Sudan University of Science and Technology

College of Graduate Studies

Photodegradation of Methyl Orange Molecules

Using Laser Photocatalysis

التكسير الضوئي لجزيئات الميثيل البرتقالي بإستخدام التحفيز الضوئي بالليزر

**A thesis Submitted for Partial Fulfillment for Requirements
of Master Degree in Laser Application in Physics**

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CHAPTER ONE

Introduction and Basic concepts

1.1 Introduction:

Human activities and human related substances and wastes introduced into rivers, lakes, groundwater aquifers and the oceans modify the environmental water quality and make huge quantities of water unsuitable for various uses. This is the case not only for human –related uses such as drinking, bathing, agricultural irrigation and industrial production but also for terrestrial and aquatic ecosystem for which clean, fresh water is a prerequisite for life.

Water pollution is a serious problem for human health and the environment. The extent of the problem has been confirmed by many reports from UN organizations and related statistics (Ganoulis.J, 2009).

Dyes and pigments are widely used, mostly in the textiles, paper, plastic, leather, food and cosmetic industry to color product. textile industries generate 100- 170 lit dye effluent per kg of cloth processed which could be characterized by strong odour, the effluent from the textile, paper, and food industries containing dye is strongly colored and reveals harmful effects on living things. In order to reduce water pollution, the degradation of dye into non – toxic form is desirable.

The treatment of waste water from textile dyeing is an environmental problem that has received considerable attention. The conventional technologies currently used to degrade the color of the dye contaminated water include primary (adsorption, flocculation), secondary (biological methods) and chemical process (chlorination, ozonization) (Mohabansi.N & Yenkie.N, 2011).

However, these techniques are non- destructive since they only transfer the non-biodegradable matter into sludge; giving rise to a new type of pollution which needs further treatment, photocatalysis is a probable solution of the world wide problems like environmental pollution, wastewater treatment. Advanced oxidation processes (AOPs) have been considered as an effective technology in treating organic chemical dyes in waste water.

AOPS are a group of processes that are based on the generation of hydroxyl radicals, which are highly reactive oxidants. AOPS are able to oxidize a wide range of compounds that are otherwise difficult to degrade. Photo catalytic systems are the combination of a semiconductor like (TiO_2, ZnO, Al_2O_3, RuO_2, ZrO_2, CdS etc.) and UV light and can be defined as the acceleration of a chemical transformation by the presence of a catalyst with light.

The catalyst may accelerate the photoreaction by interaction with substrate in ground or excited state or with primary photoproduct, depending upon the mechanism of the photoreaction and itself remaining unaltered at the end of each catalytic cycle. Heterogeneous photocatalysis is a process in which two active phases solid and liquid are present. The solid phase is a catalyst, usually a semiconductor. The molecular orbital of semiconductors has band structure. The bands of interest in photocatalysis are the populated valence band and it's largely vacant conduction band, which is commonly characterized by band gap energy (Haque.M, Muneer.M & Bahnemann.D, 2012)

1.2 Aims of this work:

This work aimed to:

1. Determination of the effect of the ZnO amount on the process of photodegradation of methyl Orange dye in waste water. 2. Study the effect of the exposure time of UV light on the photodegradation of methyl Orange dye in waste water.

1.3 Thesis Structure:

This thesis contains three chapters; chapter one contains an introduction about the subjed aims of work, pollutions, photodegradation, effect of temperature, effect of light exposure, principles of photocatalysis and mechanistic pathways, radiation sources for photo- catalysis, dyes - types and uses, and literature review. Chapter two describes the experimental part; finally chapter three contains the results, discussion, conclusions and recommendations.

1.4 Pollutions:

Pollution is the contamination of the environment in such a way that it create hazard or potential hazards to the health, safety and welfare of living or nor living species. It is caused mainly by human activities.

1.4.1Types of pollution:

Different types of pollution are: Water pollution, air pollution, soil pollution, noise pollution and radioactive pollution.

1.4.1.1 Water pollution:

Due to the growth of industrial area and modernization water resources are more and more polluted and mostly water from natural water reservoirs is used to full fill the daily needs of peoples and industries, thus, water pollution directly related to different public issues among which health is most important, water pollution takes place most major source is industrial effluent (dying processes) domestic sewage from rural areas, waste from the effluent treatment plant.

The large amount of waste is introduced into the natural resources of water which consist of phenolic compounds, dyes, carcinogenic and heavy metal, suspended matter. (Grabowaska.L, 2007)

Waste Water pollution gives bad effects on public water supplies which can cause health problem such as diarrhea, allergic dermatitis, skin irritation, dysfunction of kidney, reproductive system, liver, brain, central nervous system.

Water pollution due to effluents from textile dyeing industry is a cause of serious concern. The techniques for detection of dyes are cost intensive and futile because the dyes undergo chemical changes under environmental conditions and the transformation products may be more toxic and carcinogenic than the parent molecule.

Color is an important aspect of human world. We like to wear clothes of all kinds of colors and hues, eat food decorated with color, even our medicines are colorful, today there are more than ten thousand dyes available commercially and seven tons of dyes are produced annually. (B. Padhi, 2012)

Approximately 10-15% dyes are released into the environment during dyeing process making the effluent highly colored and aesthetically unpleasant. The

effluent from textile industries thus carries a large number of dyes and other additives which are added during the coloring process (Wang et.al, 2002). These are difficult to remove in conventional water treatment procedures and can be transported easily through sewers and rivers especially because they are designed to have high water solubility.

1.4.2 Air pollution:

Air pollution is one of the major health problems confronting humans today. The accumulation of air pollutants in the atmosphere in large quantities and of longer duration poses harm to human health, affect man-made structures as well as change the patterns of weather and climatic systems (Ali.L.G & Haruna.A, 2015).

The origin of air pollution on the earth can be traced from the times when man started using firewood as a means of cooking and heating. With discovery and from increasing use of coal, air pollution becomes more pronounced especially in urban areas.

The greatest industrial disaster leading to serious air pollution took place in Bhopal where extremely poisonous methyl isocyanide gas was accidentally released from the Union Carbid's pesticide manufacturing plant. The effects of this disaster on human health and the soil are felt even today (Bharucha.E, 2005).

1.4.1.3 Soil Pollution

Soil sustains all life on earth. Roots of plants grow in the soil and absorb nutrients and water which is used during the photosynthesis process, and also for the growth and development of the plants. Consumers, like herbivores and omnivores, eat plants. Herbivores are eaten by carnivores and omnivores in the food web, so nutrients that are absorbed from the soil will benefit all organisms.

Soil provides a habitat for many organisms. When people abuse the land through careless acts, irresponsible behavior, greed and pollution, the soil is harmed and so too all the organisms that directly and indirectly require fertile soil to survive. Forms of soil pollution are litter, dumping of toxic waste, deforestation etc. Litter is a major problem of modern society because man-made materials, like plastic, glass and tin, are non-biodegradable. Litter results when wastes are not disposed in a regulated and proper manner. Rubbish should be placed in disposal containers for collection and dumped in landfills that are covered with soil. Exposed litter is the breeding ground for rats, mosquitoes and flies, apart from being unsightly, unhygienic and a danger to animals and plants. Toxic chemicals must be disposed of in sealed containers that are buried in special cemented landfills. If these landfills are not managed properly, containers may leak. This will result in streams and rivers becoming contaminated, causing people and animals that drink the water, to be poisoned. Crops may absorb the toxins and when eaten by people, birds and animals, cause diseases and toxic poisoning. Unscrupulous people illegally dump containers of toxic chemicals into these a where the containers eventually corrode and leak, releasing the toxic waste. This will directly impact on the marine plant and animal life in the area.

1.4.1.4 Noise Pollution:

Noise may be defined as unwanted sound; sound waves propagate through an elastic medium at speed intrinsic to that material. In gaseous medium such as air, sound waves produce significant changes in the density of the air which produces pressure changes.

Noise is playing an ever-increasing role in our lives and seems a regrettable but ultimately avoidable corollary of current technology. The trend toward the use of

more automated equipment, sports and pleasure craft, high- wattage stereo, larger construction machinery, and the increasing numbers of ground vehicles and aircraft has created a gradual acceptance of noise as a natural byproduct of progress (Wang. L.K & Hung. Y.T, 2005).

1.5 Photodegradation:

The word "photocatalysis" is of Greek origin and composes of two parts: the prefix "photo" (phos: light) and the word "catalysis (katalyo: brake apart, decompose). The term can be generally used to describe a process in which light is used to activate a substance, the photocatalyst, which modifies the rate of a chemical reaction without being involved itself in chemical transformation. Photocatalysis can be defined as the acceleration of a photoreaction by the presence of a catalyst (Dimitris.K, 2006).

Photocatalytic degradation of organic pollutants for water treatment has attractive wide attention due to its effectiveness, easy operation and ideally producing nontoxic end product.

Photo-catalysis is normally based on the light absorption of semiconductor oxide photo-catalyst, to excite electron- hole pairs. These electrons and holes can migrate and initiate redox reactions with water and oxygen, and then degrade organic molecules absorbed on the surface of the photo-catalyst. Currently a major limitation to achieve high photo-catalytic efficiency is the quick recombination of photo-generated charge carries. Recombination has faster kinetics than surface redox reactions and greatly reduces the quantum efficiency of photo-catalysis. Therefore, to enhance the photo-catalytic efficiency, it's essential to retard the recombination of the charge carriers, currently a particularly attractive option is to

design and develop hybrid materials based on semiconductor oxide to solve the above problem (T. Likun pan& L. Xinjuan& Z. Guang, 2011)

Photocatalytic degradation influenced by the presence of oxygen or air, the degradation becomes less in the absence of oxygen and this has been attributed to the recombination of photo-generated hole- electron pairs. Oxygen adsorbed on the surface of a semiconductor prevents the recombination process by trapping electrons according to the reaction:

$$H_2O + h^+ \rightarrow \quad {}^{\cdot}OH + H^+ \quad (1\text{-}1)$$

$$O_2 + e^- \rightarrow O_2^{-\cdot} \quad (1\text{-}2)$$
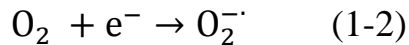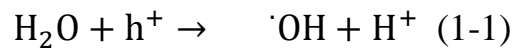
1.6 Effect of temperature:

Increase in temperature increases the recombination of charge carriers and also the desorption process of adsorbed reactant species. Thereby result a decrease of photocatalytic activity. Higher temperature is significantly helpful to decompose the pollutants in waste water; this is probably due to the fact that the activation energy gets increased with increasing operating temperature (Kunal.M & Ashutosh.S, 2002)

1.7 Effect of light exposure:

Low light levels over a long period of time can cause equal or even greater degradation as intense light for a short period. Damage occurs because light is radiant energy, this energy causes irreversible change either through radiant heating or photochemical action.

Radiant heat may create a rise in temperature that causes a reaction on the surface of an object such as cracking and change in color.

Photochemical action is a chemical change at the molecular level and is more profound transformation resulting from the exposure to light. We can observe the effect of UV light in degradation of methyl orange with defferent times.

1.8 Principles of Photocatalysis and Mechanistic Pathways:

Photocatalytic degradation is a part of AOP which has proven to be a promising technology for degrading organic compounds.   The technique is more effective as compared to other AOPs because semiconductors are inexpensive and can easily mineralize various organic compounds.

1.8.1 The Mechanism:

When a catalyst (usually, semiconductor) is exposed to UV radiation or other radiation sources, electrons are promoted from the valence band to the conduction band   as a result of this, an electron- hole pair is produced.
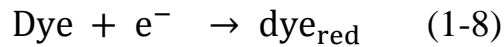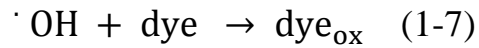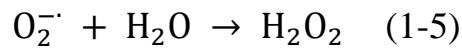
$$Catalyst + hv \rightarrow e^- + h^+$$
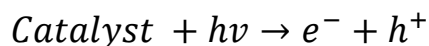
Where e- and h+ are the electron conduction band and electron vacancy in the valence band, respectively. Both these entities can migrate to   the catalyst surface, where they can enter in a redox reaction with other species present on the surface.

In most cases h+ can react easily with surface bound H_2O to produce OH radicals, whereas e- can react with O_2 to produce superoxide radical of oxygen.

$$H_2O + h^+ \rightarrow \quad {}^{\cdot}OH + H^+ \quad (1\text{-}3)$$

$$O_2 + e^- \rightarrow O_2^{-\cdot} \qquad\qquad (1\text{-}4)$$
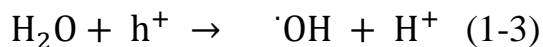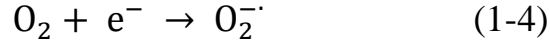
This reaction prevents the combination of the electron and the hole which are produced in first step, The OH and O_2^- react with the dye to form other species and is thus responsible for the discoloration of the dye (Rauf.M & Ashraf.S, 2009).

$$O_2^{-\cdot} + H_2O \rightarrow H_2O_2 \quad (1\text{-}5)$$

$$H_2O_2 \rightarrow 2\,^{\cdot}OH \qquad\quad (1\text{-}6)$$

$$^{\cdot}OH + dye \rightarrow dye_{ox} \quad (1\text{-}7)$$

$$Dye + e^- \rightarrow dye_{red} \qquad (1\text{-}8)$$

A schematic presentation of the mechanisms of generation of oxidative species in a photocatalytic process is shown in Figure (1.2)

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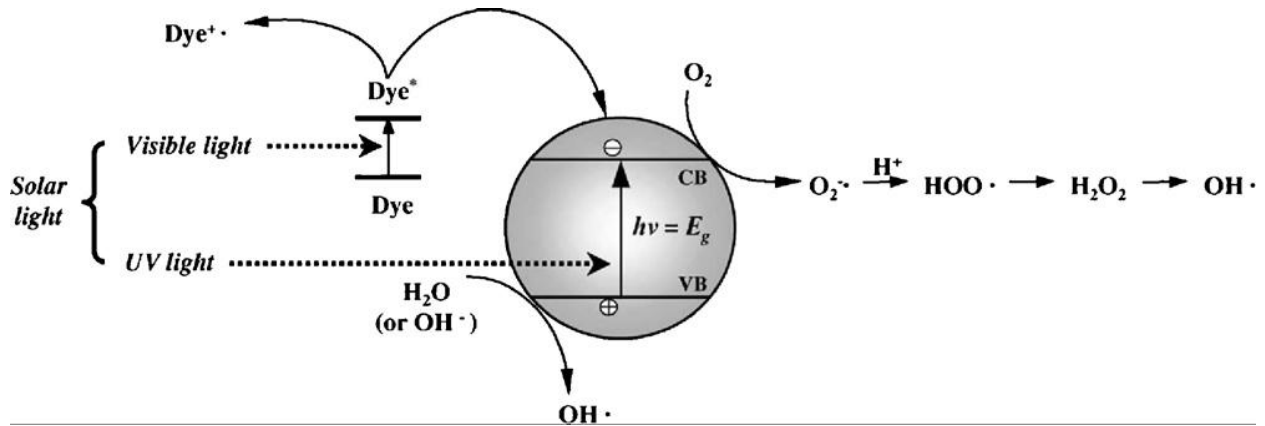
Figure (1.2): Schematic diagram showing the generation of oxidative species in a photocatalytic process (Rauf.M & Ashraf.S, 2009).

1.9 Radiation Sources for Photocatalysis:

The mechanism of photodegradation depends on the radiation used. Charge injection mechanism takes place under visible radiation whereas charge separation occurred under UV light radiation. (Koustautinou.I& Albanis.T, 2004)

There are six types of radiation sources: arc lamps, solar irradiation, Fluorescent lamps, light emitting diodes (LED), incandescent lamps and lasers.

1.9.1Arc Lamps:

Arc lamps are the most common used sources of UV and visible irradiations for photocatalytic process. The emission is obtained by activation of gas by collision with e⁻ accelerated by an electric discharge between two electrodes, Arc lamps are high power and need to be cooled by air or circulating liquid around them.

1.9.2 Solar Photocatalytic Reactor:

Solar light was used as the energy source for catalyst excitation. The reactor assembly was placed on a magnetic stirring plate to further enhance the agitation, and at periodic intervals samples were drawn from reactor and analyzed after centrifugation (Neppolian.B & choi.H, 2002).

1.9.3 Fluorescent Lamps: (FLs)

These sources are used as household illumination, offer a new promising source because of their safety, long time and efficiency electricity to light conversion, **FLs**

are filled with gas mixture of low pressure mercury vapor and argon, the inner surface of lamp is coated with fluorescent coating made of varying blending of metallic and rare- earth phosphor salts. When the light turned on the tungsten cathode is heated to produce e⁻, this e⁻collide with gases to emit light. Fluoutorescent lighting is efficient because low pressure Hg emits about 65% of their total light at 254 nm. The UV light is then absorbed by the fluorescent coating which re-radiates the energy at higher wavelength to emit visible light. (Lam.S, 2014)

1.9.4 Light emitting diodes (LEDs):

LED is a semiconductor device which emit light of different wavelength (Infrared, Visible or near ultraviolet) based on the composition and condition of the Semiconductor materials, it is solid-state technology based entirely on p-n junction devices made of semiconductor materials such as GaAs.

Current progress in the area of photocatalysis using energy efficient light emitting diodes as an irradiation source, LEDs are small in size, have a longer span than conventional light sources, and can operate in a direct current (Tayad.R.J, 2014).

1.10 Dyes, types and uses:

Dye effluents also contain chemicals that are carcinogenic, mutagenic or teratogenic to various organisms (Novotny et. al., 2006, Mathur & Bhatnagar, 2007). This is especially serious because many chemicals can cause damage to genetic material without being expressed immediately.

Azo and nitro compounds have been reported to be reduced in sediments of aquatic bodies giving rise to potentially carcinogenic amines (Chen, 2006). Many dyes are

made from known carcinogens like benzidine and are also known to accumulate, thus posing a serious threat (Baughman & Perenich, 1988).

Many dyes are also known to get reduced to toxic substances inside living organisms. The carcinogenicity of azo dyes, which constitute a significant proportion of textile dyes, is well known (Weisberger, 2002, Umbuzeiro et. al., 2005). Some azo dyes have been linked to bladder cancer in humans; to splenic sacromas, hepatocarcinomas and nuclear anomalies in experimental animals and to cause chromosomal aberration in mammalian cells (Mendevedev, 1988, Percy et. al., 1989).

Dyes are colored organic compounds used   to impart color to various substrates, including paper, leather, drugs and textile materials.

The two major types of colorants produced today are dyes and pigments. Dyes are normally water- soluble or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance.

The dyes molecules are usually chemically bonded to the surface and become   a part of the material on which is applied, the primary use of dyes in the textile industry.

The color intensity of dye molecules depends on how strongly it absorbs radiation in the visible region, which extends from 400 to 700 nm (Alí, M.F, 2005).

1.10.1 Classification of Dyes:

Dyes may be classified   according to their chemical structure or by the method by which they are applied to the substrate.

Classification by application or usage is the principal system adopted by the color index. The diverse classes of dyes include the acridine dyes, azo dyes, arylmethane dyes, anthroqinone dyes, nitro dyes etc.

The classification of dyes according to their usage is summarized in table (1.1)

Table (1.1): Application Classification of Dyes:

Class	Principal substrates	Method of application	Chemical Types
Acid	Nylon, wool, silk, paper,inks, and leather	Usually from neutral toacidic dyebaths	Azo(including premetalized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso
Azoic components and compositions	Cotton, rayon, celluloseacetate and polyester	Fiber impregnated withcoupling component and treated with a solution ofstabilized diazonium salt	Azo
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks	Applied from acidic Dyebaths	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine and anthraquinone
Direct	Cotton, rayon, paper,leather and	Applied from neutral or	Azo, phthalocyanine, stilbene, and

	nylon	slightly alkaline baths containing additional electrolyte	Oxazine
Disperse	Polyester, polyamide,acetate, acrylic andplastics	Fine aqueous dispersions often applied by high temperature/pressure orlower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	Azo, anthraquinone, styryl, nitro, and benzodifuranone
Fluorescent Brighteners	Soaps and detergents,and all fibers, oils,paints, and plastics	From solution,dispersion or suspension in mass	Stilbene, pyrazoles, coumarin, andnaphthalimides

1.11 Literature review:

In 2003, Mladen Franko and Polonca Trebse and Lea Pogacnik are studied laser-indused degradation of organophosphates and monitoring of their toxicity by cholinesterase biosensors. Rapid decomposition has been achieved within two hours following the irradiation for range of concentration (Franko.M & Trebse.P, 2003).

In 2005, Gondal et.al. Studied the laser induced photocatalytic degradation of phenol using WO_3 for the first time. Effect of WO_3 concentration and laser energy

on photocatalytic removal of phenol from waste water were studied. They concluded that laser enhanced photodegradation can be used as an efficient method for removal of phenol present in wastewater (Gondal.M.A, 2005).

In 2010, M. H. Ehrampoush, et.al, studied photocatalytic degradation of methylene sing different concentrations of TiO_2 nano-particles (diameters less than 21 nm) and ultraviolet (UV-C) radiation in a tubular reactor. Different concentrations of catalyst (0.3-1.2 g/L), different pH conditions (3, 7 and 9) and dye concentration (15, 30 and 60 mg/L) as well as sample rotation level (125mL/min) were studied. The sample passed 1-7 times through the quartz reactor exposed to UV-C ray (constant intensity = 2.8 mW/cm2) (every rotation time was 8 min) Results of this research showed clearly that methylene blue is significantly degradable by TiO2 and UV-C radiation. Increasing dyeconcentration resulted in decreased efficiency and thus, as more samples passed through quarts' tube, removal efficiency increased. Methylene blue with concentration of 15 mg/L and after 7 rotations in the reactor 56 min (Ehrampoush.H, 2010).

In 2013 Saravanan and Karthikeyan studied the degradation of methyl orange and methyl blue by coupled semiconductor ZnO/CuO possesses higher photocatalytic degradation when compared to ZnO under visible light. Since coupling of ZnO/CuO reduces the band gab, extending the wavelength range to visible light region leading to electron-hole pair separation under visible light irradiation and consequently, achieving a higher photocatalytic activity.

The maximum efficiency is observed for 5% CuO loaded on ZnO. This environmental friendly composite material was used for the degradation of real textile dye effluent under visible light illumination. The catalyst exhibits high

photocatalytic activity not only in decolorization but also in mineralization of coolourless organic pollutants (Saravanan.R & Karthikeyan.S).

In 2016 Amani Mohamed studied the photodegradation of Malachite green molecules using CuO photocatalyst under UV light. The results showed that the complete removal was achieved when 1000 mg of CuO was added and irradiated for 40 minute (Mohmed.A.M.Y, 2016).

Chapter Two

The Experimental Part

2.1 Introduction:

This chapter presents the equipment's, tools and materials used in the experimental work in addition to the experimental procedure.

2.2 Equipment's, Tools and Setup:

The experimental setup that was used in this work consists of UV light source, magnetic stirrer, glass beaker, UV/Visible spectrophotometer and Quartz cell. Figure (2.1) shows a schematic diagram of the setup.

Figure (2.1): a schematic diagram of the setup

2.3 The UV light source:

In this work the UV light source used was composed of light emitting diode (LED) with wavelength 365 nm and output power 1200 mW, forward current 700 m A, LED is a two-lead semiconductor light source, it's a p-n junction diode that emits light when activated. It was manufactured by LED ENGIN. Figure (2.2) shows the UV source used in this work.
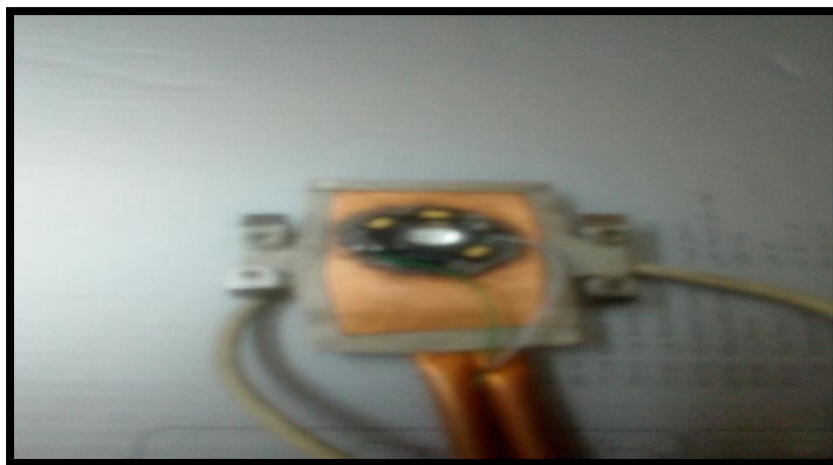
Figure (2.2): UV Light Source

2.4 Magnetic Stirrer:

The magnetic stirrer is a laboratory device used to stir solution faster, it's very common in experimental chemistry and biology, this device is very efficient and quite.

It is used to mix components to get homogeneous liquid mixtures. Magnetic stirrers use a motor to rotate an internal magnet very quickly, which attracts and

pulls a metal stir stick into a circular motion to stir a liquid. In this work this device was used to make homogenous solution by mixing the semiconductor powder (ZnO) with the Methyl orange solution. The magnetic stirrer used made in china its speed between 1-10 rpm.Figure (2.3) shows the magnetic stirrer.

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Figure (2.3): Magnetic Stirrer

2.5 The UV/Visible spectrophotometer:

Spectrophotometer is measurement of how much a chemical substance absorbs or transmits and measure the amount of the intensity of light absorbed after it passes through sample solution. In this work this device was used to measure the

absorption spectrum of the solution before and after irradiation by UV light, in the wavelength region from 190- 1100 nm with auto lamp switch from visible to ultraviolet, wavelength display 0.1nm, Accuracy ± 1.0 nm, wavelength repeatability ± 0.3nm. The UV/Visible spectrophotometer used in this work was supplied from SHIMADZU Company-Japan. Figure (2.4) shows the UV/visible spectrophotometer.

A UV-Visible spectrometer is normally used to measure the absorbance of a chemical solution. The Beer- Lambert law states that the fraction of the incident light absorbed by the solution is proportional to its molecular concentration and the law is expressed as(Christin, 1994; Rao, 1975)

$$A = \log_{10} (I_0/I) = \varepsilon cl \qquad (2\text{-}1)$$

Where:

A = Absorbance

I_0 = the intensity of the incident light

I = the intensity of light after passing through the solution

ε = the absorption coefficient

C = concentration of solution

L = the path length of sample cell

Figure (2.4): UV/Visible spectrophotometer

2.6 A cuvette:

Is a small tube of circular or square cross section, made of plastic, glass and quartz and designed to hold samples for spectroscopic experiments. In this work we used a quartz cell as a liquid sample container. Its dimensions and width are 1 cm, height 4.2 cm.

2.7 The materials:

2.7.1 Zinc oxide:

Zinc oxide is an inorganic compound with formula ZnO. It is white powder that is insoluble in water, and it's widely used as an additive in numerous materials and products including rubbers, plastic, ceramics, and glass. Figure (2.6) shows photo of the Zinc Oxide.

Figure (2.6): Zinc Oxide

ZnO used in various applications like chemical sensor, superconductor, photo catalyst. ZnO is a wide band gap semiconductor having high optical transparency and Luminescence in visible and near ultraviolet range of spectrum. It is used   in solar cell and light emitting diodes. Zinc Oxide is environmental friendly and ease synthesize, ZnO has an direct band gap 3.37 eV   and density about 5.606 g/cm3 , melting point 1,975 ℃ , molar mass 81.38 g/mol (W.Shen & Y.Liu, 2008), It was used in this work as catalysts to produce the h-e pairs after irradiation by the UV source.

2.7.2 Methyl Orange:

Chemical structure:

Methyl orange $C_{14}H_{14}N_3NaO_3S$ is an intensely colored compound used in dyeing and printing textiles. It is also known as C.L acid orange 52, orange III, and gold orange.

This dye is highly toxic for humans and Causes skin irritation, serious eye irritation, respiratory irritation, gastrointestinal tract, harmful if swallowed, inhaled, absorbed through skin, may cause nausea, vomiting, headache and diarrhea.

Chemists use MO as an indicator in the titration of weak bases with strong acids It changes from red (at pH 3.1) to orange- yellow (at pH 4.4).

Methyl Orange is acid (azo) dye, acid dyes are water soluble they can applicable to all kind of natural fibers like wool, cotton, silk. They are also used in paints, inks, plastic. Orange acid azo dyes produce an orange- pink color. They are used in coloring foods and drugs. Physical state is orange fine crystalline powder; melting point 300℃, soluble in water (insoluble in alcohol), stable under ordinary conditions, and its molecular weight is 327.3344 g/mol. Figure (2.7) shows the photo of methyl orange dye.

Figure (2.7) methyl orange

2.8 The experimental procedure:

The experimental procedure was done as follows:

- 5 mg from Methyl Orange was added to 100ml of distil water. Then the mixture was divided to three identical samples.

- 1000mg from catalyst (ZnO) was added to the first sample and 1500mg from (ZnO) was added to the second sample while 2000mg from (ZnO) was added to the third sample.

- A small portion from Methyl Orange (MO) was placed in the UV spectrophotometer and the absorption spectrum was recorded and used as reference.

- The first sample was irradiated, with stirring, by UV light source with wavelength 365 nm and output power 1200 mW for ten minutes. The absorption spectrum of this sample was recorded after irradiation using UV spectrometer.

-The same step was repeated for the first sample with irradiation time of 20 and 30 minutes and the absorption spectrum of the irradiated sample was recorded.

- The above steps were repeated for the second sample and the third sample, individually.

- The degradation of (MO) was deduced from the decrease in the intensity of its absorption peaks in the spectra.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Introduction:

This chapter presents the obtained results and the discussion of each parameter (exposure times and ZnO amount) that affect the degradation of Methyl Orange.

The obtained Result reflects:

-The effect of the irradiation time (Using the UV source) by study the relation between exposure times and degradation percentage.

-The effect of the amount of semiconductor (ZnO) added to the Methyl Orange.

 The degradation of Methyl Orange can be observed using different weights of ZnO (1000 mg, 1500 mg and 2000 mg) under UV light source with different irradiation times (10, 20 and 30) minutes. The data are presented as absorption spectra where the intensity of the absorption peak of methyl Orange before irradiation was compared with the peak intensity after irradiation.

3.1.1 Absorption spectrum of Methyl orange without irradiation and without semiconductor:

The absorption spectrum of methyl Orange (MO) recorded without irradiation and without addition of semiconductor and used as a control to compare it with absorption spectrum after addition of ZnO and irradiation for different time.

UV/visible spectrophotometer recorded a strong absorption band at 464 nm. This peak represents the finger print of the (MO) molecules. Figure (3.1) shows the absorption intensity of (MO) versus wavelength.
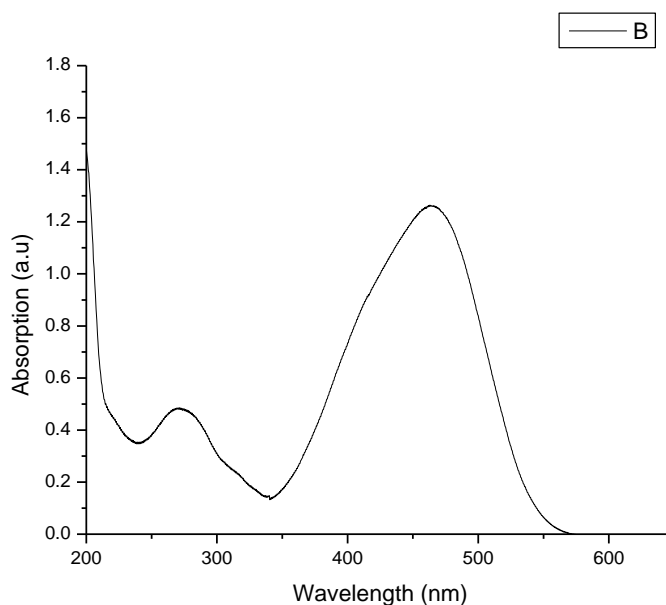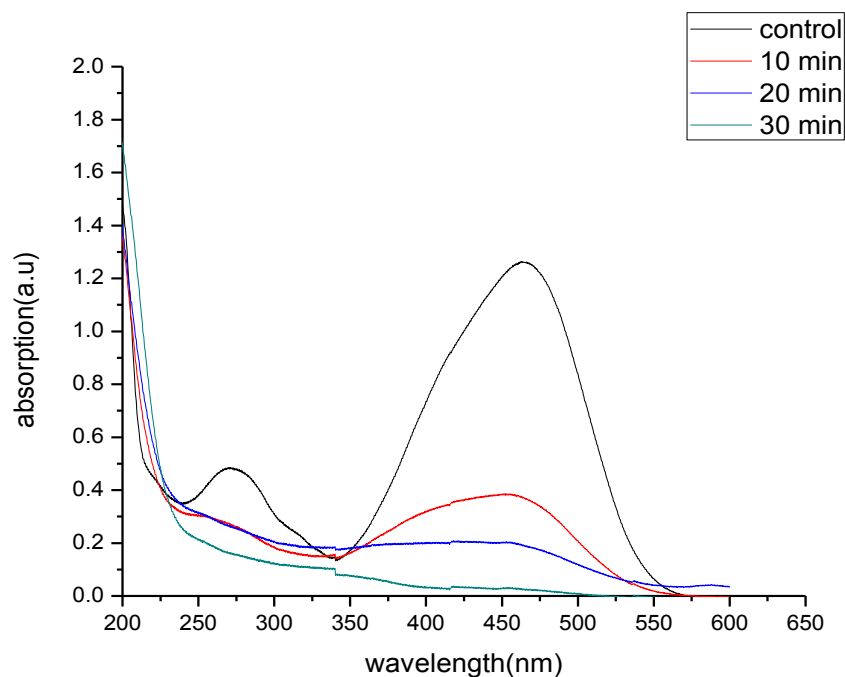
Figure (3.1): the absorption spectrum of (MO) without irradiation and without semiconductor

3.1.2 Absorption spectra of (MO) with addition of 1000 mg ZnO irradiated by UV light for different times:

The sample consists of 1000 mg of ZnO irradiated for (10, 20 and 30) minutes and recorded the spectrum, the decrease in the intensity indicate the degradation of methyl orange. Figure (3.2) shows the absorption spectra of (MO) mixed with 1000 mg of ZnO after different exposure times.

Table (3.1) lists the intensity of the peak at 464 nm for different irradiation times; the decrease in the peak at 464 nm is due to the increment in the exposure time.

Figure (3.2): The absorption spectra of (MO) mixed with 1000 mg of ZnO irradiated by UV light for different exposure times.
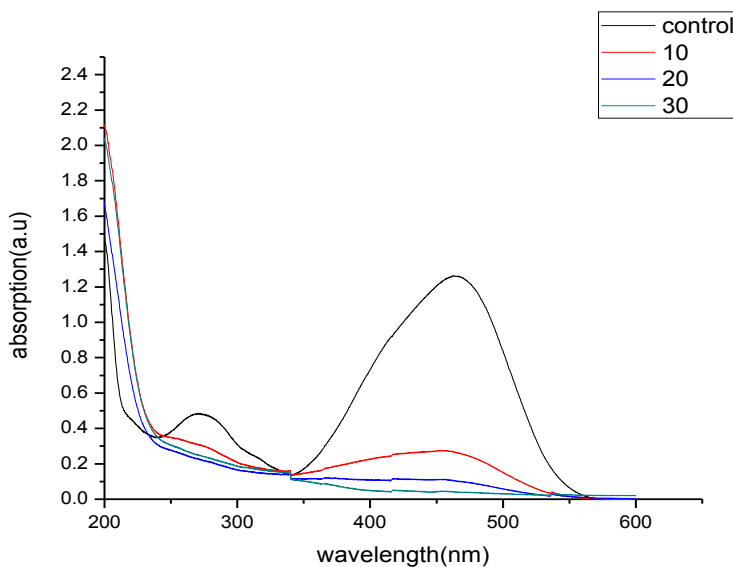
Table (3.1) the intensity of the peak at 464nm after addition of 1000 mg ZnO and different exposure times:

Irradiation time (min)	Intensity of the 464 nm (a.u)	Degradation Percentage %
0	1.2623	0.00
10	0.3732	70.43
20	0.1935	84.67
30	0.0597	95.27

3.1.3 The absorption spectra of Methyl Orange with addition of 1500 mg of ZnO and irradiation times (10, 20, and30 minutes):

Figure (3.3) shows the spectra of Methyl Orange mixed with 1500 mg of ZnO irradiated by the UV light for different exposure times.

Table (3-2) lists the intensity of the peak at 464 nm for each irradiation time.

Figure (3.3): the absorption spectra of Methyl Orange mixed with 1500 mg of ZnO irradiated by UV light for (10, 20 and 30) minutes.
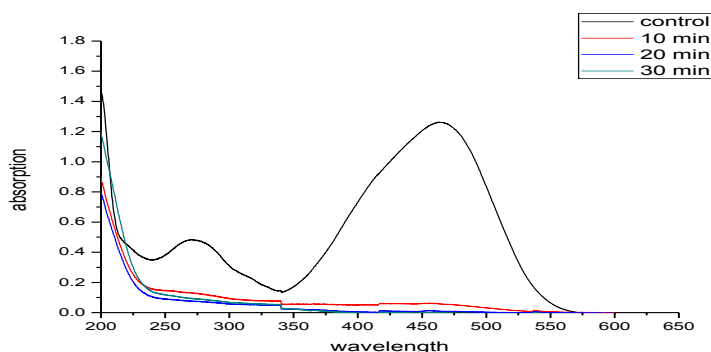
Table (3.2) the intensity of the peak at 464 nm and degradation percentage after addition of 1500 mg ZnO and irradiation of 10, 20, and 30 minutes:

Irradiation time (min)	Intensity of the 464 nm (a.u)	Degradation percentage %
0	1.2623	0.00
10	0.2578	79.57
20	0.1063	91.57
30	0.043	96.59

3.1.4 The absorption spectra of Methyl Orange mixed with 2000 mg of ZnO irradiated by UV light for different times:

The absorption spectra of the Methyl Orange mixed with 2000 mg of ZnO after irradiation by UV light is shown in figure (3.4). The effect of the irradiation time on the degradation of Methyl Orange can be observed through the decrease in the intensity of the peak at 464nm with increment time.

Table (3-3) illustrates that 100% of the Methyl orange was degraded after irradiation time of 30 minutes with 2000mg of ZnO.

Figure (3.4): the absorption spectra of (MO) mixed with 2000mg of ZnO irradiated by UV light for different times

Table (3.3) The degradation percentage and the intensity of the peak at 464 nm after addition of 2000 mg ZnO and irradiation for 10,20 and 30 minutes

Irradiation time (min)	Intensity of the 464 nm (a.u)	Degradation percentage (%)
0	1.2623	0.00
10	0.0275	97.82
20	0.0112	99.11
30	0.0000	100

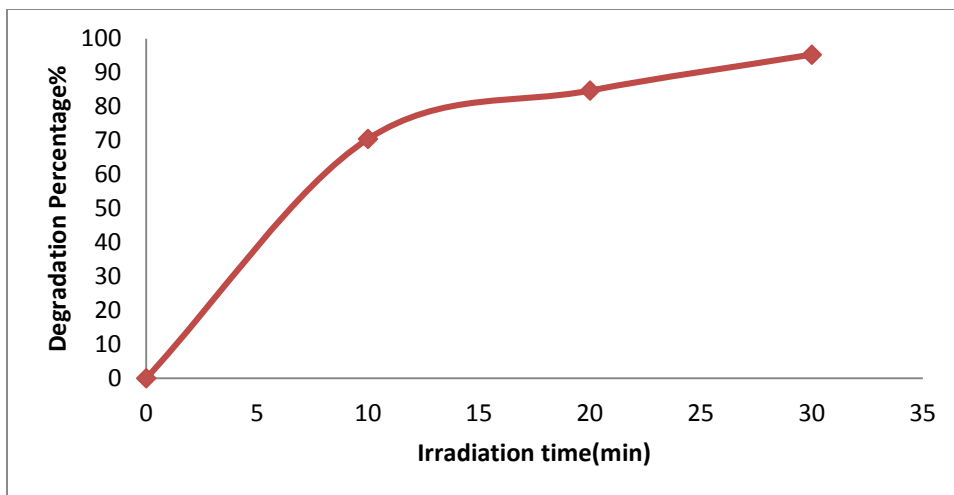## 3.2 The Relation between Exposure time and Degradation Percentage:

The mathematical relation for degradation of methyl orange with different amount of ZnO is:

Degradation percentage % $= 1 - A_t/A_o$

$A_t =$ the absorbance after time (t)

$A_o =$ the absorbance at t $= 0$ minutes.

From table (3.1) one can obtain the relation between the exposure time and the degradation percentage of methyl Orange with addition of 1000mg ZnO irradiated by UV light for different exposure times. Figure (3-5) shows this relation.
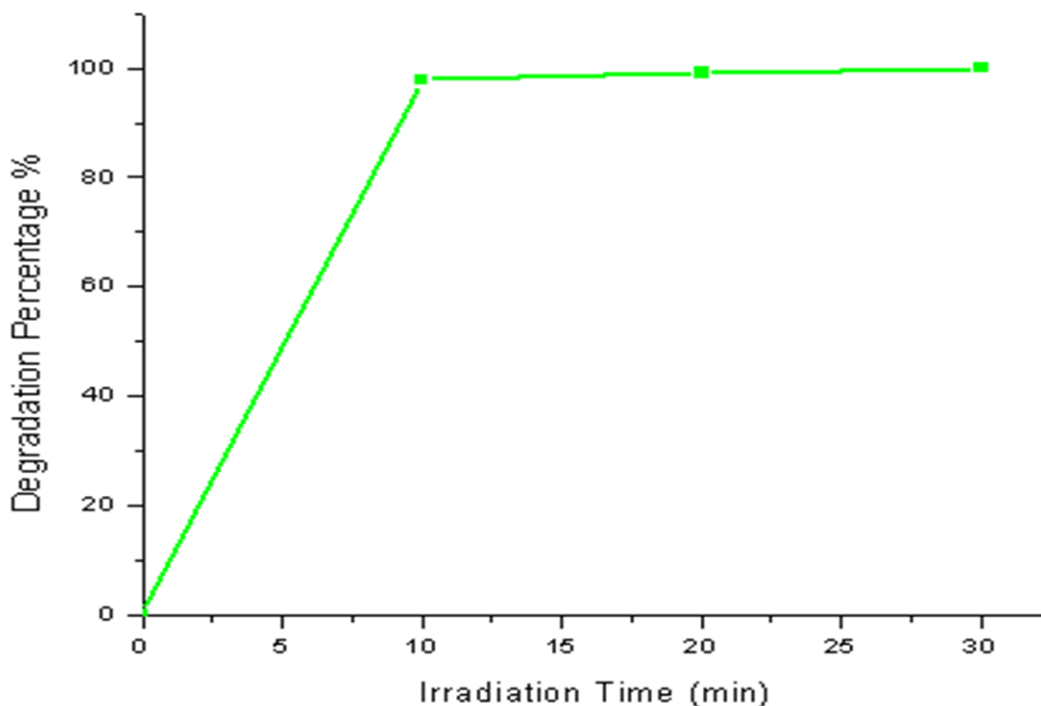
Figure (3.5) the relation between the exposure time and the degradation percentage of methyl Orange with addition of 1000mg ZnO irradiated by UV light for different exposure times.

Figure (3.6) was plotted using data in table (3.2). The relation between the degradation percentage and the exposure time of a mixture composed of methyl orange and 1500 mg of ZnO irradiated for different times is indicated.
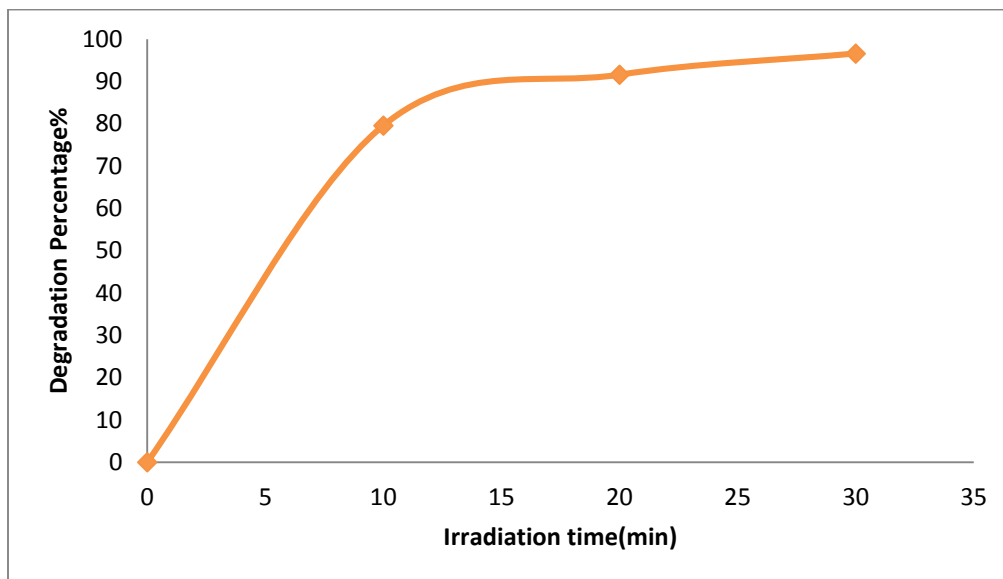
Figure (3.6) the relation between the degradation percentage and the exposure time of 1500 mg of ZnO irradiated for different times.

Using the data in table (3.3), the relation between the exposure time and the degradation percentage of methyl orange with 2000mg of ZnO irradiated for different times was drawn as in figure (3.7)


Figure (3.7**) the relation between exposure time and degradation percentage of methyl orange with 2000 mg of ZnO irradiated for different times.**

From figures (3.5), (3.6), (3.7), it can be noticed that the degradation in methyl orange is increasing exponentially with increasing the exposure time.

Table (3.4) lists the degradation percentage of methyl orange at different exposure times with different weights of ZnO. This deduced result is demonstrated graphically in figure (3-8).

Table (3-4) the relation between the amount of ZnO and the degradation percentage in different irradiation times:

Irradiation time (min)	ZnO Weight (mg)	Degradation percentage%
10	1000	70.43
	1500	84.67
	2000	95.27
20	1000	79.57
	1500	91.57
	2000	96.59
30	1000	97.82
	1500	99.11
	2000	100
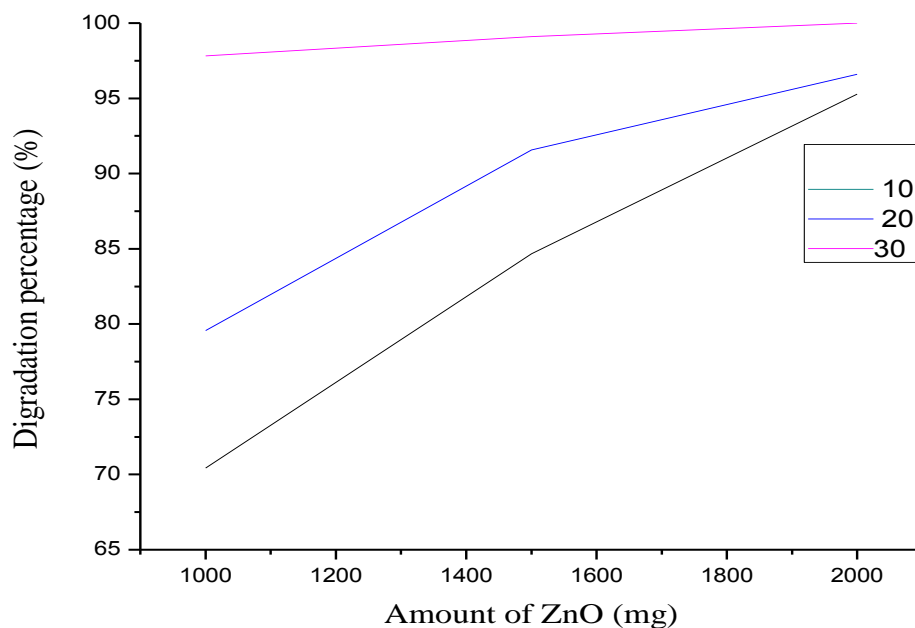
Figure (3.8) the relation between the amount of ZnO (mg) and degradation percentage of a mixture composed of methyl orange and 1000, 1500, 2000 mg of ZnO irradiated for (10, 20 and 30) minutes

3.3 The Discussion:

 The results in this study indicated that when ZnO is irradiated by light with energy greater than or equal to its band gap (3.37 eV), an electron in the valence band can be excited to the conduction band, with the simultaneous generation of hole in the valence band (Eq. 3-1). These photogenerated electron-hole pair can either recombine (Eq.3-2) or interact separately with other molecules. The holes in the valence band can react with water on the surface of ZnO or hydroxide radical to form highly reactive hydroxyl radicals (*OH) (Eq.3-3) and (3-4). while electrons are accepted by adsorbed oxygen to form superoxide radical (O2*), (Eq.3-5).

This radical may form organic peroxides or H_2O_2 (Eq.3-6). The hydroxyl radical is a powerful oxidizing agent and attacks the (MO) molecule to give the oxidized product (Eq. 3-7) (Kaur.J & Bansal.S, 2013). The reactions are summarized as follows:

$$ZnO + hv \rightarrow h^+ + e^- \qquad\qquad (3-1)$$

$$h^+ + e^- \rightarrow heat \qquad\qquad (3-2)$$

$$H_2O + h^+ \rightarrow H^+ + {}^*OH \qquad\qquad (3-3)$$

$$h^+ + OH^- \rightarrow OH^* \qquad\qquad (3-4)$$

$$e^- + O_2 \rightarrow O_2^{*-} \qquad\qquad (3-5)$$

$$O_2^{*-} + HO_2 + H^+ \rightarrow HO_2 + O_2 \qquad\qquad (3-6)$$

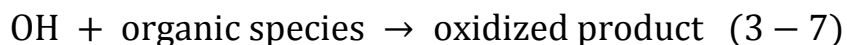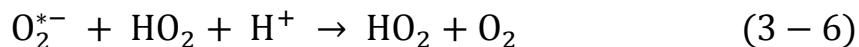$$OH + organic\,species \rightarrow oxidized\,product \quad (3-7)$$

Figure (3-2): showed the decrease of the peak at 464 nm after irradiation for 10 minutes. The significant decrease was happened with increasing the time to 20

minutes and 30 minutes. Increasing the weight of ZnO from 1000 mg to 1500 mg and increasing the exposure time from 10, 20 to 30 minutes lead to more production of electron − hole pairs which react with methyl orange in the solution and increasing its degradation. After the increasing of ZnO amount to 2000 mg to the solution, the intensity of the peak at 464 nm become zero after 30 minutes, as shown in figure (3-4). This means a total removal of methyl orange. From table (3.4) and figure (3.8), it can be noticed the degradation of methyl orange was increased exponentially with the increasing of ZnO amount.

In other study the ZnO nanoneedles (ZNNs) were grown in large quantity by thermal evaporation technique and their catalytic properties were investigated for the photo-catalytic degradation of methyl orange dye. This shows that the ZNNs have enhanced catalytic activity with UV illumination. A fast decomposition of the (MO) dye was observed with a degradation rate of 95.4%   within 140 min due to the rapid formation of oxygenated radicals via capture of electrons and holes generated in ZNNs by UV irradiation. Therefore, ZNNs with high crystallinity and better optical property might be a good tool for the reduction and mineralization of diluted textile dye wastewater and polluted water (Tripathy.N & Ahmed.R, 2014)

3.4 Conclusions:

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

The degradation of (MO) depends on parameters such as, initial concentration of dye, amount of catalyst and exposure time.

- The methyl orange dye could be successfully degraded by ZnO under UV irradiation.

- The degradation of (MO) increased exponentially with increasing the exposure time from 10 minutes to 20 and 30 minutes.
- Increasing the ZnO amount increased exponentially the degradation of methyl orange (MO).
- The maximum degradation percentage of (MO) was achieved with 2000 mg of ZnO and 30 minutes' irradiation time.

3.5 Recommendations

The followings can be recommended as future work:

- Degradation of other molecules, like methyl red.

- study the effect of temperature in the degradation of methyl orange.

- Usage of other semiconductors such as; CdS, CuO, Al_2O_3.

- Utilization of UV laser with high power to irradiate the sample (Nitrogen laser).

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