

Chapter One

Basic Concepts

1.1 Introduction:

The twenty-first century is being called the environment century. There has been an intensification of global warming as well as air and water pollutants including toxic organic compounds like chlorinated and nonchlorinated aliphatic and aromatic compounds, dyes, detergents and surfactants, agro wastes like insecticides, pesticides and herbicides, disinfection byproducts, volatile organic compounds, plastics, inorganic compounds like heavy metals, noxious gases like NO_x , SO_x , CO and NH_3 , and pathogens like bacteria, fungi and viruses associated with industrialization; this is due in a large part to the rapid economic growth of developing countries such as China, first and foremost, and then India and Brazil. In addition, a new strain of influenza has spread throughout the world, becoming a major social issue. Photocatalyst technology is said to be an environmental cleanup technology. Using the natural energy of sunlight, it contributes to the cleaning of air and water, and it is attracting attention as an approach to environmental cleanup by fighting bacteria and providing sterilization to combat influenza and other outbreaks of illness [1].

The word photocatalysis is a composite word which is composed of two parts, “photo” and “catalysis”. Catalysis is the process

where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy.

Generally, photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself. In other words, the photocatalyst is the substance which can modify the rate of chemical reaction using light irradiation [2].

Photocatalysis is a process that can be used to destroy pollutant. It refers to the acceleration of threats of chemical reactions (oxidation/reduction) brought about by the activation of a catalyst, usually a semiconductor oxide, by ultraviolet (UV) or visible radiation.

1.2 Brief history of photocatalysis:

There is generally a conception that Photocatalysis originated with the discovery of Photoelectrochemical decomposition of water by Fujishima and Honda in 1972. In 1921, years ago from Fujishima and Honda, Renz reported that titania was partially reduced when it was illuminated with sunlight in the presence of organic substrates like glycerol. In 1924, Baur and Perret probably were the first to report the photodecomposition of silver salt on ZnO to produce metallic silver. Probably Baur and Neuweiler were the first to recognize that both oxidation and reduction are taking

place simultaneously on the production of hydrogen peroxide on ZnO. This was followed by the work of Renz in 1932 who reported the photocatalytic reduction of silver nitrate and gold chloride on TiO₂. Goodeve and Kitchener studied the photocatalytic decomposition of dye on titania surfaces and even reported the quantum yields. In 1953, it has been recognized that the organic substrate was oxidized and oxygen was reduced [3].

All these studies culminated in the photoelectrochemical decomposition of water by Fujishima and Honda which opened up means for solar energy conversion and also for the generation of hydrogen fuel. Fujishima and Honda discovered the first photocatalytic water splitting simultaneously oxidized to oxygen and reduced to hydrogen, when a bias potential is applied to an “illuminated” TiO₂ single crystal electrode [3].

The Fujishima - Honda effect is one of the most important discoveries in chemistry and opened up and extensively promoted the research field of photocatalysis, it cannot be an origin of photocatalysis. Actually, reports on photocatalytic oxidation of organic compounds by titania powders had been published before the discovery of this effect. In other words, the paper published in Nature in 1972 is undoubtedly an origin of research activity of photocatalysis but not an origin of heterogeneous photocatalysis in the bibliographic sense. Therefore, it is scientifically incorrect to state that photocatalytic reaction with titania particles was discovered by Fujishima and Honda in 1972 [4].

In 1977, Frank and Bard showed the photocatalytic oxidation of CN^- and SO_3^{2-} using different semiconductor materials like TiO_2 , ZnO , CdS , Fe_2O_3 and WO_3 . This was followed by the demonstration of the TiO_2 catalyzed photodegradation of chlorinated organic compounds by Ollis in the early 1980s. Later, O'Regan and Grätzel, in 1991, showed the first high efficiency solar cell based on dye-sensitized colloidal TiO_2 films for photovoltaic power generation. Among the different approaches for pollutants removal from water, some of them are recognized as mainly efficient for pesticide degradation. Ozonation and ozone related processes ($\text{O}_3/\text{H}_2\text{O}_2$, UV/O_3), heterogeneous photocatalysis (TiO_2/UV), homogeneous photocatalysis (Fenton and Fenton-like processes) and electrochemical oxidation are considered as the most efficient for pesticide degradation in water (Somich et al., 1990; Scott). Thus, a brilliant start in TiO_2 photocatalysis was followed by some notable developments including, metal ion doped TiO_2 (1994), super hydrophilic TiO_2 films (1997), anion doped TiO_2 (2001), and visible light responsive TiO_2 thin films for large scale water splitting (2006) [5].

Photocatalysis is widely employed in water and air purification, self-cleaning surfaces, self sterilizing surfaces, antifogging surfaces, anticorrosive surface treatments, lithography, photochromic materials, microchemical systems, selective and green synthesis of organic compounds, and the generation of hydrogen. Photocatalysis, as a research area, has witnessed a sea change over the past two decades with significant advancements

being made in the synthesis of novel materials and nano-structures, and the design of efficient processes for the degradation of pollutants and the generation of energy. This is evident from the evolution of the number of international journal publications since 1990 to the current date, as depicted in Figure (1-1) which shows that there is an exponential growth in the publications and hence the knowledge in photocatalysis [5].

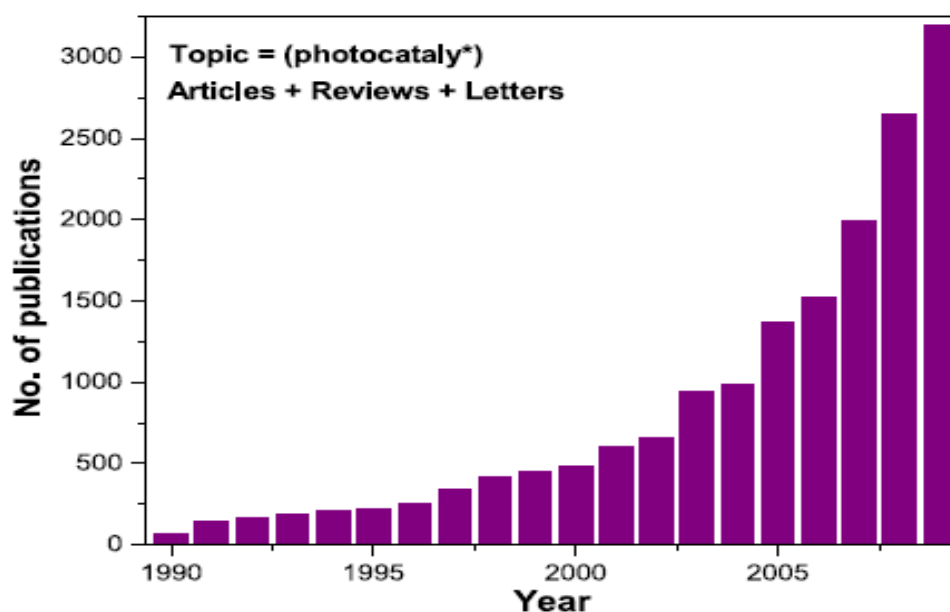


Figure (1-1): Evolution of international journal publications in the field of photocatalysis since 1990.

1.3 Mechanism of UV photocatalysis:

Semiconductor photocatalysis is initiated by electron-hole pairs after band gap excitation. When semiconductor photocatalysis is illuminated by light with energy equal to or higher than 3.2 eV (wavelengths lower than ~ 390 nm). Generation of excited high energy states of electron and hole pairs occurs when wide band gap semiconductors are irradiated higher than their band gap

energy, the valence band electrons (e_{CB}^-) can be excited to the conduction band, leaving a positive hole (h_{VB}^+) in the valence band. The excited electron-hole pairs can recombine, releasing the input energy as heat, with no chemical effect. However, if the electrons (and holes) migrate to the surface of the semiconductor without recombination, they can participate in various oxidation and reduction reactions with adsorbed species such as water, oxygen, and other organic or inorganic species. These oxidation and reduction reactions are the basic mechanisms of photocatalytic water/air remediation and photocatalytic hydrogen production, respectively. The h_{VB}^+ reacts with organic compounds resulting in their oxidation producing CO_2 and H_2O as end products. The h_{VB}^+ can also oxidize organic compounds by reacting with water to generate $\cdot OH$. Hydroxyl radical ($\cdot OH$) produced by has the second highest oxidation potential (2.80 V), which is only slightly lower than the strongest oxidant fluorine. Due to its electrophilic nature (electron preferring), the $\cdot OH$ can non-selectively oxidize almost all electron rich organic molecules, eventually converting them to CO_2 and water. A simplified mechanism for photocatalytic process on a semiconductor is presented in Figure (1-2) [7].

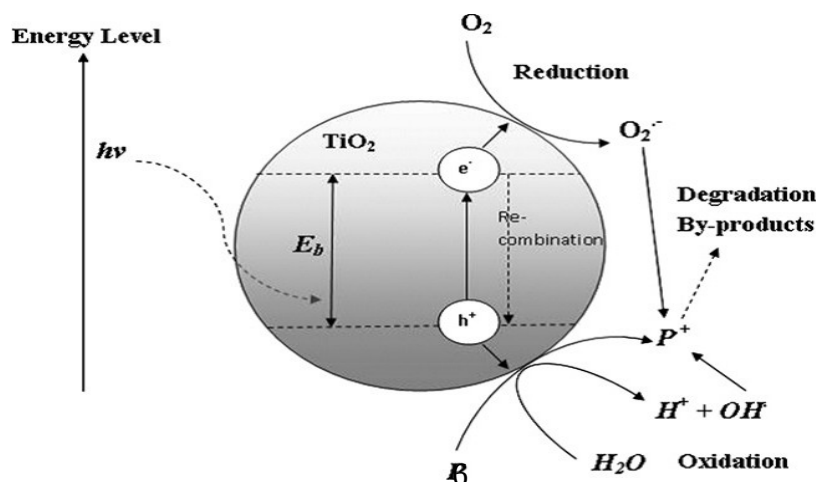
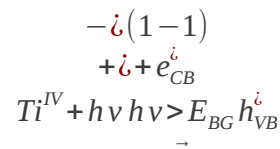


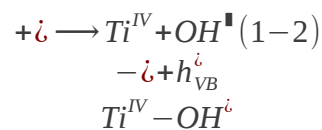
Figure (1.2): The mechanism of photocatalysis using TiO₂ in presence of UV light.

The following steps provide a detailed mechanism of photocatalytic degradation of organic compounds, which is well documented. While TiO₂ has been used as the semiconductor photocatalyst for the sake of representation, most of the following reactions are applicable for other semiconductor photocatalysts as well [5].

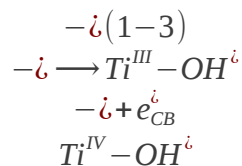
□ charge carrier generation:



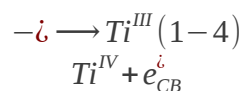
□ charge carrier trapping:



□ surface trap:

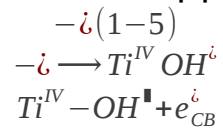


□ deep trap:

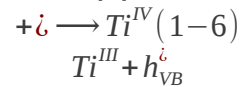


□ electron-hole recombination:

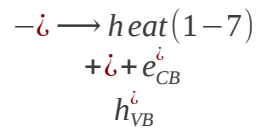
- free electron with a trapped hole:



- free hole with a trapped electron:

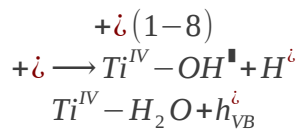


- free hole with free electron:

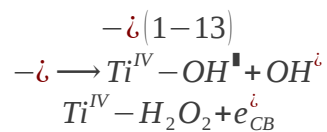
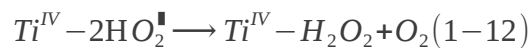
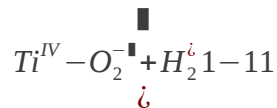
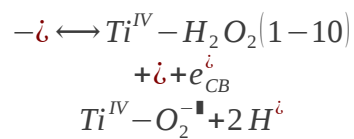
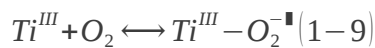


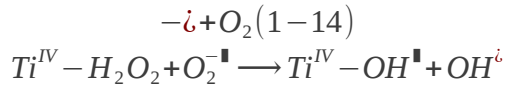
- generation of hydroxyl radicals in the aqueous medium:

- hole pathway:



- electron pathway :

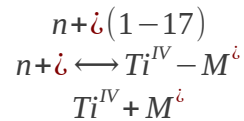




- adsorption-desorption of a reductant (any organic substrate S):

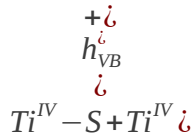


- adsorption-desorption of an oxidant (eg. metal ion):

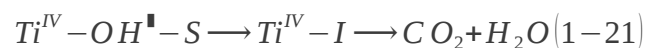
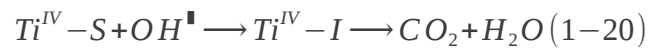
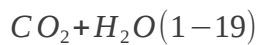
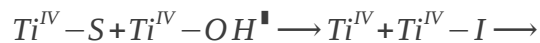


- photooxidation of a reductant:

- direct hole attack:



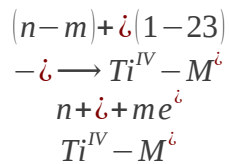
- hydroxyl radical attack:



- adsorption-desorption of the organic intermediate:



□ photoreduction of a metal ion:



In all the above reactions, **Ti^{IV}** denotes the four coordinated surface functionality of TiO₂ or the “active site” and **I** denote organic intermediates. The charge carriers thus generated gets trapped to the TiO₂ surface, which occurs over a time scale of tens of nano seconds (ns).

Reaction (1-2) represents the trapping of the holes by the surface hydroxyl groups present in TiO₂, while reactions (1-3) and (1-4) represent the reversible trapping of the electrons in the surface of TiO₂ (shallow traps), and the irreversible trapping or relaxation of the electrons to the bottom of the CB (deep traps), respectively. Reactions (1-5) – (1-7) represent the electron-hole recombination reaction, which occurs at surface states of the TiO₂, or in the bulk medium due to the delocalization of the electrons and holes. This is one of the detrimental reactions in photocatalysis as this affects the interfacial charge transfer processes and hence the quantum efficiency of the photoprocess. Reaction (1-8) represents the generation of hydroxyl radicals (OH[•]) by the reaction of surface adsorbed water molecules with the holes, and reactions (1-9) – (1-14) show the formation of superoxide (O⁻²), hydroperoxy (HOO[•]) and hydroxyl species through the electron pathway. All the above

radical species are referred to as the “active species”. When the reactions are carried out in non-aqueous (organic) medium, the surface bound hydroxyl species present in the semiconductor plays a major role (reaction (1-2)), and the contribution of reactions (1-8)-(1-14) for the overall oxidation of the substrate is negligible. Once the active species are generated, the reactants are adsorbed onto the surface of the photocatalyst (reactions (1-15) - (1-17)). This is followed by the oxidation of the reductant and the concomitant reduction of the oxidant by the attack of the hydroxyl radicals and CB electrons, respectively (reactions (1-18) -(1-21)) [4].

The above two processes occur at characteristic time scales of 100 ns and milliseconds, respectively. This means that, the oxidizing power of the VB hole or the hydroxyl radicals is always higher than that of the reducing power of the CB electrons. Moreover, these interfacial electron transfer steps compete with the electron-hole recombination reaction (10 ns) and hence, the practical efficiency or quantum yield is always lesser than that of the theoretical yield. The organic compounds degrade through the formation of intermediates (I), which transform finally to CO₂ and H₂O. Reaction (1-22) shows that the products desorbed from the surface thereby freeing the TiO₂ active site. Similarly, when metal ions are present in the system, they are reduced to their thermodynamically stable oxidations states by the CB electrons (reaction (1-23)). Therefore, the overall photocatalysis reaction can be depicted as follows, wherein, the oxidants are reduced and

the reductants are oxidized by the action of UV radiation on the semiconductor photocatalyst.



Photocatalysis has become an integral part of the advanced oxidation processes (AOPs), i.e., processes which employ oxidizing agents like hydrogen peroxide (H₂O₂), ozone (O₃) and Fenton's reagent (H₂O₂ + Fe²⁺) for the effective detoxification of the pollutants. Invariably, the above oxidants are used in conjunction with UV radiation and/or photocatalysis in order to accelerate the rate of degradation of the pollutants. Recently, ultrasound (US), microwave radiation and electrolysis are being coupled to the above AOPs in order to further enhance the decomposition of the pollutants. A common feature that all the above advanced oxidation processes (AOPs) share is the generation of reactive hydroxyl radicals (OH[•]), which are the precursors of degradation of any organic or inorganic compound. These hydroxyl species possess a higher oxidation potential (2.80V) compared to the other common oxidants like atomic oxygen (2.42 V), O₃ (2.07 V), H₂O₂ (1.78 V), hydroperoxy radicals (1.70 V) and chlorine dioxide (1.57 V). Thus the hybrid AOPs, which involve a combination of two or more techniques, aim to synergistically produce more hydroxyl radicals to effectively degrade the pollutants [4].

1.4 Semiconductor photocatalytic materials:

A wide range of semiconductors may be used for photocatalysis, such as TiO₂, ZnO, MgO, WO₃, Fe₂O₃, CdS. The ideal photocatalyst should possess the following properties (i) photoactivity, (ii)

biological and chemical inertness, (iii) stability toward photocorrosion, (v) suitability towards visible or near UV light, (vi) low cost, and (vi) lack of toxicity. TiO_2 is known to have an excellent pigmentary properties, high ultraviolet absorption and high stability which allow it to be used in different applications, such as electroceramics, glass and in the photocatalytic degradation of chemicals in water and air. It has been used in the form of a suspension, or a thin film in water treatment. According to the thermodynamic requirement, the VB and CB of the semiconductor photocatalyst should be positioned in such a way that, the oxidation potential of the hydroxyl radicals ($E_0(\text{H}_2\text{O}/\text{OH}^\bullet) = 2.8 \text{ V vs NHE}$) and the reduction potential of superoxide radicals ($E_0(\text{O}_2/\text{O}_2^{\bullet-}) = -0.28 \text{ V vs NHE}$), lie well within the band gap. In other words, the redox potential of the VB hole must be sufficiently positive to generate hydroxyl radicals and that of the CB electron must be sufficiently negative to generate superoxide radicals. Figure (1-3) depicts the band structure diagram of different materials, along with the potentials of the redox couples.

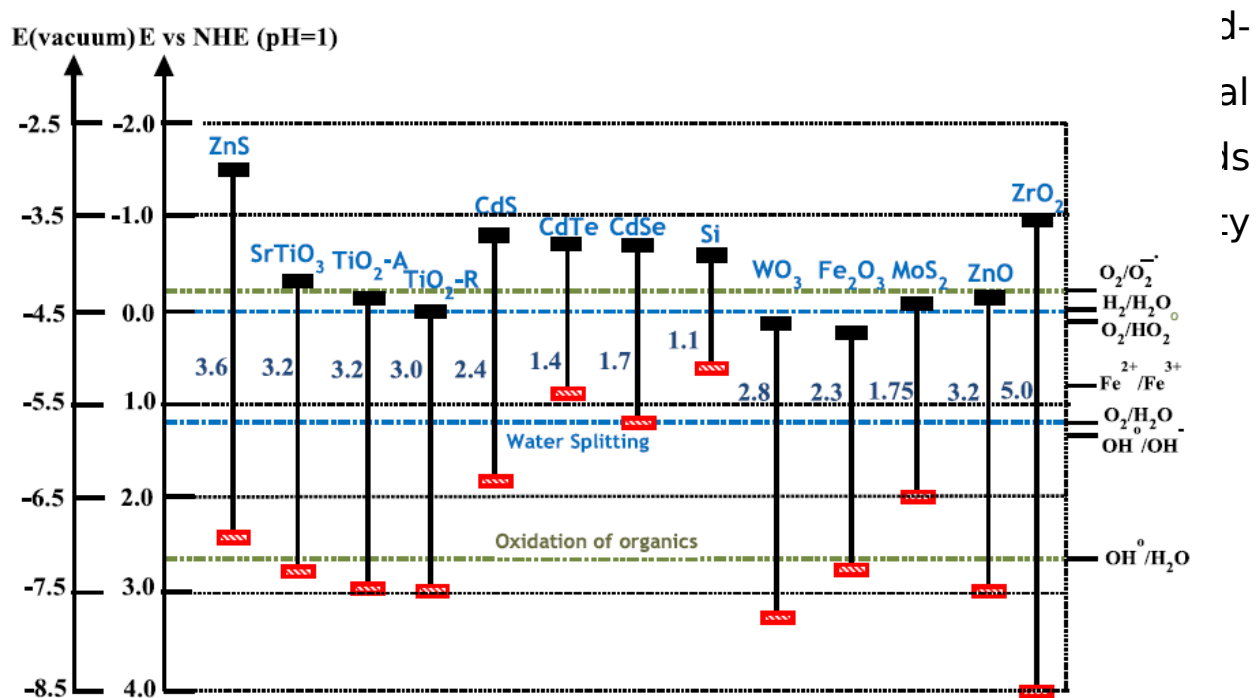


Figure (1.3): The energy band gap and band edge positions of different semiconductors, along with selected redox potentials.

Table (1-1): The band gap energy and wavelength sensitivity of semiconductors.

Semiconductors	E_{BG} (eV)	λ (nm)
Fe ₂ O ₃	2.3	539
TiO ₂ (rutile)	3.0	413
TiO ₂ (anatase)	3.2	388
WO ₃	2.8	443
ZnO	3.2	388

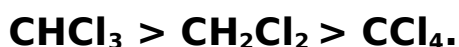
1.5 UV photocatalytic degradation of organic compounds:

An organic compound is any of a large class of chemical compounds whose molecules contain carbon, with the exception of carbides, carbonates, Cyanides and carbon oxides. Organochlorine compounds like dichloromethane (CH_2Cl_2), chloroform (CHCl_3), carbon tetrachloride (CCl_4) and trichloroethylene (TCE, C_2HCl_3) were, in fact, the first organic pollutants to be degraded using photocatalysis. These toxic organic compounds are widely used as solvents, pesticides, refrigerants, and in plasticizers and plastics [10].

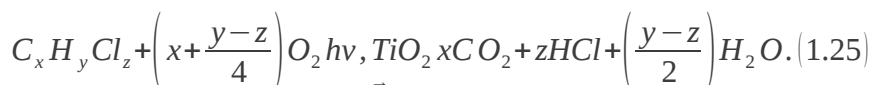
The photo-transformation of a compound in surface water may result from light absorption by the pollutant itself (direct photolysis) or may be photo-induced by the dissolved natural organic matter or nitrate ions present in water, as these chromophores are known to photoproduce reactive species (indirect photolysis). In an aquatic environment, the processes of direct and indirect photolysis occur concurrently. The presence of microorganisms, algae or humic substances accelerates photochemical reactions due to the fact that these components are capable of absorbing sunlight. Some non-ionic organic compounds, particularly pesticides, undergo photodegradation much faster in the presence of photosynthesising microorganisms. The photocatalytic activity of TiO_2 is greatly influenced by the crystalline form (anatase or rutile), and the size of the particles. This of course also is important for water

purification processes. According to Yu et al in his studied of Characterization, activity and kinetics of a visible light driven photocatalyst in 2010, TiO_2 has been applied as a promising environmentally friendly photo catalyst in many fields such as environmental remediation, hydrogen production and solar energy utilization. It is valued for its chemical stability, lack of toxicity and low cost [11].

Photocatalytic oxidation with TiO_2 , catalyst is of equivalent oxidizing power to OH radical reactions in aqueous solution. The reaction may be driven by electrically powered U.V. or natural solar U.V to destroy organic pollutants in water with the formation of harmless mineral products. The catalyst may be used in free suspension or immobilized. The degradation of TCE involved the formation of trichloroacetaldehyde as the intermediate. They found that chloride ions generated during the degradation inhibits the conversion of the above compounds. The orders of degradation exhibited by the chloromethane follow:



A general stoichiometric reaction for the photocatalytic degradation of the organo-chlorine compounds can be written as:



Many studies have been devoted to the photocatalytic degradation of chlorinated aromatic compounds like chlorophenols and chlorobenzenes, chlorinated pesticides like DDT, hexachlorobenzene, atrazine and parathion, surfactants like

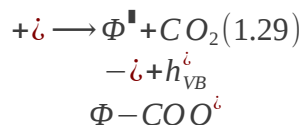
sodium dodecyl benzene sulfonate and trimethyl phosphate, aliphatic and olefinic compounds, dyes, nitrogenous compounds like nitrophenols and nitrobenzenes, carboxylic acids, alcohols and heteroatom compounds[12].

In the following subsection, the photocatalytic degradation of common water pollutants, like dyes and pesticides, are discussed.

1.5.1 Dyes:

photocatalytic degradation in recent years has attracted increasing attention as cleaner and greener technology for removal of toxic organic and inorganic pollutants in water and wastewater . Semiconductor photocatalysis appears to be a promising technology that has a number of applications in environmental system such as air purification, water disinfection, water purification, and hazardous waste remediation. TiO_2 catalyzed photochemical degradation of organic pollutants in general, and a dye in particular in wastewater is a favored and promising technique. The organics are completely mineralized into H_2O and CO_2 without generating any harmful byproducts. This technique has been employed for the photomineralisation of large number of dyes such as methylene blue, direct acid dyes, azo dyes and reactive black. The photocatalytic degradation of organic compounds on TiO_2 has been analysed in terms of Langmuir-Hinshelwood kinetics for the compound (Mathews, 1988; Pruden and Ollis, 1983; Hsiao et al., 1983; Ollis et al., 1984; Sabate et al., 1991; Hidaka et al., 1992) [13]. However, despite its promise, the development of a practical treatment system based on the heterogeneous photocatalysis has not yet been successfully achieved because of many operational parameters

that must be considered. The initial step in the TiO₂ mediated photocatalysed degradation is proposed to involve the generation of electron hole pair, which migrates to the photocatalyst surface to yield hydroxyl and super oxide radical anion. It has commonly accepted that the hydroxyl and super oxide radical's anions can initiate redox processes of the adsorbed substrate. Mechanistically, it is now commonly accepted that the photocatalyst TiO₂ is first excited by UV light and subsequently initiates the photo degradation processes. The degradation of a dye can be characterized in two ways: percent decolorization and percent mineralization. Decolorization refers to the reduction in concentration of the parent dye molecule under consideration at its characteristic wavelength, but does not refer to the complete removal of the organic carbon content. This is due to the formation of colored dye intermediates, which absorb at different wavelengths. Hence, complete degradation or mineralization occurs when all the organic carbon is converted to CO₂. Therefore, analyzing the mineralization of the dyes in terms of the total organic carbon (TOC) content assumes importance. The mechanism of CO₂ evolution follows the photo-Kolbe decarboxylation mechanism [13], which is given by:



Where Φ denotes the organic component of the dye or the dye intermediate. The radical Φ° form as a result of this reaction and can undergo further transformation to yield other intermediates with smaller size.

1.5.2 Pesticides:

Due to the world-wide general application of intensive agricultural methods during the last few decades and to large-scale development of the agrochemical industry, variety and quantities of agrochemicals present in continental and marine natural waters has dramatically increased. Most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions. In recent years, the scientific community has shown a great concern about the possible adverse effects that the presence of these pesticides in water and food may have for human health and for the equilibrium of ecosystems. Such concern, which has recently been highlighted, is supported by results from major monitoring studies already performed over 20 years ago, and confirmed by more recent investigations. Among the possible chronic effects of these compounds are carcinogenesis, neurotoxicity, effects on reproduction and cell development effects, particularly in the early stages of life. With increasing global demand for vegetables, the situation does not look likely to improve. In fact, the current situation might worsen with the appearance of new and more sophisticated Substances. Most pesticides show UV-Vis absorption

bands at relatively short UV wavelengths. Since sunlight reaching the Earth's surface (mainly UV-A, with varying amounts of UV-B) contains only a very small amount of short wave-length UV radiation, the direct photodegradation of pesticides by sunlight is expected to be, in general, of only limited importance. Abundant studies are available, however, with steady state and/or laser-pulsed UV radiation. Direct irradiation will lead to the promotion of the pesticides to their excited singlet states, which may then intersystem cross to produce triplet states. Such excited states can then undergo, among other processes: (i) homolysis, (ii) heterolysis or (iii) photoionization.

Photochemical degradation is one of the major transformation processes and one of the factors controlling the fate of pesticides in the environment. Photodegradation can destroy pesticides on foliage, on the soil surface, and even in the air. Based on the chemical structure, pesticides are classified as organochlorine compounds, organo phosphorous compounds and carbonate compounds, which contain nitrogen, phosphorous, sulfur, chlorine and heterocyclic nitrogen atoms in their molecules. Therefore, the mineralization of the pesticides should result in the conversion of these hazardous compounds to innocuous products of N, S and P, along with CO₂ and H₂O [14].

Many studies have elucidated the pathway of degradation of commonly used pesticides like atrazine, pyridaben, methyl parathion, methamidophos, triazophos, dicofol, etc. using TiO₂, by monitoring the formation intermediates by HPLC/ MS/ MS and GC/

MS techniques. It was found that, during mineralization, phosphorous is converted to orthophosphoric acid (H_3PO_4), nitrogen to NO^{-3} and NH^{+4} ions, and sulphur to SO_2^{-4} ions [15,16].

1.6 Visible light degradation of organic compounds:

Undoubtedly, the first generation TiO_2 or pristine TiO_2 is an efficient photocatalyst in the UV region. Visible light driven photocatalysts are expected to be developed in order to utilize solar and household light for the degradation of pollutants or harmful compounds and water splitting. Visible degradation of volatile organic compounds (VOCs) In the presence of a semiconductor photocatalyst has been extensively studied as a potential method for reducing the severe atmospheric pollution all over the world. TiO_2 acts as a photocatalyst during irradiation by only UV light shorter than around 400 nm because it has a band gap energy of about 3.2 eV of anatase TiO_2 , corresponding to an absorption threshold of 390 nm, restrains its use in the visible range (400–800 nm) for practical applications using solar radiation as the light source. Hence, the second generation TiO_2 photocatalysts encompass a wide variety of the cationic and anionic substituent (or dopants) in TiO_2 , by This way, sunlight and indoor light can be utilized more efficiently in the photocatalytic oxidation (PCO) process Doping of anions (N, F, C, S etc.) in TiO_2 crystalline could shift its photo response into visible light spectrum. Unlike metal ions (cations), anions are less likely to

form recombination centers and, therefore, are more effective at enhancing photocatalytic activity [17, 18].

1.7 Literature review:

Wide spread contamination of water by carcinogen materials has been recognized as an issue of growing importance in recent years. All studies are concentrated at how to degrade, remove or reduce pollutants on wastewater. Photocatalysis process is one of most importance methods used to remove the carcinogen materials like phenol, 2,4-dichlorophenol, chlorothalonil and Rohdamine B from pollutant water. It was found that the photocatalysis is efficiency process. The photocatalysis processes used in this research to remove Rohdamine 6G from waste water according to previously studies in the same field. The following articles are published in international journals.

M. A. Gondal, and coworkers studied the laser induced photocatalytic degradation of phenol using WO_3 in 2005 for the first time. Effect of WO_3 concentrations and laser energy on photocatalytic removal of phenol from waste water were studied. They concluded that laser enhanced photo-degradation can be used as an efficient method for the removal of phenol present in waste water [19].

Umar Ibrahim Gaya, in 2010, studied the photocatalytic degradation of 2,4-dichlorophenol in presence of ZnO. The primary process parameters, such as catalyst concentration, 2,4-dichlorophenol concentration and pH, were recommended to be

1.5 g l⁻¹, 50 mg l⁻¹ and PH 7, respectively. Under these experimental conditions, mineralization of DCP 2,4-dichlorophenol was achieved in 180 min [20].

Rajesh J. Tayade, and coworkers in 2007 studied the Photocatalytic degradation of dyes and organic contaminants acetophenone, nitrobenzene, methylene blue and malachite green present in aqueous solutions using nanocrystalline anatase and rutile TiO₂. They calculated the initial rate of degradation to compared the photocatalytic activity of anatase and rutile nanocrystalline TiO₂ for the degradation of different substances under ultraviolet light irradiation. And concluded that the higher photocatalytic activity was obtained in anatase phase TiO₂ for the degradation of all substances as compared with rutile phase of TiO₂ [21].

V. Sakkas, and coworkers studied the photocatalytic degradation of the organophosphorus insecticide diazinon in percence of TiO₂ catalysts under simulated solar irradiation. They found that the insecticide diazinon disappeared after 9.7 minutes under simulated solar irradiation [22].

Falah H. Hussein and Ahmed F. Halbus in july 2012 studied the photocatalytic decolorization of cobalamin in aqueous solution of different types of catalysts including ZnO, TiO₂ (Degussa P25), TiO₂ (Hombikat UV100), TiO₂ (Millennium PC105), and TiO₂ (Koronose 2073) by using UVA source of irradiation and from their results shown that the activity of different types of catalysts used in photocatalytic process was of the sequence: ZnO > TiO₂

(Degussa P25) > TiO₂ (Hombikat UV100) > TiO₂ (Millennium PC105) > TiO₂ (Koronose 2073). They found that the complete decolorization of cobalamin was achieved in less than thirty minutes [23].

1.8 Aim of the work:

The aim of this work is:

- To study the effect of the amount of TiO₂ on the process of photodegradation of Rhodamine 6G in waste water.
- To study the effect of the exposure time of UV light on the process of photodegradation of Rhodamine 6G in waste water.

Chapter Two The Experimental Part

2.1 Introduction:

In this work the effect amount of semiconductor (TiO₂) and the exposure time of UV light (270-280nm) on the photodegradation of Rhodamine 6G in waste water were studied. This chapter presents the materials, the equipments, tools and setup that were used and followed by the experimental procedure.

2.2 The materials:

The materials used in this experiment were:

2.2.1 Titanium dioxide (TiO₂):

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium with chemical formula TiO₂. When used as a pigment, it is called titanium white, Pigment White 6 (PW6). It has a wide range of applications [24].

2.2.1.1 Physical properties and Chemical properties:

Titanium (IV) dioxide, or titania, is a kind of powder whose color is white. Titanium dioxide is a soft solid and melts at 1800 Degrees Celsius. It has special performance, such as insulation, corrosion, flags, etc. It is polymorphous and it exists in three types of crystal structures: (a) rutile, (b) anatase and (c) brookite. It is insoluble in dilute alkali, dilute acid, but soluble in hot concentrated sulfuric acid, hydrochloric acid, nitric acid. The solubility of titanium dioxide is related to solutes. Titanium is insoluble in water. Table (2.1) shows the physical properties of TiO₂.

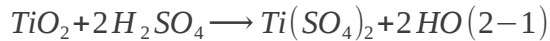
Table (2.1): The physical properties of TiO₂

Atomic mass	47.90 g.mol ⁻¹
Atomic number	22
Density Atomic mass	4.23 g/cm ³ 47.90 g.mol ⁻¹
Melting point	1660 °C
Boiling point	3287 °C

Titanium dioxide is non-toxic and the chemical activity is stable, it almost has no reaction with other materials produce under normal temperature. It is a partial acid sexual oxide. It has no reaction with oxygen, hydrogen sulfide, sulfur dioxide, carbon dioxide and ammonia and is not soluble in water, fatty acids, other organic acids and weak inorganic acids except for alkali and hot nitric acid. But, in some specific conditions, titanium dioxide can get reaction with some substances. For example, these reactions are as follows [25]:

1) Only in the circumstance of long time boiling it may be totally

soluble in strong sulfuric acid and hydrofluoric acid. The reaction equations are as follows:

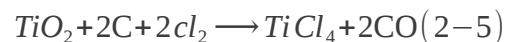


2) Titanium dioxide can melt in the alkali (sodium hydroxide, potassium hydroxide) or alkali metal carbonate (sodium carbonate, potassium carbonate). Any one of which have mentioned with Titanium dioxide can be transformed into soluble acid titanate. For example, Titanium dioxide and sodium hydroxide's reaction equations:



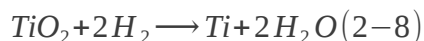
3) At high temperature, if a reductant (carbon, starch, petroleum coke) exists, titanium dioxide can be chlorinated into titanium tetrachloride by chlorine.

The response equation is as follows:



4) Titanium dioxide under high temperature can be restored into Low-valent titanium compounds by hydrogen, Na, Mg, aluminum, zinc, calcium, and some elements of the constant. If we put the dry hydrogen into red titanium dioxide, it can get Ti_2O_3 ; In 2000 °C and 15.2 MPa of hydrogen, it also can get TiO_2 . If the rutile titanium dioxide is injected into the plasma chamber, it will be reduced to titanium metal through hydrogen [25]. The reaction equations are as follows:





2.2.2 Rhodamine 6G:

Rhodamine 6G is known as Rhodamine 590, R6G, Rh6G, C.I. Pigment Red 81, C.I. Pigment Red 169, and Basic Rhodamine Yellow. It is a highly fluorescent Rhodamine family dye and it often used as a tracer dye within water to determine the rate and direction of flow and transport. Rhodamine dyes fluoresce can be detected easily and inexpensively with instruments called fluorometers. Rhodamine dyes are used extensively in spectroscopic applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy and enzyme-linked immunosorbent assay (ELISA) [26].

2.2.2.1 Physical properties and chemical properties:

Rhodamine 6G usually comes in three different forms. Rhodamine 6G chlorides is a bronze/red powder with the chemical formula $\text{C}_{27}\text{H}_{29}\text{ClN}_2\text{O}_3$ and Perchlorate, ($\text{C}_{27}\text{H}_{29}\text{ClN}_2\text{O}_7$), comes in the form of red crystals, while Rhodamine 6G tetrafluoroborate, ($\text{C}_{27}\text{H}_{29}\text{BF}_4\text{N}_2\text{O}_3$), appears as maroon crystals. The molar mass of Rhodamine 6G is 479.02 g/mol. Although is highly soluble in Butanol, Ethanol, Methanol, and water 20 g/l (25 °C), It appears as dark reddish purple, brown or black crystalline solid. Its structure is shown in figure (2- 1)[27].

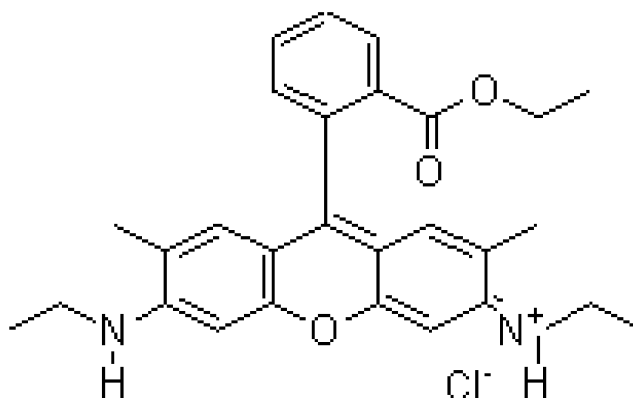


Figure
Chemical
Rohdamine
2.2.2.2

(2.1):
structure of
6G.
Health and

environment effects of Rhodamine 6G:

Toxicology and carcinogenesis studies of Rhodamine 6G were conducted because of potential human exposure resulting from it

when used as a dye for natural and synthetic fibers and in biomedical research and because of the absence of information on Rhodamine 6G toxicity and potential carcinogenicity. Rhodamine 6G can cause severe eye irritation, respiratory tract and skin irritation, might be harmful if absorbed through skin or if swallowed, may be harmful if inhaled, and the laboratory tests indicate that this material may be carcinogenic. Rhodamine 6G is toxic to eukaryotic cell mitochondria and it depending on cellular concentration. In two-stage skin models of carcinogenesis, activation of protein kinase C by a promoter, such as 12-O-tetradecanoyl-phorbol-13-acetate (TPA), it is considered to be an integral event associated with the promotion and development of skin neoplasms (papillomas or carcinomas). O'Brian and Weinstein in (1987) found that Rhodamine 6G inhibited rat brain protein kinase C after activation with the tumor promoter TPA, presumably through a chemical-lipid interaction and the induction of cytotoxicity, but not in the absence of lipid cofactor. There is no reported evidence that Rhodamine 6G inhibits protein kinase C isolated from epidermal cells. However, inhibition of rat brain protein kinase C in vitro suggests Rhodamine 6G should not induce skin neoplasms or promote spontaneously occurring skin neoplasms.[28,29]

2.3 Equipments, tools and setup:

The experimental setup that was used in this work consists of UV light source, magnetic stirrer, glass beaker and spectrometer. Figure (2.2) shows a schematic diagram of the setup arrangement.

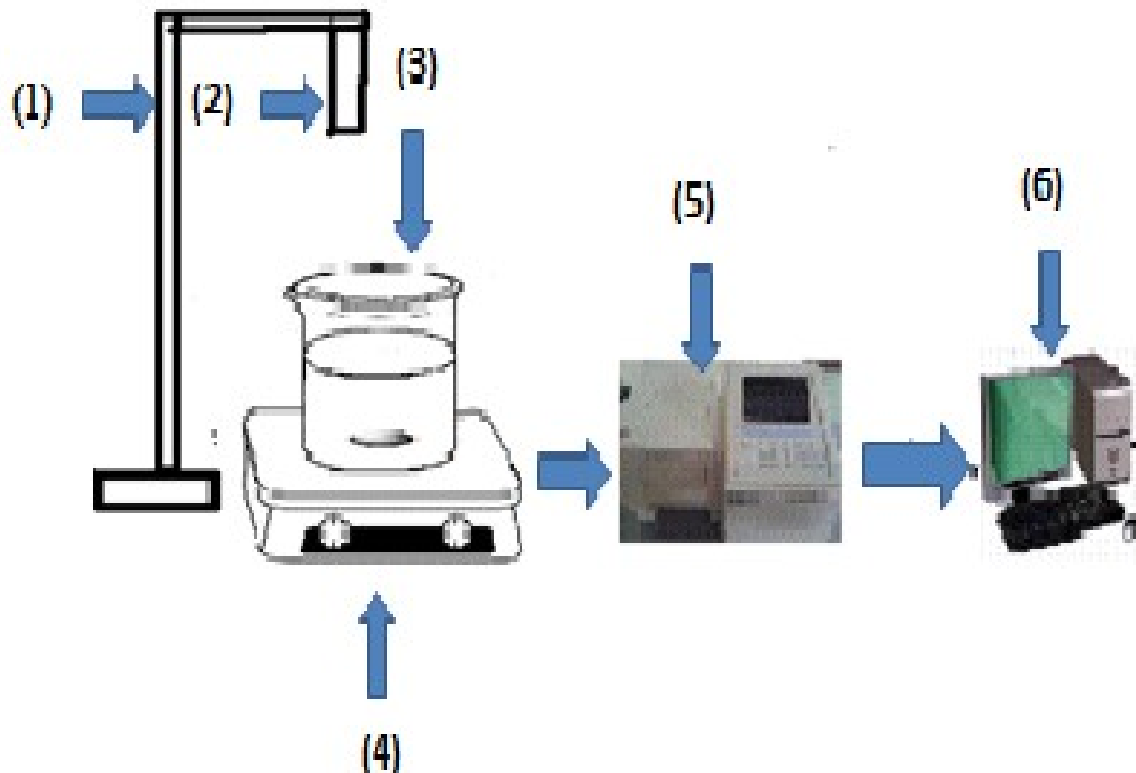


Figure (2.2): Schematic diagram of setup used in this work.

- (1) Holder, (2) The UV light source, (3) The glass beaker, (4) The magnetic stirrer, (5) The UV/Vis. spectrometer and (6) Computer.

2.3.1 The UV Light Source:

The UV light source used in this work was generating from Multiclear laser device used in derma treatment. It emits a tunable UVB/UVA1/BLUE Light targeted selective phototherapy system for the treatment of multiple medical and aesthetic skin disorders. The UV light is produced using proprietary high-power xenon plasma light source. The Multiclear emits the narrowest effective wavelengths between (270-280 nm).



Figure (2.3): The UV light source.

2.3.2 The Magnetic Stirrer:

The magnetic stirrer device is used to make homogenous solution by mixing the semiconductor powder with the Rhodamine 6G solution. This enables semiconductor molecules to exposure to UV radiation. A rotation field of magnetic force is employed to induce variable speed a stirring action within either closed or opened vessels. The stirring is accomplished with the aid of small permanent magnets sealed in Pyrex glass. This device was manufactured by Scott science and healthcare limited it speed 60 to 1500 pm.

2.3.3 The Glass beaker:

Glass beaker was used to hold the sample during irradiation with capacity 100 ml.

2.3.4 The UV -VIS 1240 Spectrophotometer:

This device was used to measure the absorption of the solutions before and after irradiation by UV light. It is covering a wavelength from 190-1100 nm with auto lamp switch from visible to ultraviolet. The UV-VIS spectrophotometer used here was supplied from SHIMADZU contains a quartz cell of thickness 1 cm as a sample holder. Figure (2-4) shows a photo for this spectrometer.



Figure (2.4): The UV-VIS 1240 spectrometer.

2.3.5 The Experimental methodology:

The experimental work was done in steps as follows:

1. Three samples were prepared by dissolving 7mg from Rhodamine 6G in 100 ml of distilled water.
2. 100mg from semiconductor catalyst (TiO_2) was added to the first sample and then 300mg from the same semiconductor was added to the second sample and finally 600mg of TiO_2 was added to the third sample.
3. A small portion from the first sample was put in the quartz cell and placed in the compartment of the UV spectrometer and the spectrum was recorded and used as references a spectrum.
4. Step (3) was repeated for the second and the third sample, separately.
5. The first sample was irradiated with 750 mJ of UV light with wavelengths of (270-280 nm) and spot size of 4cm^2 for 10 minutes, then the absorption spectrum of this sample was recorded using the UV spectrometer.
6. The above step was repeated with irradiation time of 20 and 30 minutes. The absorption spectra were recorded for the two cases.
7. The second sample was irradiated with 750 mJ of UV light of wavelength (270-280 nm) and spot size of 4cm^2 for 10 minutes,

and then the absorption spectrum of this sample was recorded using the same spectrometer.

8. Step (7) was repeated with irradiation time of 20 and 30 minutes and two more spectra were recorded.
9. The third sample was irradiated with 750 mJ of the same light source with spot size of 4cm² for 10 minutes, and then the absorption spectrum of the sample was recorded.
10. The above step was repeated with irradiation time of 20 and 30 minutes which resulted two more spectra.
11. The effects of the amount of TiO₂ and irradiation times were deduced from the comparison between the intensity of the absorption bands of Rhodamine 6G in the recorded spectra for each case.

Chapter Three

Results and Discussion

3.1 Introduction

This chapter presents the results obtained from the experimental part. In addition that the discussion of the effect of each parameter on the degradation of Rhodamine 6G, will be presented as well.

The results obtained in this study are classified into two categories:

1. The effect of the amount of the semiconductor (catalysis) on the degradation of Rhodamine 6G.
2. The dependence of the degradation of Rhodamine 6G on the irradiation time.

The data concerning the degradation of Rhodamine 6G was obtained for three different irradiation times (10, 20 and 30

minutes), respectively. And three different weights of TiO_2 semiconductor (100, 300 and 600 mg) were added to 100ml of Rhodamine 6G solution. The data presented as absorption spectra in which the intensity of absorption peak of Rhodamine 6G is compared for all irradiation times and all amounts of TiO_2 catalyst.

3.2 Absorption spectrum of Rhodamine 6G in 100 ml of water without irradiation:

The absorption spectrum of Rhodamine 6G was recorded without addition of semiconductor and without irradiation. Seven mg of Rhodamine 6G was dissolved in 100 ml of distilled water. Figure (3-1) shows the absorption intensity verse wavelength for Rhodamine 6G, It can be observed from the figure, Strong absorption occurred at 525nm.

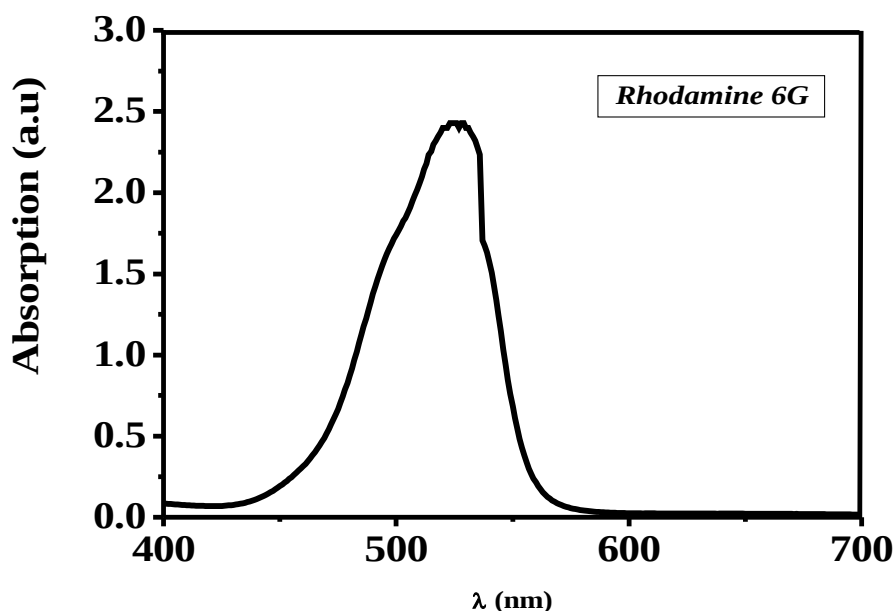


Figure (3.1): the absorption spectrum of Rhodamine 6G in 100 ml of distilled water without irradiation and without semiconductor.

3.3 Absorption spectra of Rhodamine 6G mixed with 100 mg of TiO_2 irradiated by UV light source for different times:

Table (3.1) lists the absorption intensity at 525 nm for different irradiation times and Figure (3.2) shows the absorption spectra of Rhodamine 6G mixed with 100 mg of TiO_2 at different exposure times. It can be observed from the figure (3.2) and table (3.1) the effect of the irradiation time on the degradation of Rhodamine 6G can be noticed through the decrease of the absorption intensity of Rhodamine 6G with time increasing. The decrease in the intensity of the peak at 525nm means that the amount of Rhodamine 6G was decreased due to its degradation because of photocatalysis process.

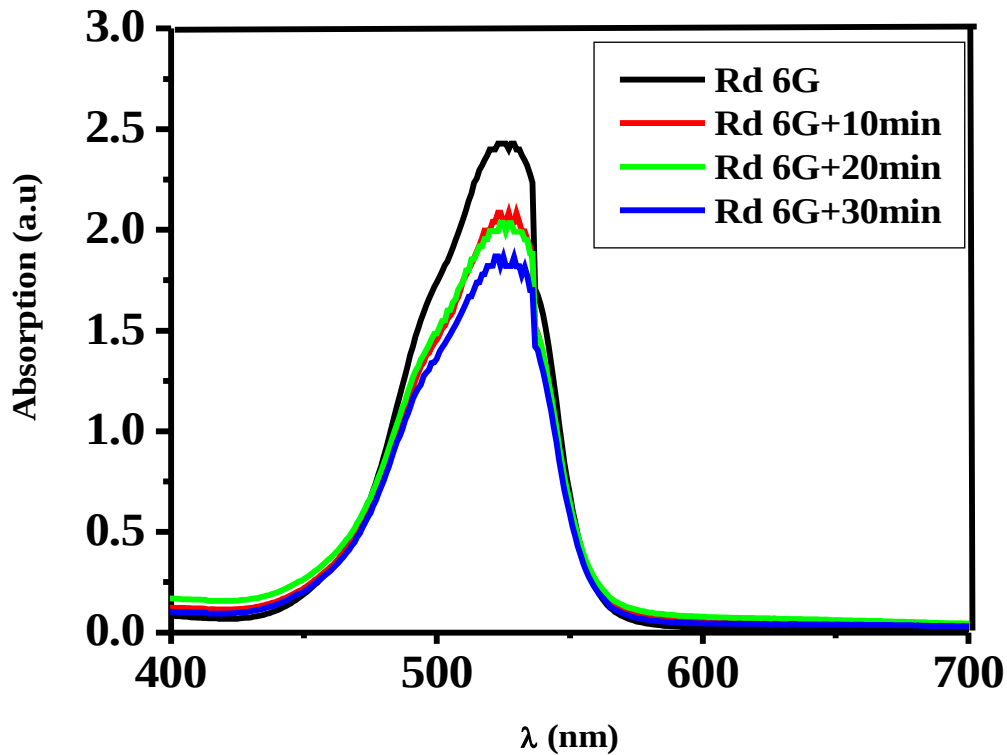


Figure (3.2): The absorption spectra of Rhodamine 6G mixed with 100 mg of TiO₂ irradiated by UV light for different exposure times.

Table (3.1): The peak absorption intensity at 525nm of Rhodamine 6G mixed with 100 mg of TiO₂ after irradiated for different exposure times.

Irradiation time (min)	Intensity (a.u)
0	2.4284
10	2.0393
20	2.0300
30	1.8669

Figure (3.3) shows the effect of irradiation times of uv light on the ratio between the amount of Rhodamine 6G after and before irradiation

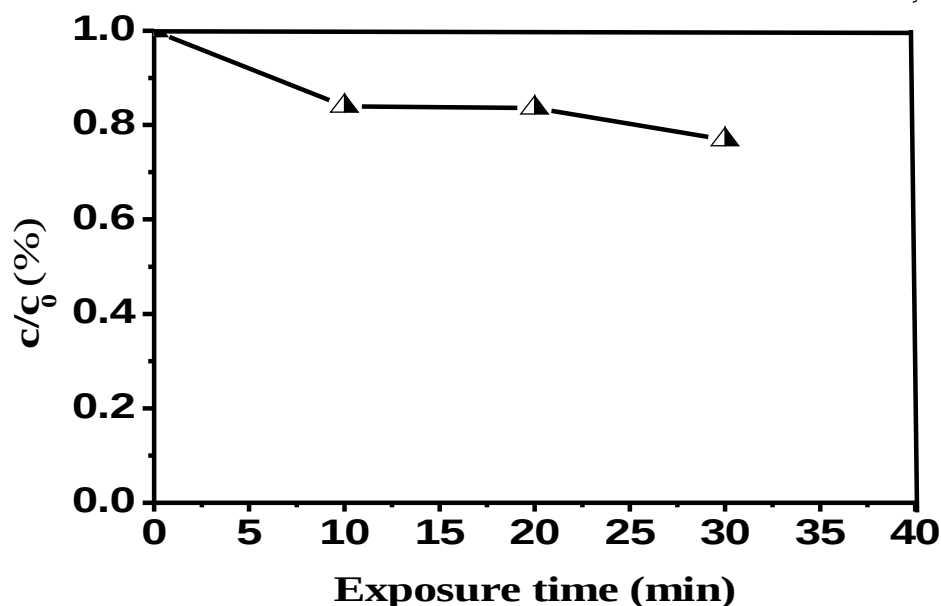


Figure (3.3): The ratio between the amount of Rhodamine 6G after and before irradiation mixed with 100 mg of TiO₂ and irradiated for different exposure times.

It can be observed from figure (3.2) and table (3.1) that the intensity of the absorption peak of Rhodamine 6G at 525 nm is not significantly decreased with increasing the irradiation time and from figure (3.3) it can be seen that it slightly affected the ratio between the amount of Rhodamine 6G after and before irradiation.

3.4 Absorption spectra of Rhodamine 6G mixed with 300 mg of TiO₂ irradiated by UV light source for different times:

The absorption spectra of Rhodamine 6G mixed with 300 mg of TiO₂ after irradiated for different exposure times, are shown in figure (3.4). The effect of the irradiation time on the degradation of Rhodamine 6G can be noticed through the decrease of the absorption intensity of Rhodamine 6G at 525 nm with time increasing. Table (3.2) lists the absorption intensity at 525 nm for different irradiation times.

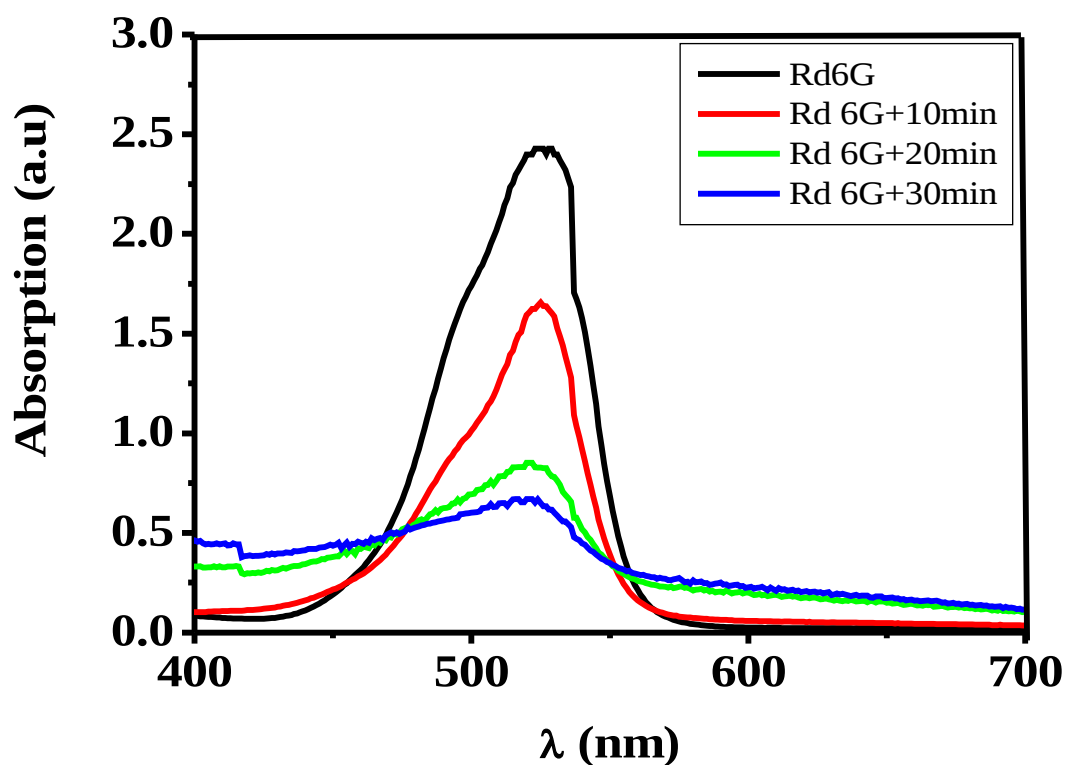


Figure (3.4): The absorption spectra of Rhodamine 6G mixed with 300 mg of TiO₂ irradiated by UV light for different times.

Table (3.2): The absorption intensity at 525nm of Rhodamine 6G mixed with 300 mg of TiO₂ irradiated with different exposure times.

Irradiation time (min)	Intensity (a.u)
------------------------	-----------------

0	2.4284
10	1.6569
20	0.8272
30	0.6510

Figure (3-5) shows the effect of irradiation times of uv light on the ratio between the amount of Rhodamine 6G after and before irradiation.

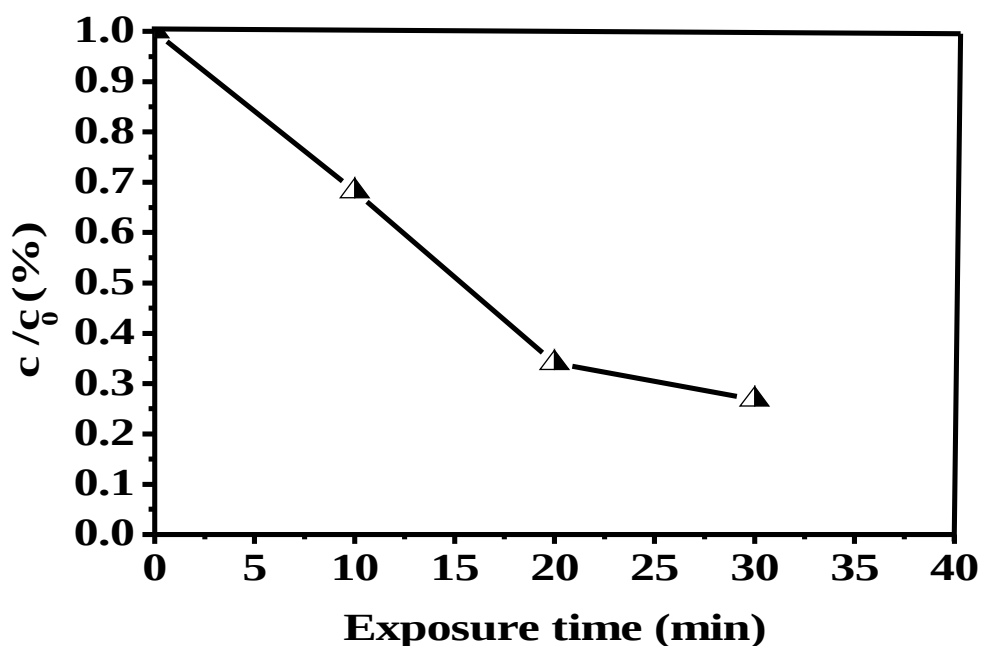


Figure (3.5) The ratio between the amount of Rhodamine 6G after and before irradiation mixed with 300 mg of TiO_2 and irradiated for different exposure times.

From figure (3.4) and table (3.2) it can be seen that the decreasing in intensity of absorption peak of Rhodamine 6G at 525 nm was because of increasing the irradiation time and from figure (3.5) one can noticed that the ratio of the amount of

Rhodamine 6G after and before irradiation was decreased with increasing for different exposure times.

3.5 Absorption spectra of Rhodamine 6G mixed with 600 mg of TiO₂ irradiated by UV light source for different times:

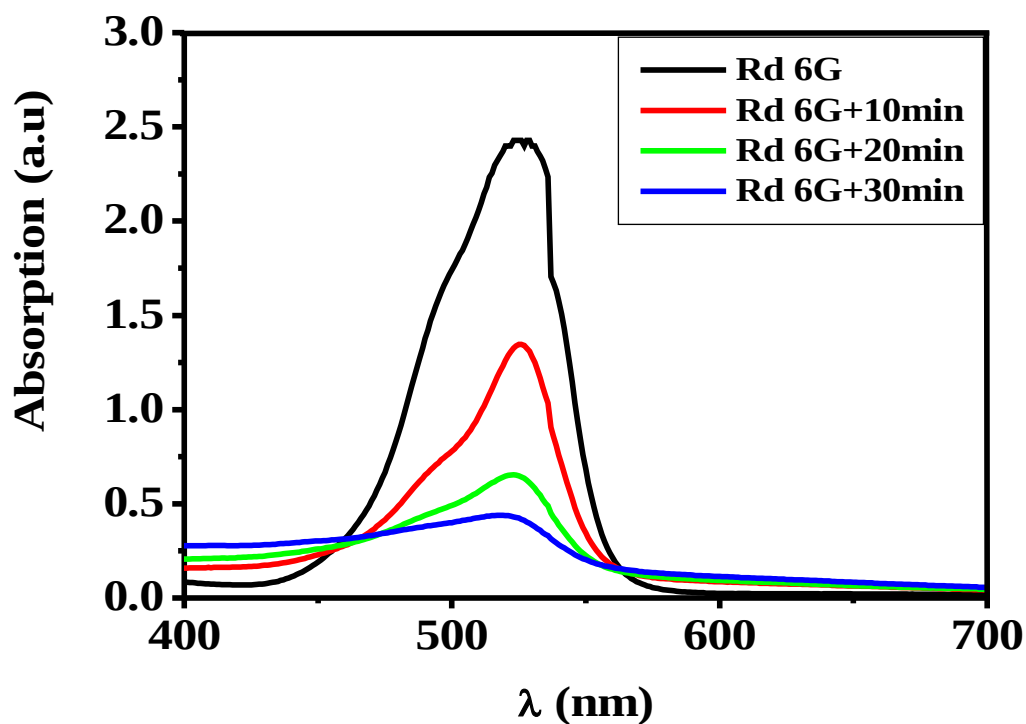


figure (3-6) shows the absorption spectra of the Rhodamine 6G mixed with 600 mg of TiO₂ after different exposure times, The effect of the irradiation time on the degradation of Rhodamine 6G can be noticed through the decrease of the absorption intensity at 525nm of Rhodamine 6G with time increasing. Table (3.3) illustrates the absorption intensity at 525 nm in different irradiation times.

Figure (3.6): The absorption spectra of Rhodamine 6G mixed with 600 mg of TiO₂ irradiated by UV light for different exposure times.

Table (3.3): The absorption intensity at 525nm of Rhodamine 6G mixed with 600 mg of TiO₂ for different exposure times.

Irradiation time (min)	Intensity (a.u)
0	2.4284
10	1.3452
20	0.6489
30	0.4238

Figure (3-7) shows the effect of irradiation times of uv light on the ratio between the amount of Rhodamine 6G after and before irradiation.

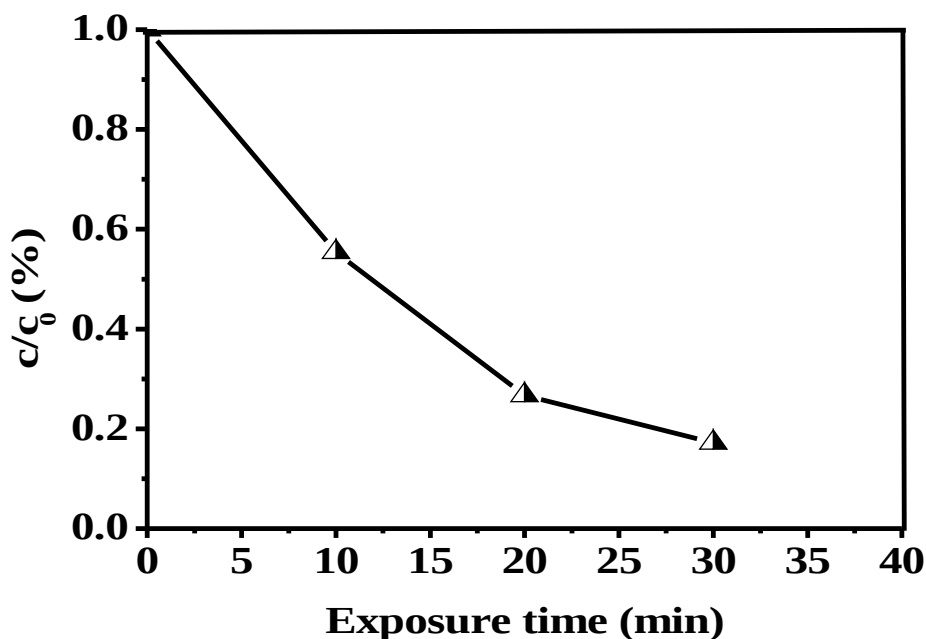


Figure (3.7): The ratio between the amount of Rhodamine 6G after and before irradiation mixed with 600 mg of TiO₂ and irradiated for different exposure times.

the intensity of the absorption at 525 nm was decreased significantly with increasing the irradiation time as shown in figure (3.6) and table (3.3) .As can be seen from figure (3.7) the ratio of the amount of Rhodamine 6G after and before irradiation is approximately decay to zero with increasing irradiation time. Rhodamine 6G was highly degraded after 30 minutes of irradiation when mixed with 600mg of TiO₂.

3.6 Comparison of the degradation rate of Rhodamine 6G with different irradiation times and different TiO₂ weights:

Table (3.4) show the comparison of the degradation percentage of Rhodamine 6G in wast water. Figure (3.8) shows the degradation percentage of Rhodamine 6G at different exposures times with different wieghts of TiO₂.

Table (3.4): The degradation percentage of Rhodamine 6G at different exposure times with different wieght of TiO₂.

Irradiation time (min)	degradation percentage of Rhodamine 6G mixed with 100mg of TiO ₂	degradation percentage of Rhodamine 6G mixed with 300mg of TiO ₂	degradation percentage of Rhodamine 6G mixed with 100mg of TiO ₂
0.00	00.0%	00.0%	00.0%
10	16%	31%	44%
20	16.5%	65%	73%
30	23%	73%	82%

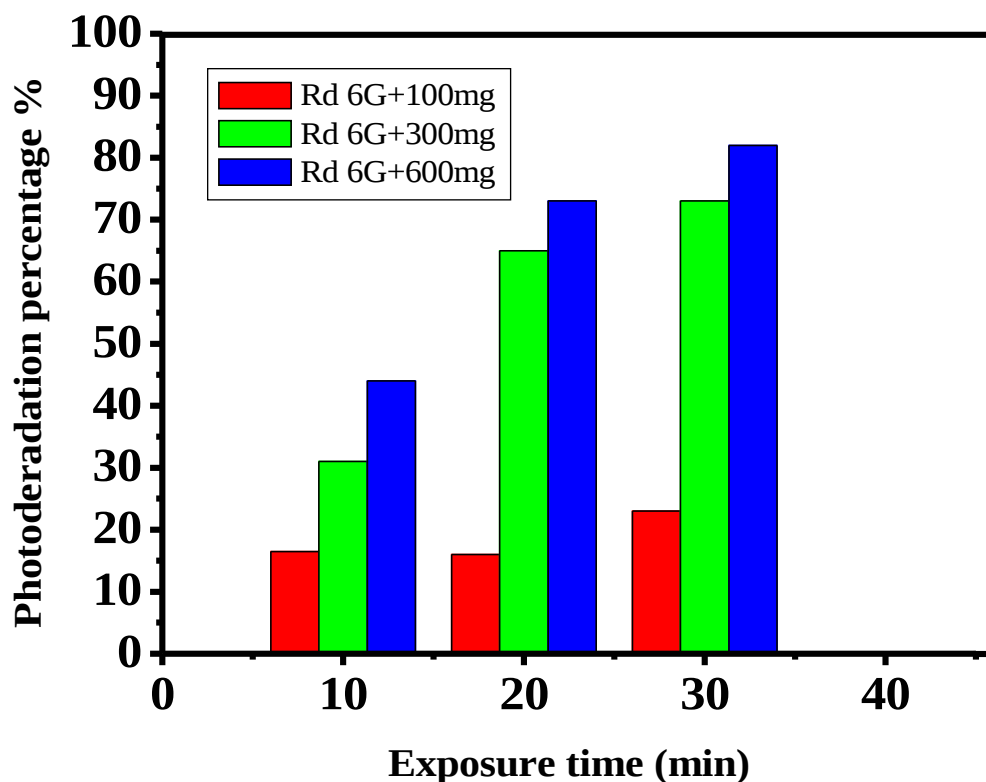


Figure (3.8): The degradation percentage of Rhodamine 6G at different exposure times with different weight of TiO_2 catalyst.

3.7 Discussion:

The photodegradation occurred when the semiconductor catalyst is activated by absorption of external energy from UV light that

lead to acceleration of chemical reactions (oxidation/reduction). The mechanism depends on the generation of valence band holes (h^+_{VB}) and conduction band electrons (e^-_{CB}), when a semiconductor photocatalyst absorbs light photon of energy greater than or equal to its band gap ($h\nu \geq E_{BG}$). The holes mediate the oxidation of Rd 6G solution by the formation of hydroxyl radicals, and the electrons mediate reduction and oxidation reactions by the formation of superoxide radicals according to reaction formulas ((1-1) - (1-24)) shown in chapter one.

As can be observed from absorptions spectra of Rd 6G measured by UV-Vis spectrometer, the dependence of removing molecules of Rd 6G from wastewater was affected by irradiation times and semiconductor weight that was mixed with Rd 6G and this can be noticed through decreasing of intensity of the peak absorption at 525nm.

The photodegradation percentage of Rd 6G mixed with 100mg of TiO_2 was 16% when irradiated for 10 minutes and it was slightly increased to 16.5% when irradiated for 20 minutes and finally increased to 23% at 30 minutes .The amount of TiO_2 mixed with Rd 6G and the exposure time are not efficient for photodegradation process in this case.

For the case of Rd 6G mixed with 300mg of TiO_2 shown in figure (3.4) and (3.5), one can see that the number of Rd 6G molecules absorbing light is decreased significantly. The percentage of photodegradation process was increased to 31%, 65% and 73% at 10, 20 and 30 minutes, respectively.

As it can observed from figures (3.6) and (3.7), that the absorption spectra of Rd 6G mixed with 600mg of TiO_2 showed the highest decreasing of Rd 6G and there was a significant increase in the percentage of photodegradation process of Rd 6G which was 43% when irradiated for 10 minutes, 73% for 20min while was 82% for 30 minutes. The photodegradation process for Rd 6G mixed with 600mg of TiO_2 was the most efficient than those with 100 mg and 300mg.

These results are in agreement with the results of [M. Qamar](#), [M.A. Gondal](#), and [Z.H. Yamani](#) [30], where they studied the Removal of Rd 6G induced by laser and catalyzed by Pt/ WO_3 nanocomposite, and the results of Tanmay K. Ghorai, Niladri Biswas [31], in their

studies of photodegradation of Rd 6G in aqueous solution via SrCrO₄ and TiO₂ nano-sphere mixed oxides.

3.8 Conclusions

From the results obtained in this work the followings can be concluded:

1. The degradation of Rhodamine 6G increased with the increasing of semiconductor weight.
2. The degradation of Rhodamine 6G increased with the increasing of exposure time.
3. The degradation is very efficient in case of Rhodamine 6G mixed with 600mg TiO₂ and irradiated with incoherent UV light for 30 minutes.

3.9 Recommendation

The followings can be suggested as future work:

1. Usage of UV lasers in photocatalysis processes.
2. Usage of other types of semiconductors like: ZnO, Fe₂O₃, NiO and WO₃.
3. Filter paper can be used to filtrate the semiconductor molecules from wastewater before recording the spectra.

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