initial Dye Concentration and Initial pH
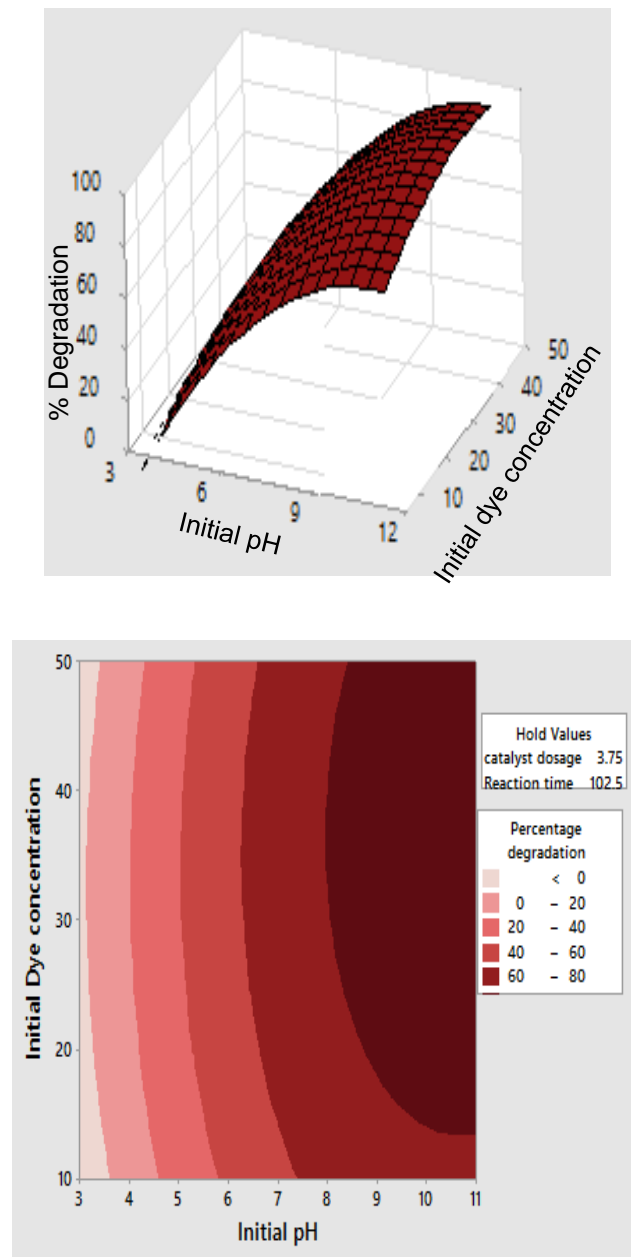
Figure 4.2: Response surface and contour plot for dye concentration and pH interaction

The response surface shown in Figure 4.3 indicates that as the pH increase from 3 to 10, the percentage degradation also increases. From a pH of 11, the percentage

degradation is generally constant. There is a limited increase in percentage degradation as the initial dye concentration is increased from 10 to 38 ppm. Beyond a value of 38 ppm the percentage degradation decreases. Comparatively, initial pH influences the percentage degradation more than the initial dye concentration. The contour lines in the plot are elliptical which suggest that the interaction between initial pH and initial dye concentration is significant (Jadhav et al., 2013). It shows that the optimum initial dye concentration is > 10 and the optimum initial dye concentration is the region 30-40 ppm.

4.2.2 Interaction Effect of Initial pH and Catalyst Dosage
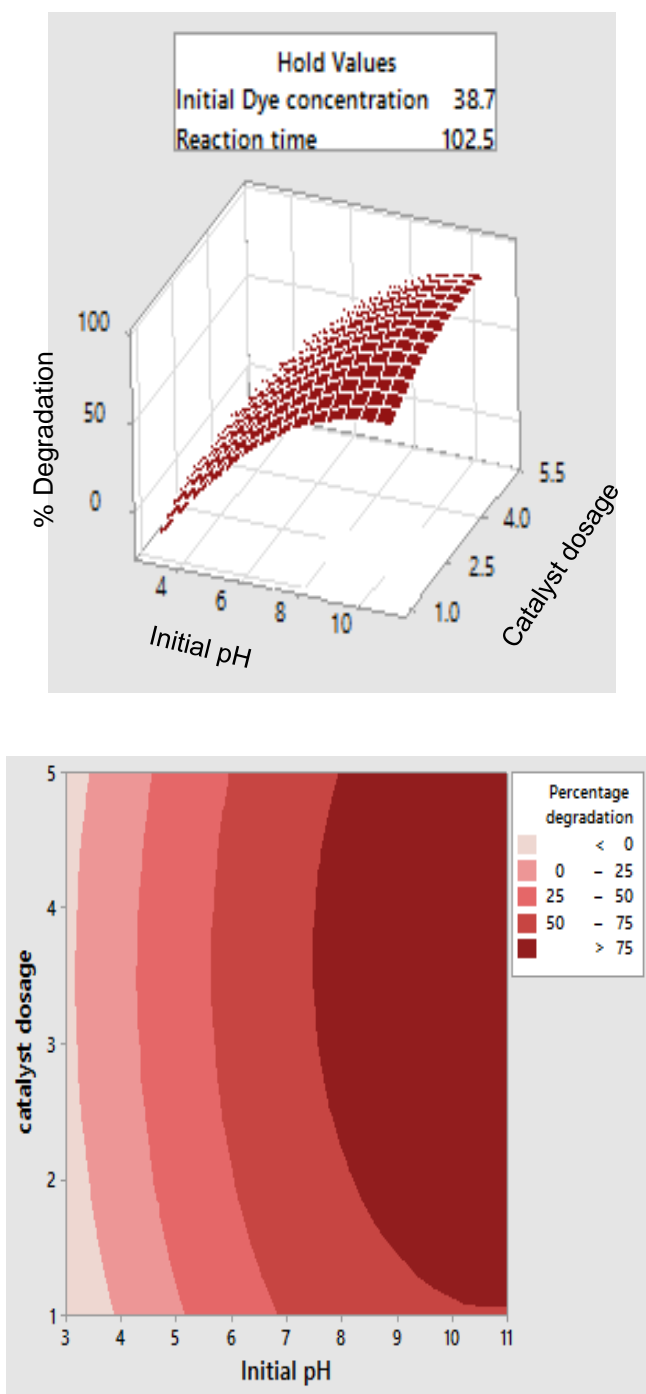
Figure 4.3: Response surface and contour plot for initial pH and Catalyst dosage.

From Figure 4.4, it can be seen that percentage degradation increases as initial pH is increased from 2 to 10. There is a limited increase in percentage degradation for catalyst dosage range of 1 to 4 g/l. Thereafter percentage degradation drops slightly as the catalyst dosage is increased to 5 g/l. This is attributed to increased opacity inside the reactor because increased catalyst particles causes light dispersion and prevents light from reaching the catalysts active sites. In the regression equation, the coefficient in the initial pH and catalyst dosage interaction is 0.01708. This implies that for every unit increase in initial pH, catalyst dosage increases by 0.01708. The contour plot is also elliptically shaped implying that the interaction is significant. From the contour plot, the highest degradation lies between a catalyst dosage of 3 to 5 and an initial pH range of > 8.

4.2.3 Interaction Effect of Initial pH and Reaction Time
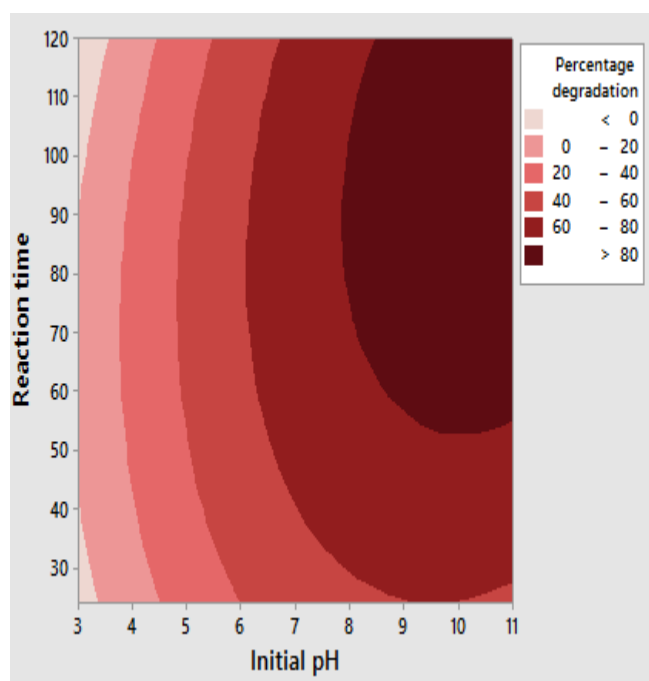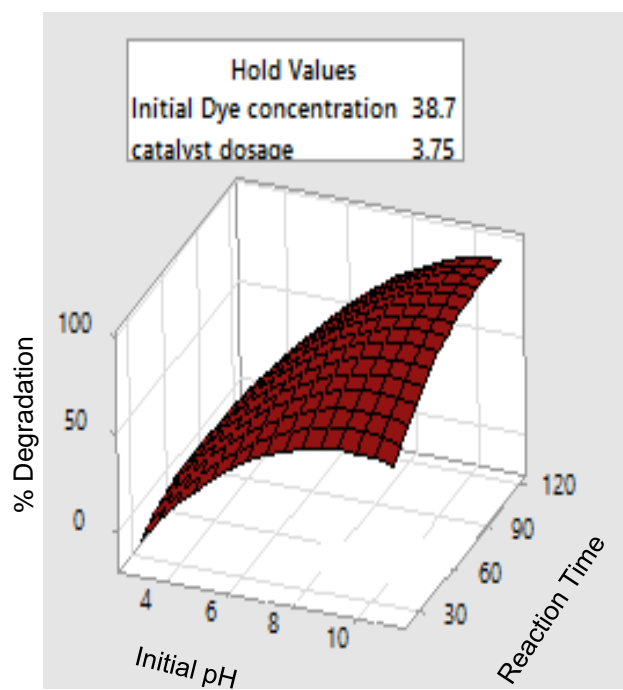
Figure 4.4: Response surface and contour plot for initial pH and Reaction Time.

The percentage degradation increases with an increase in the initial pH from 3 to 11. At the same time the percentage degradation also increases when the reaction time is increased to 120 minutes. From the contour plot, the percentage degradation is greater than 80% when the reaction time is in the range of 60 to 120 minutes at the initial pH range of > 9. Optimizing reaction time is therefore important so that the catalyst surface is efficiently utilized in the reaction process. The contours are elliptical and therefore the interaction is significant.

4.2.4 Interaction Effect of Initial Dye Concentration and Catalyst Dosage
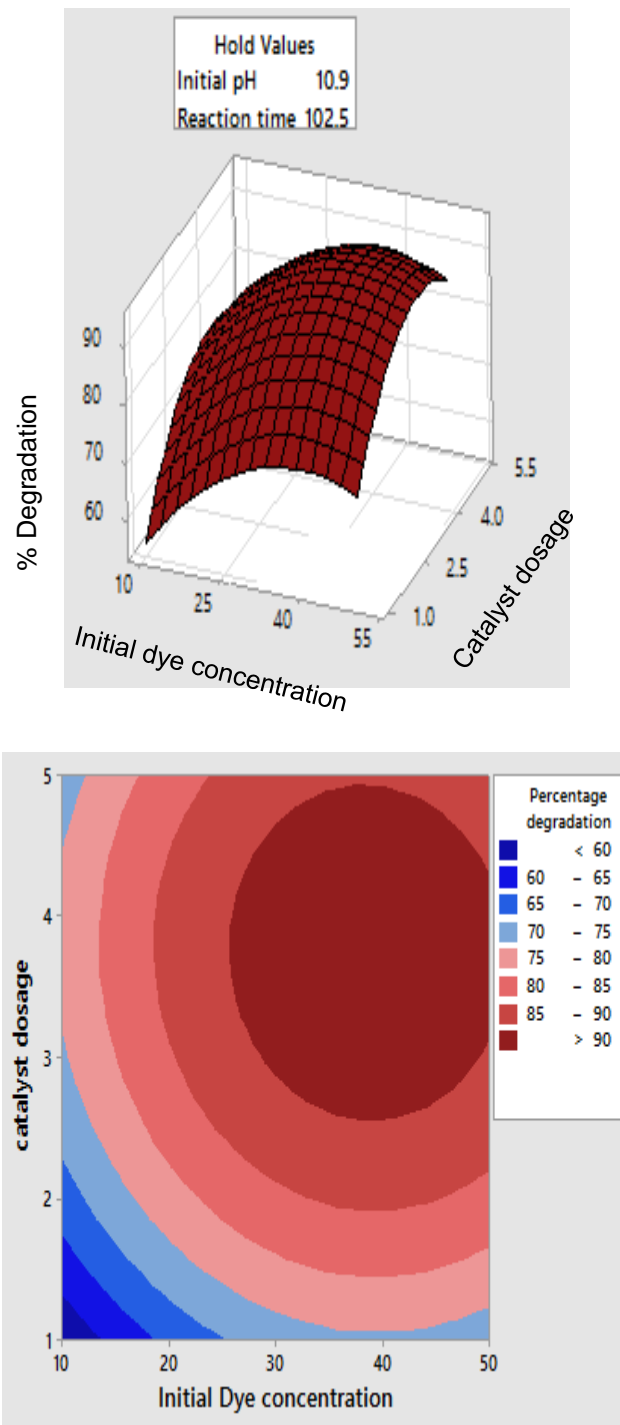
Figure 4.5: Response surface and contour plot for dye concentration and Catalyst dosage.

Surface response shown in Figure 4.6 indicates that the highest percentage degradation occur at initial dye concentration of 38 ppm and a catalyst dosage of 3.75g/l. there is increased percentage degradation when the catalyst dosage is increased from 1g/l to 3.7g/l then it drops as catalyst dosage is increased. The effect of initial dye concentration is almost similar in magnitude to that of the catalyst dosage. The shapes of the contour lines are elliptical though tending to circular meaning that the effects are significant but with a low magnitude of significance. In fact the p-value on the ANOVA table is 0.037 which is slightly less than 0.05 confidence level. This means that for optimum percentage degradation, when the initial dye concentration is increased, the catalyst dosage should be increased almost by the same magnitude to maintain the optimum.

4.2.5 Interaction Effect of Initial Dye Concentration and Reaction Time
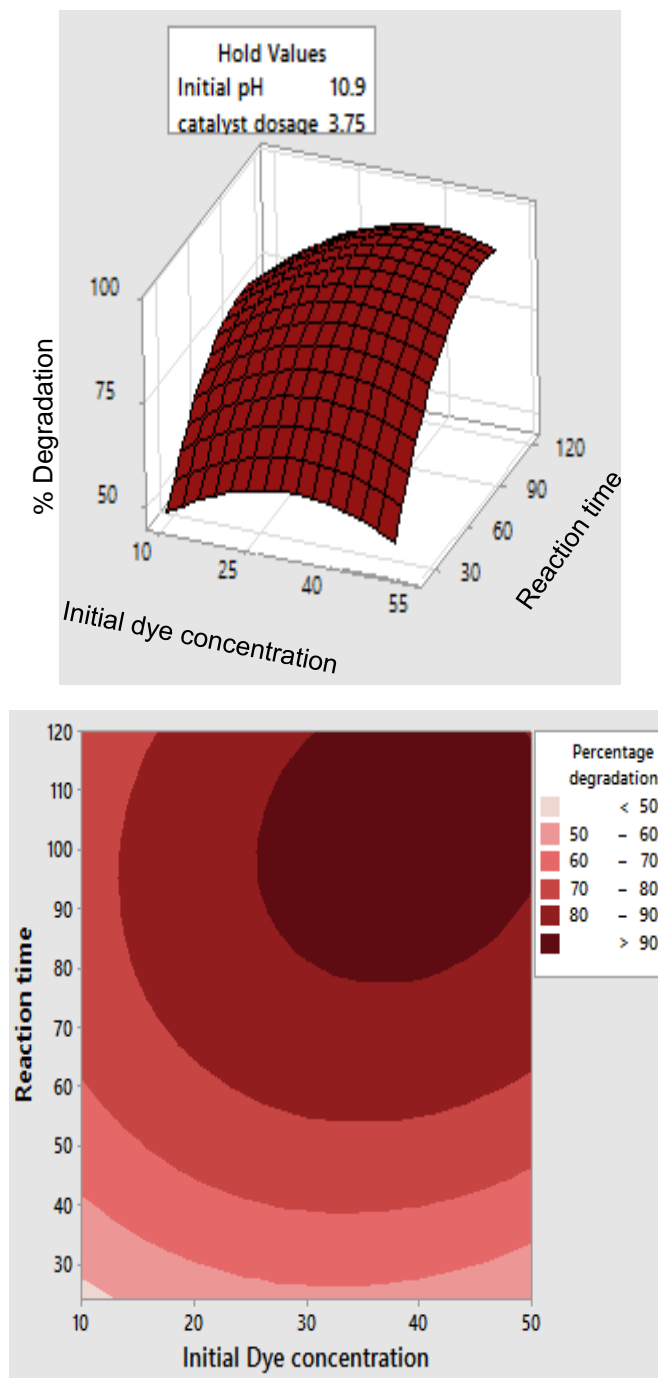
Figure 4.6: Response surface and contour plot for dye concentration and Reaction Time.

From the response surface graph, shown in Figure 4.7, the percentage degradation increase with an increase in initial concentration from 10 ppm to 38 ppm then drops as initial dye concentration is increased to 50 ppm. The percentage degradation also increases with increase in reaction time from 30 minutes to 100 minutes. It then drops as reaction time increases to 120 minutes. The reaction time has more effect on degradation compared to the initial dye concentration. In the contour plot, the lines are elliptical meaning that the interaction is significant. Reaction time must be optimized to allow the catalyst time to produce hydroxyl radicals to attack the dye molecules. As time progresses in the reaction process, the catalyst active sites become exhausted and degradation rate drops.

4.2.6 Interaction Effect of Catalyst Dosage and Reaction Time
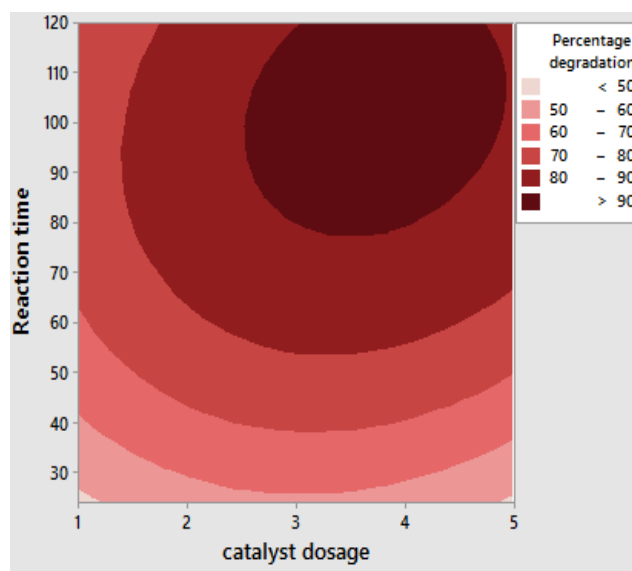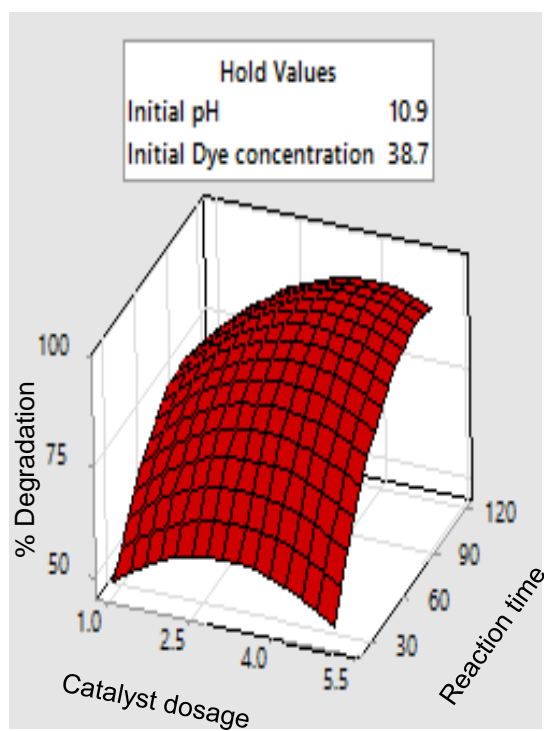
Figure 4.7: Response surface and contour plot for catalyst dosage and Reaction Time.

From Figure 4.8, at high reaction time of 120 minutes there is an increase in percentage degradation from 70% to >90%. At high catalyst dosage, the percentage degradation increases from about 50% to >90%. The reaction time has greater effect on percentage degradation than the catalyst dosage. The highest percentage degradation is at a catalyst dosage of 3.75g/l and a reaction time of 100 minutes. The contours are also elliptical meaning that the interaction is significant in determining the percentage degradation. Sufficient time should be given for the catalyst to effectively use its active sites.

4.3 OPTIMIZATION OF REACTION CONDITIONS

After running the experimental data on the response optimizer on the statistical tool, the results shown in Table 4.3 were generated.

Table 4.3: Optimum conditions for photo-degradation of methylene blue

Parameter	
Response	Percentage Degradation
Goal	Maximize
Weight	1
Importance	1
Multiple response optimization	
Initial pH	10.9192
Initial dye concentration, ppm	38.6869
Catalyst dosage, g/l	3.7474
Reaction time, min	102.545
Percentage degradation fit	93.3972
Composite desirability	1

From the table it can be seen that the optimum operating condition for the photo-catalytic process is an initial pH value of 10.92, an initial dye concentration of 38.7 ppm, a catalyst dosage of 3.75 g/L, and a reaction contact time of 102.55 minutes. To confirm this result, an experiment was done with this optimum conditions and the percentage degradation was found to be 90%.

A comparison was made to determine the degradation rate by using pure (undoped) titanium dioxide with illumination, doped titanium dioxide with illumination and doped titanium dioxide without illumination. The catalyst dosage was kept constant at the optimum amount of 3.75 g/L and the initial pH of 10.9. The initial concentration of the dye was kept at 38.7 ppm and the total reaction time of 120 minutes. Three experimental trials were run and the average values of the absorbance of the samples were plotted on the graph shown in Figure 4.9.
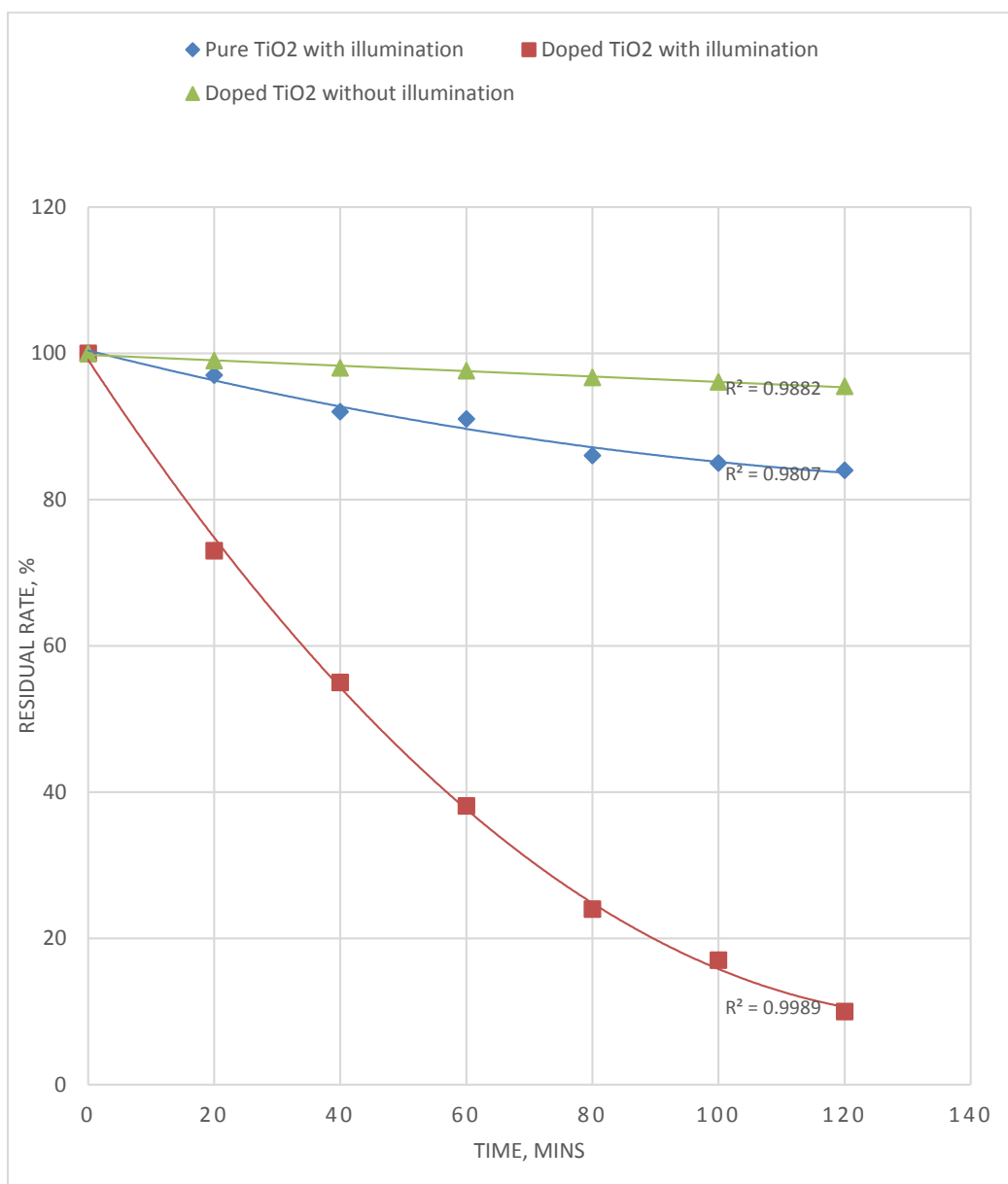
Figure 4.8: Graph for photo-degradation against catalyst types

From the graph it is seen that the highest degradation (90%) occur when the dye was subjected to the silver-doped catalyst with fluorescent light illumination. There was a slight degradation (16%) of the dye when pure photo catalyst was used with the same illumination. There was a negligible (4.5%) degradation of the dye when the process was carried out in the dark using the same doped catalyst. This means that the doping

of the titanium dioxide using silver greatly enhanced the catalytic activity of the catalyst when it was excited by the fluorescent light.

Doping of the catalyst shifts the absorption spectra of the catalyst into the visible region. The band gap of the catalyst is reduced and therefore the electrons produced in the valence band can be excited into the conduction band by visible light (Richards, 2006). This enables the catalyst to produce hydroxyl radicals that attacks the complex dye molecule and breaks it down into smaller and less harmful compounds. The photo degradation activity of the pure titanium dioxide can be attributed to self-photosensitization under visible light which causes a slight photo degradation of the dye (Zulkarnain et al., 2005).

4.3.1 Determination of Chemical Oxygen Demand (COD)

The COD was determined at the optimum conditions. Before degradation of the waste water, the COD was found to be 1030 mg/l and after degradation, it reduced to 46 mg/l representing 95.5% COD reduction. Environmental Management and Coordination Regulations on water quality standards recommends a COD level of not more than 50 mg/l for all the waste water effluent (EMCA, 2006). A COD of 46mg/l is therefore within the recommended standard.

The absorbance of actual waste water from the dyeing of the fiber was found to be 2.159 representing a concentration of 40ppm determined from the graph shown in Figure 4.2. The initial concentration of the dye before dyeing was 200 ppm. This means that the unfixed dye that is in the waste water represents 20% of the initial amount of methylene blue. The waste water after dyeing was degraded using 3.75g/l of silver-doped titanium dioxide, at pH of 10. After 120 minutes, the absorbance was

measured and found to be 0.259. This represents 88% degradation of the dye. The COD was also measured on the actual dye effluent after dyeing and was found to be 47 mg/l representing 92% reduction.

The COD removal is attributed to high reactivity of organic compounds with hydroxyl radicals and it is used to monitor dye mineralization (Faisal et al., 2007). Mineralization of methylene blue dye during photo degradation process therefore occurred meaning that the complex molecular structure of the dye was broken down by the hydroxyl radicals leading to the production of less harmful compounds.

4.3.2 Determination of color units

Color units were determined using R2800 UV spectrophotometer. Before degradation at initial dye concentration of 38.7ppm the color was found to be 1000 platinum-cobalt units. After degradation the color reduced to 37 platinum cobalt units. NEMA recommends that all waste water standards should have color units of not more than 40 platinum cobalt units. Color causes obstruction of dissolved oxygen and aesthetic deterioration of water bodies.

4.4 Parametric Effects on photo-degradation of methylene blue.

4.4.1 Effect of pH on photo-degradation

The photo degradation process was conducted at different pH values and the percentage degradation evaluated. The initial dye concentration was kept at the optimum of 38.7ppm a catalyst dosage at 3.75 g/L and a reaction time of 102.55 minutes. The results are presented in a graph shown in Figure 4.10:
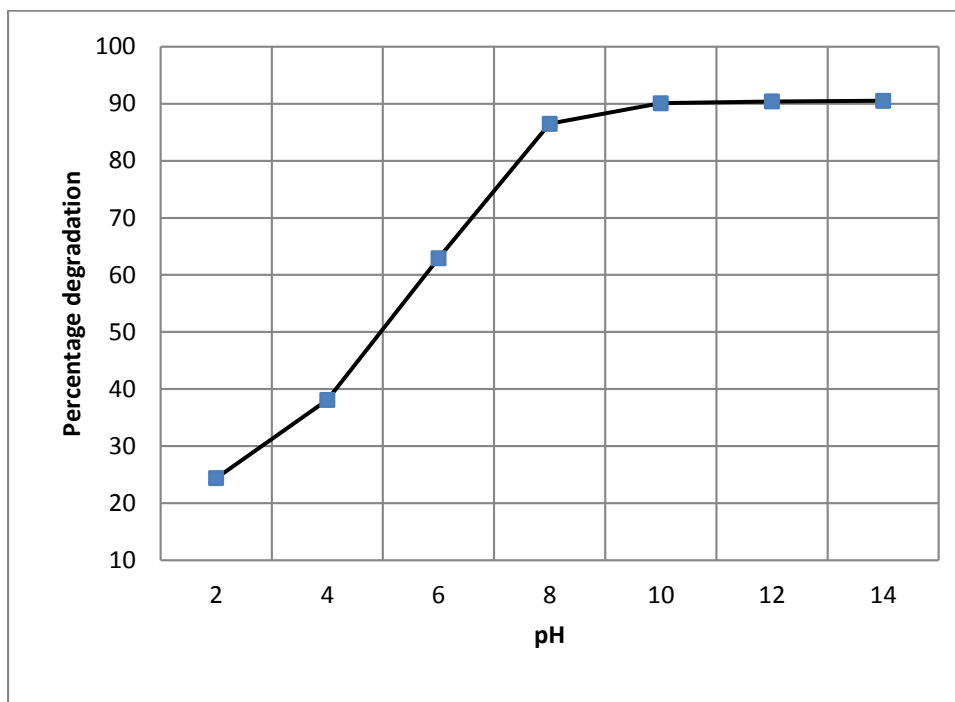
Figure 4.9: Graph showing effect of pH on percentage degradation

The highest degradation rate was seen to take place at a pH of 10 and was constant to a pH of 14. The effect of pH is related to the ionization state of dye molecules onto the TiO_2 surfaces. The TiO_2 surface is positively charged in acidic media, whereas it is negatively charged under alkaline conditions (Gnanaprakasam et al., 2015). Methylene blue is a cationic dye because its carries a positive charge. It is therefore attracted to the catalyst surface faster where reaction takes place. Hydroxyl radicals are formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels (Gnanaprakasam et al., 2015). In alkaline solutions hydroxyl radicals are generated by oxidizing more hydroxide ions available on TiO_2 surfaces and the efficiency of the process is enhanced (Faisal et al., 2007). At low pH, reduction by electrons in

conduction band may play a very important role in the degradation of dyes due to the reductive cleavage of azo bonds.

On the other hand, TiO_2 particles tend to agglomerate under acidic conditions and this leads to a decrease in surface area available for dye adsorption and photon absorption (Attia et al., 2008). Hence pH plays an important role both in the characteristics of textile waters and in the reaction mechanisms that can contribute to dye degradation.

4.4.2 Effect of catalyst dosage on photo-degradation

The main reason why catalyst dosage has to be investigated is to avoid having situations where the catalyst is being fed to the reactor in excess of the amount needed at optimum conditions. This can affect the performance of the reaction process and at the same time is an extra cost since the catalyst is wasted unnecessarily.

The amount of the catalyst fed into the reactor was varied while the pH was kept constant at a value of 10.9 and the initial dye concentration of 38.7ppm. Percentage degradation of the samples was determined when the dye was subjected to photo degradation process after a period of 102.55 minutes and the results are shown in a graph in Figure 4.11.
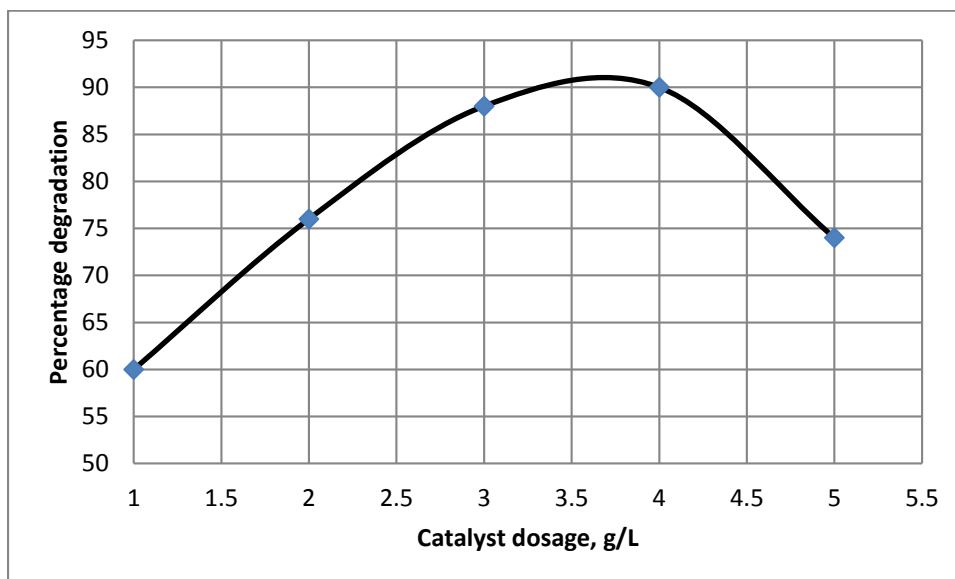
Figure 4.10: Percentage degradation against catalyst dosage

It can be seen that as the catalyst dosage was increased from 1g/L to 3.75g/L, the percentage degradation also increased. This behavior can be attributed to an increase in the amount of active sites available in the surface of photo-catalyst particles resulting to an increase in the number of dye molecule adsorbed onto the surface of photo-catalyst (Kim and Lee, 2010). This increases the rate of photo-degradation of the dye.

The highest percentage degradation was seen to take place at a catalyst dosage of 3.75g/L giving percentage degradation of 91%. As the catalyst dosage is increased to 5g/L, the degradation rate dropped to 74%. This behavior emanates from variation in the intensity of radiation entering the reaction vessel and the way the catalyst utilizes that radiation. Light scattering by catalyst particles at higher concentration lead to decrease in the passage of irradiation through the sample leading to poor light utilization (Gaya et al., 2010; Kavitha and Palanisamy, 2011). Deactivation of

activated photo-catalyst molecules colliding ground state molecules with increasing the load of photo-catalyst may also cause reduction in photo-catalyst activity (Kim and Lee, 2010).

4.5 CATALYST RE-USE

To investigate the extent of catalyst re use, several experimental runs were conducted using the same catalyst several times. This was done in order to reduce the cost of the catalyst eventually.

The percentage degradation at 20 minute time interval was determined and the results are plotted in the graph given in Figure 4.12.
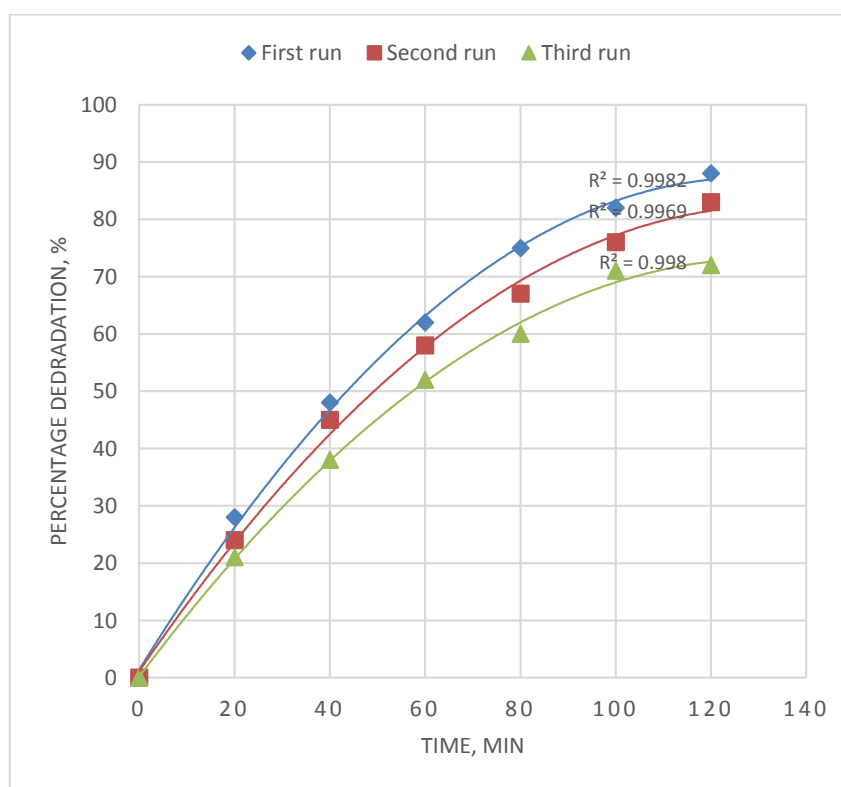
Figure 4.11: Graph for photo degradation rate against time for several catalyst re-use.

From the graph it can be seen that the highest degradation took place at the first run (88%) followed by the second run (83%) and then the third run at 72.2% after 120 minutes. As the catalyst is being used, their active adsorption site is being used up. This reduces slightly the catalytic activity of the catalyst. However, it can be seen that the catalyst can be re used three times without so much loss of its catalytic activity. This helps in reducing the overall cost of the photo degradation process because the cost of the catalyst is a major setback in catalytic processes.

4.6 PARAMETRIC REACTION KINETICS

As explained in section 3.4, the reaction parameters were tested on first order kinetics to determine whether it fits into the first order equation 3.5.   The conditions of reaction was kept at the optimum pH of 10.9, catalyst dosage of 3.75g/l, initial dye concentration of 38.7 ppm and reaction time of 100 minutes. The ratio $\ln\dfrac{A}{A_0}$ was plotted against time and the results are shown in Figure 4.13.

$$\ln\frac{A}{A_0} = -K_1 t \ldots\ldots.. \text{equation 3.5}$$

The slope of the graph was evaluated and found to be -0.025. Therefore pseudo first order reaction constant is 0.025 min^{-1}. The data points in the graph fits a straight line with a R^2 of 0.9927. It is evident that the photo degradation process follows first order kinetics well.
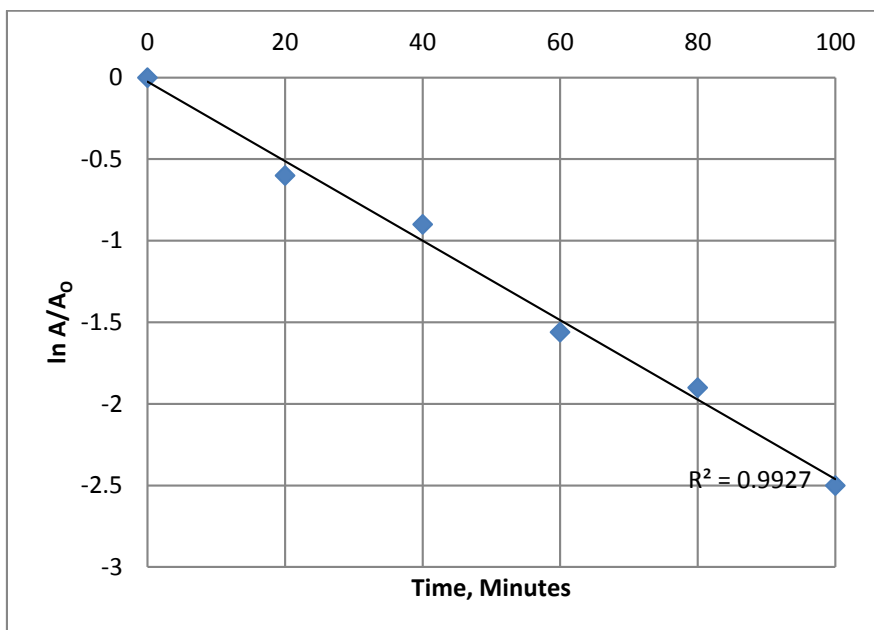
Figure 4.12: First order kinetics for the photo-degradation process

The reaction was tested to determine whether it was modeled by Langmuir-Hinshelwood (L-H) isotherm described by equation 3.8. The initial reaction rate, r_o was evaluated from the slope of the tangent of concentration-time graph at the beginning of the reaction for every initial concentration. The catalyst dosage was kept constant at 3.75g/L, pH at 10.9 and reaction time at 100 minutes. The absorbance of the samples was read off at 10 minute time interval and the concentration of the sample interpolated from the graph shown in Figure 4.2. The concentration-time graphs are presented in Figures 4.14 - 4.18.
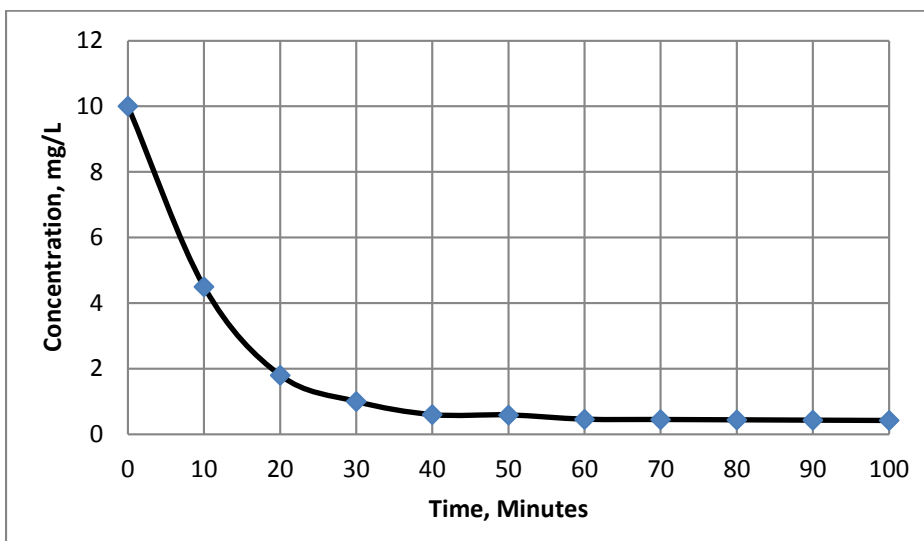
Figure 4.13: **Concentration-time graph for initial concentration of 10 mg/L (ppm)**
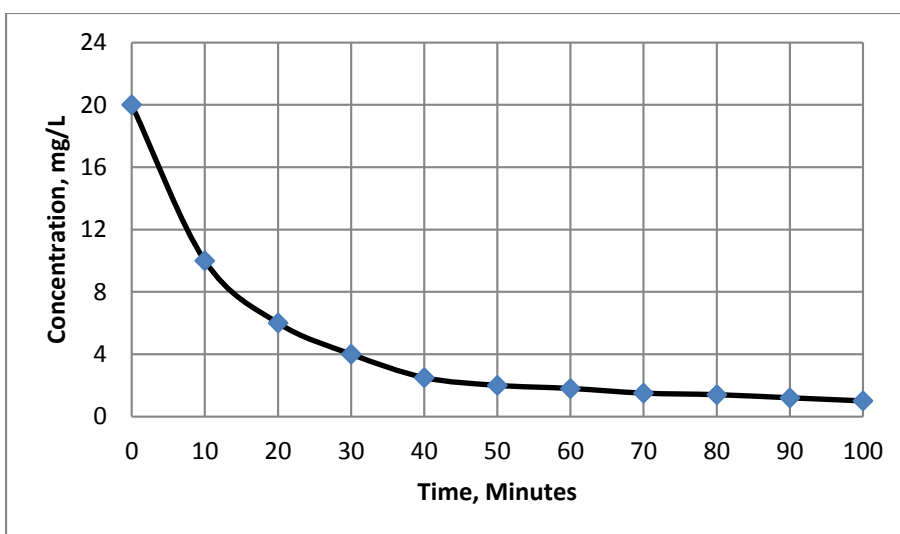
Figure 4.14: Concentration-time graph for initial concentration of 20 mg/L (ppm)
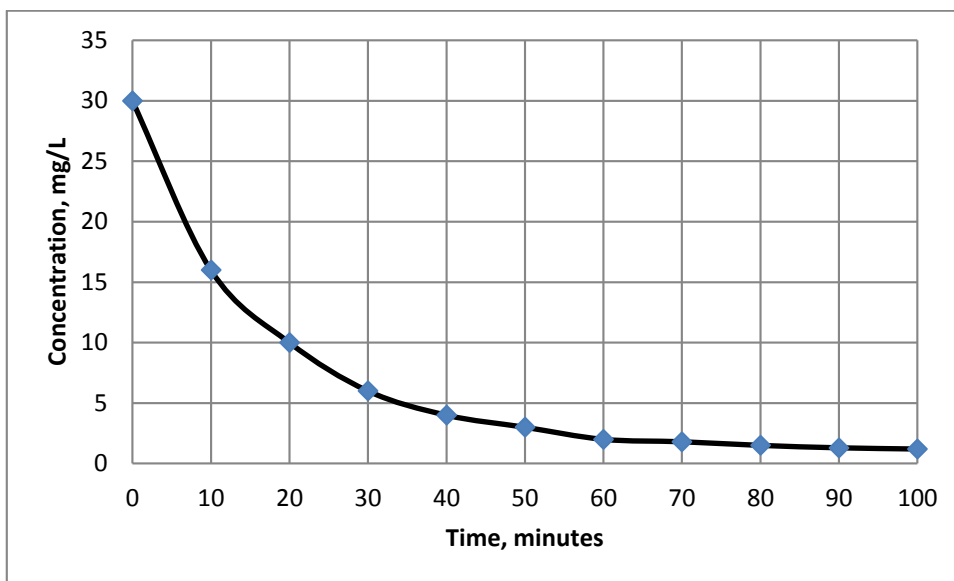
Figure 4.15: Concentration-time graph for initial concentration of 30 mg/L (ppm)
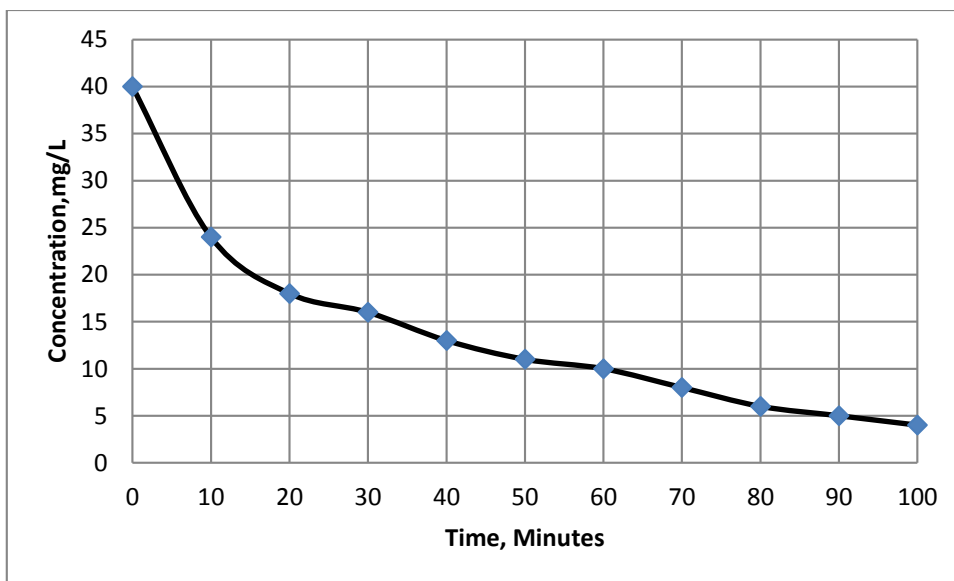
Figure 4.16: Concentration-Time graph for initial concentration of 40 mg/L (ppm)
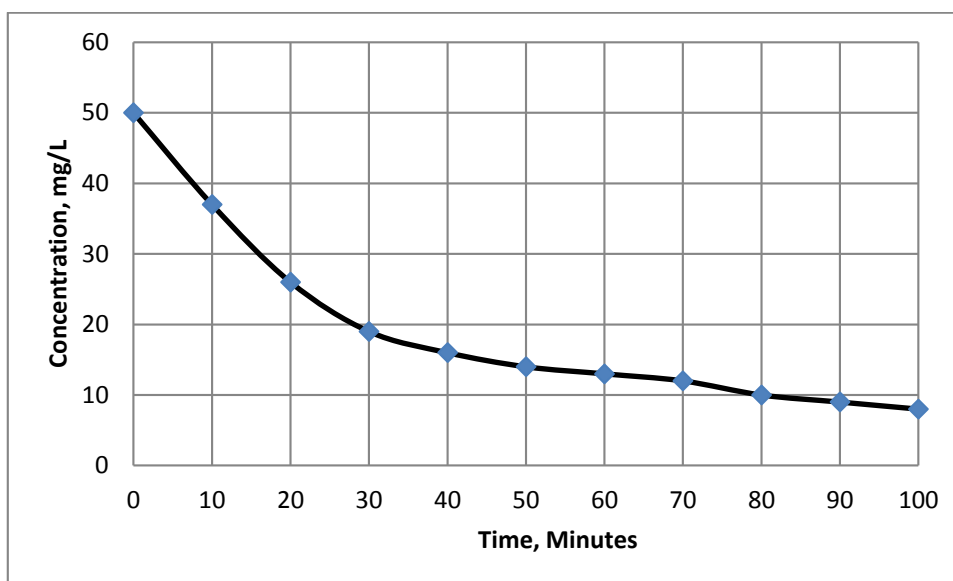
Figure 4.17: Concentration-time graph for initial concentration of 50 mg/L (ppm)

The slope of the tangent at the start of each concentration-time graph gives the initial rate of reaction, r_o for each initial dye concentration, C_o. The results are shown in Table 4.4.

Table 4.4: Initial reaction rate and initial concentration of the dye

C_0, (mg/l)	r_o, (mg/l.min^{-1})	$1/C_0$,(l/mg)	$1/r_0$, (l.min/mg)
10	0.77	0.1	1.3
20	1.33	0.05	0.75
30	1.54	0.033	0.65
40	1.92	0.025	0.52
50	1.50	0.02	0.67

The values of $1/r_0$ were plotted against $1/C_0$ and the graph shown in Figure 4.19 was obtained.
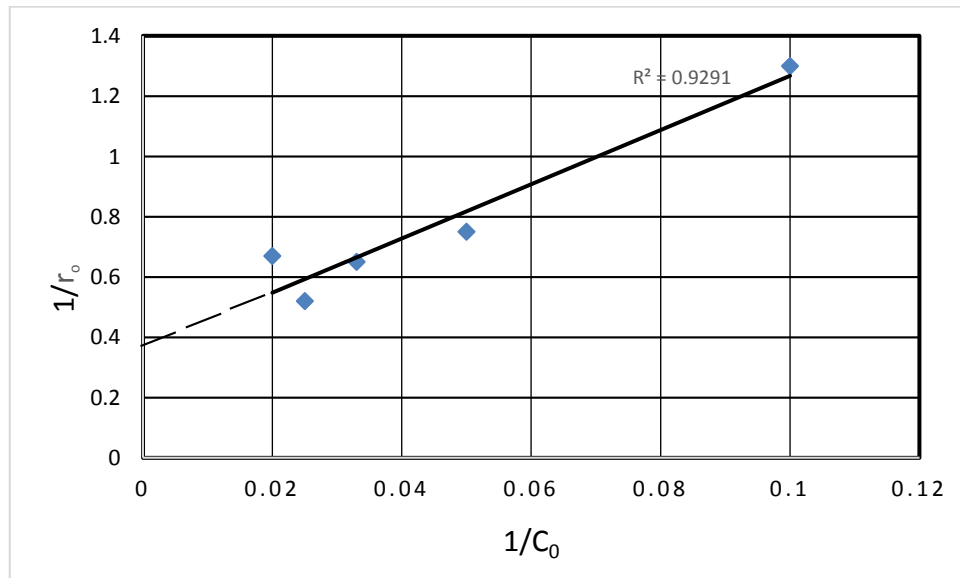
Figure 4.18: Graph to test L-H adsorption isotherm

From the graph it can be seen that the reaction fits the L-H adsorption isotherm well with R^2 statistic of 0.9291. In order to determine the reaction rate constant, k_r the line in the graph is extended as shown in Figure 4.19 to cut the y-intercept. The y-intercept of the line was found to be 0.38 and the slope, 9.189.

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K C_0} \ldots \ldots \text{equation 3.8}$$

Therefore,

$$\frac{1}{k_r} = 0.38$$

Therefore the reaction rate constant, $k_r = 2.632$ mg/Lmin

$$\frac{1}{k_r K} = \text{slope} = 9.189$$

Substituting for k_r, the value of K becomes 0.0413.

Therefore, adsorption rate constant, K = 0.0413 L/mg.

The Langmuir-Hinshelwood adsorption isotherm is used to describe the reactions occurring at the solid-liquid interface. This means that the dye is adsorbed onto the surface of the catalyst before the surface reaction takes place. In this reaction process, the surface reaction is the slowest process and therefore rate limiting. Adsorption of the reactants and desorption of the products from the catalyst surface takes place at a faster rate. The design of a photo catalytic reactor for this heterogeneous system should therefore be based on the L-H adsorption kinetics.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In this study, silver doped titanium dioxide was used as a catalyst to break down methylene blue waste water under fluorescent light illumination. The parameters investigated include initial pH, initial dye concentration, catalyst dosage and reaction time. It was found that the optimum operating conditions that maximize photo-degradation was a pH of 10.9, initial dye concentration of 38.7ppm, catalyst dosage of 3.75g/l and a reaction time of 102.5minutes. Under these conditions, the photo-degradation was found to be 90%. The COD reduced by 95.5% and the color after degradation was found to be 37 platinum cobalt units in line with Environmental management quality standards. The COD after degradation was found to be 46 mg/l implying that there was a significant mineralization of the dye effluent.

The catalyst was re-used three times without appreciable loss of its catalytic activity. The use of silver-doped titanium dioxide as a catalyst is an attractive option because it can be recovered after the reaction process, regenerated and re-used for degradation. It is a clean technology because it breaks down the dye into less harmful compounds. Doping the titanium dioxide with silver greatly enhanced the excitation energy of the catalyst into the visible region. The study of reaction kinetics showed that the reaction process is first order and fits into the Langmuir-Hinshelwood adsorption isotherm implying that adsorption of the dye onto the catalyst surface happens before the surface reaction.

5.2 RECOMMENDATIONS

More research need to be done on doped immobilized catalyst illuminated by visible light in the treatment of textile dyes because it will save a lot of cost involved in catalyst recovery. Other variables like the dopant concentration and light intensity need to be investigated to bring more light into the subject. Pilot plant design and process development should be done before actual full scale implementation.

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APPENDICES

Appendix A: Operation Worksheet

Table A.1: Operation Experimental Worksheet

Standard Order	Run Order	Blocks	Initial pH	Initial Dye concentration	catalyst dosage	Reaction time	Percentage degradation
41	1	3	5	40	2	96	34.1
48	2	3	7	30	3	72	71.0
31	3	3	5	20	2	48	35.9
35	4	3	5	20	4	48	37.3
45	5	3	5	40	4	96	39.0
34	6	3	9	40	2	48	72.0
33	7	3	5	40	2	48	35.7
49	8	3	7	30	3	72	70.9
42	9	3	9	40	2	96	80.7
44	10	3	9	20	4	96	82.0
43	11	3	5	20	4	96	36.6
40	12	3	9	20	2	96	75.0
32	13	3	9	20	2	48	70.0
36	14	3	9	20	4	48	72.1
50	15	3	7	30	3	72	70.1
47	16	3	7	30	3	72	70.2
39	17	3	5	20	2	96	31.0
38	18	3	9	40	4	48	74.0

37	19	3	5	40	4	48	36.2
46	20	3	9	40	4	96	86.7
18	21	1	7	30	3	72	71.0
4	22	1	9	40	2	48	72.1
12	23	1	9	40	2	96	80.7
11	24	1	5	40	2	96	34.0
10	25	1	9	20	2	96	75.0
7	26	1	5	40	4	48	36.3
15	27	1	5	40	4	96	38.8
16	28	1	9	40	4	96	88.0
13	29	1	5	20	4	96	36.6
9	30	1	5	20	2	96	31.0
2	31	1	9	20	2	48	69.5
8	32	1	9	40	4	48	74.0
14	33	1	9	20	4	96	81.7
6	34	1	9	20	4	48	72.0
5	35	1	5	20	4	48	37.3
1	36	1	5	20	2	48	35.9
3	37	1	5	40	2	48	35.6
20	38	1	7	30	3	72	71.0
17	39	1	7	30	3	72	71.0
19	40	1	7	30	3	72	70.9
29	41	2	7	30	3	72	71.0
26	42	2	7	30	5	72	65.0

24	43	2	7	50	3	72	66.7
28	44	2	7	30	3	120	62.0
21	45	2	3	30	3	72	6.5
23	46	2	7	10	3	72	59.4
30	47	2	7	30	3	72	71.0
27	48	2	7	30	3	24	54.0
22	49	2	11	30	3	72	87.0
25	50	2	7	30	1	72	57.6
53	51	4	7	10	3	72	59.5
59	52	4	7	30	3	72	71.0
56	53	4	7	30	5	72	65.0
52	54	4	11	30	3	72	87.0
55	55	4	7	30	1	72	57.6
51	56	4	3	30	3	72	6.5
54	57	4	7	50	3	72	66.7
58	58	4	7	30	3	120	62.0
60	59	4	7	30	3	72	71.0
57	60	4	7	30	3	24	54.0
73	61	5	5	20	4	96	36.6
68	62	5	9	40	4	48	74.0
61	63	5	5	20	2	48	36.0
67	64	5	5	40	4	48	36.3
62	65	5	9	20	2	48	69.5
77	66	5	7	30	3	72	71.0

69	67	5	5	20	2	96	31.0
74	68	5	9	20	4	96	82.0
63	69	5	5	40	2	48	35.6
76	70	5	9	40	4	96	87.0
79	71	5	7	30	3	72	71.0
65	72	5	5	20	4	48	37.0
70	73	5	9	20	2	96	75.0
64	74	5	9	40	2	48	72.0
72	75	5	9	40	2	96	80.6
71	76	5	5	40	2	96	34.0
75	77	5	5	40	4	96	38.8
78	78	5	7	30	3	72	71.0
66	79	5	9	20	4	48	72.0
80	80	5	7	30	3	72	71.0
81	81	6	3	30	3	72	6.5
86	82	6	7	30	5	72	65.0
82	83	6	11	30	3	72	87.0
90	84	6	7	30	3	72	70.9
84	85	6	7	50	3	72	66.7
83	86	6	7	10	3	72	59.4
85	87	6	7	30	1	72	57.6
87	88	6	7	30	3	24	54.0
88	89	6	7	30	3	120	62.0
89	90	6	7	30	3	72	71.0

Appendix B: Experimental Pictorials

Figure B.1: Titanium isopropoxide solution and Drying oven

Figure B.2: Furnace used to calcine the catalyst

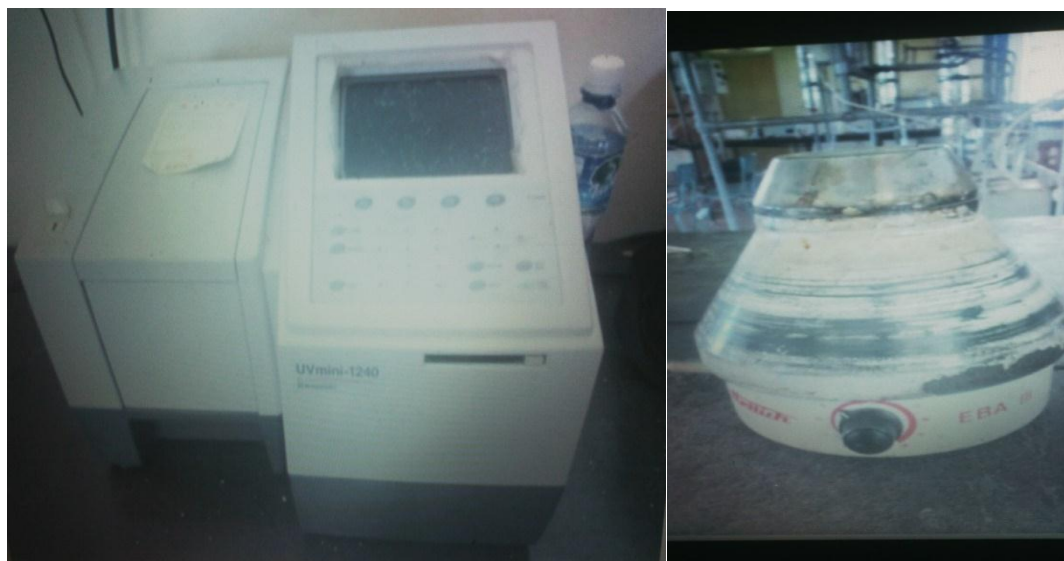**Figure B.3: UV spectrophotometer and Centrifuge**

a)   b)   c)

a) Methylene blue waste water after dyeing of acrylic fibre; b) Dyeing of acrylic fibre; c) UV Spectrophotometer for color determination`

Figure B.4: Waste water and UV spectrophotometer for color determination

a)   b)   c)

a) Samples before and after degradation; b) Vials used for COD determination; c) COD block digester

Figure B.5: Samples, sample vials and COD Digester

Figure B.6: Custom made photo-catalytic reactor.