

Chapter One

Photocatalysis, Basic Concepts

1.1 Introduction:

Water is the most precious natural resource in the world embracing over 75 % of the earth surface. The accessibility to safe drinking water is a high priority issue for the survival of human as well as wildlife. This is due to the fact that water resources such as rivers, lakes and oceans are being contaminated as a result of industrialization and urbanization processes leading to population growth, deforestation and pollution. Consequently, various international and local regulations are becoming stricter with time to control the amounts of pollutants discharged into the water as well as to ensure the quality of the treated effluents disposed into the aquatic environment. Nevertheless, many natural and synthetic pollutants are not generally controlled and monitored, although they are known or suspected to cause harmful ecological effects and can be deleterious to human health (S. Lam, 2014).

Common water pollutants include: textile dye; herbicides and pesticides; alkanes; haloalkanes; aliphatic compounds; alcohols; carboxylic acids; aromatic compounds; detergents and surfactants; agro waste like insecticides, pesticides and herbicides; inorganic compounds like heavy metals, such as mercury, cadmium, silver, nickel, lead; noxious gases; and pathogens like bacteria, fungi and viruses. Both organic and inorganic contaminants can be found in ground water wells and surface waters; these residues can cause adverse effects to the environment and to human health (M. Jesus, 2011).

Paper, dyeing, plastic and textile industries use color for dyeing their products and thus use a huge amount of water which results in the production of adye-containing wastewater with hazardous effects on the environment.

Photocatalysis has emerged as a probable solution to some of the world wide problems like environmental pollution, wastewater treatment, etc (M. H. Ehrampoush, et.al, 2010).

1.2 Aims of the work:

This work aimed to:

- study the effect of the amount of CuO on the process of photodegradation of Malachite green dye in waste water. This dye is highly toxic for humans and animals and can cause permanent injury to eyes.
- study the effect of the exposure time of UV light on the photodegradation of Malachite green dye in waste water.

1.3 Thesis structure:

This thesis contains three chapters, chapter one contains introduction of research (aim of the work, what is photocatalyst, semiconductor photocatalyst materials, mechanism and fundamentals of photocatalyst reactions, photocatalyst process, radiation sources for photocatalyst, effect of light source on photocatalyst degradation, effect of temperature, effect of pollutant concentration, photocatalyst treatment of organic compounds, dye, and literature review), chapter two describes the experimental part, finally chapter three contains the results, discussion, conclusions and recommendations.

1.4 What is photocatalyst:

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 (K.Dimitris,2006).

1.5 History of Photocatalysis:

We are surrounded by photochemistry everyday; we see it in the green color of grass and leave every summer day. However, the first mention of photocatalysis was by Plotnikov in the 1930's in his book entitled *Allgemeine photochemie*. The next major development followed in the 1950's when Markhani and Laidler performed a kinetic study of photo-oxidation on the surface of zinc oxide in an aqueous suspension. By the 1970's researchers started to perform surface studies on photocatalysts like Zinc Oxide and Titanium dioxide. Titanium Dioxide may come in the anatase or the rutile form. Degussa P25 Titanium Dioxide contains both the anatase and rutile form. Curiously, this mixture long stood as the standard in photocatalysis with high reactivity. In the 1970's solar energy was being studied due to a need for more available renewable resources and environmental concerns; photochemistry was looked upon for the storage and usage of solar energy. In 1972 Fujishima and Honda had a breakthrough for the photolysis of water with a semiconductor electrode, which could also be a solar powered cell. The next big breakthrough in photochemistry occurred in 1976 when Carey and Oliver developed a method for measuring the variation in quantum efficiency with intensity. The interest in using Titania as a photocatalyst has since been revived in the 1990. In the 1980's and 1990's there came an increasing concern for environmental preservation and cleanup. As a result some environmental scientists have looked at photochemistry for air, water, and soil cleanup TiO_2 catalyzed photochemistry can accomplish the mineralization, which is the degradation of organic compounds to H_2O and CO_2 and its inorganic substituents if the organic compound should have any, of many different organic compounds. During the last few years, semiconductor

mediated photocatalysis has been reported as a promising route to destroy toxic and hazardous organic substances in industrial wastewater and drinking water. In most cases, a complete oxidative destruction of pollutants has been observed and the end products include CO₂, H₂O and inorganic ions. The harvest of sunlight for photo catalysis has been a tremendous boon to the process, on account of the economic feasibility, ease of large scale operation and process efficiency (R. Chhotu, 2008).

1.6 Semiconductor Photocatalyst Materials:

Semiconductor solids such as TiO₂, ZnO₂, CdS etc.. as photocatalysts, have been extensively studied. These solids have special electronic and optical properties which are determined by the band structure. Solids with different band widths give distinct properties and they are classified as: metals, semiconductors and insulators. When the band gap is overlapped, solids behave like metal (conductor) and regardless of temperature. Between the band gaps, higher band is called conduction band because only when electrons are excited to the conduction band is the solid electrically conductive. The lower band is called the valence band by analogy with the valence electrons of individual atoms. Both insulators and semiconductors have a band gap between the conduction band and the valence band. The difference is that the band gap in insulators is much larger and this is called forbidden band gap where it is difficult to excite electrons from their valence band to their conduction band. The present theory of the excitation of the electrons in valence band to conduction band is mainly due to thermal energy. Therefore, conductivity of semiconductors is strongly dependent on the temperature of the material. For the photocatalysis reaction on semiconductors, the absorbed irradiation functions as thermal energy and excites the electrons from valence band to conduction band. Therefore, the width of band gap is one of the most important properties which strongly

influence the electrical and optical properties of the material. Broader band gap needs more energy to excite the electrons which means only the irradiation carrying higher energy such as ultraviolet light can be used for the energy source during the reaction process. The irradiation with lower energy, visible light and infrared for example, can only drive catalysts with narrow band gap. these differences are shown in Figure (1-1).

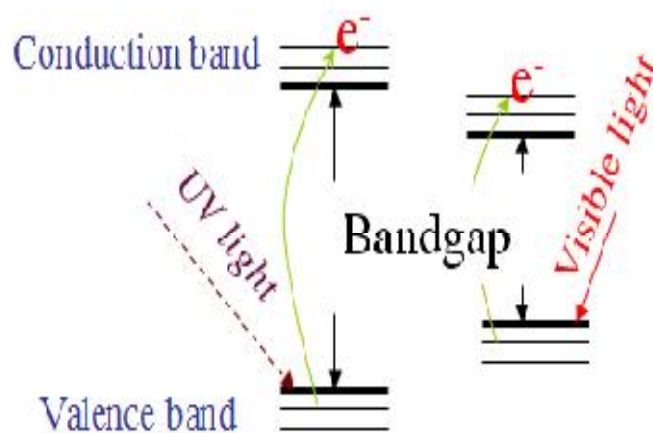


Figure (1-1) Different band gaps and their light absorption

Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes, after which the TiO_2 was widely studied as a photocatalyst. When the energy of incident light is larger than the band gap, electron will be excited from “hole”, at the valence band which can obtain electrons. Most of the separated electrons and holes recombine to release energy in the heat form. Table (1-1) lists bandgap energies for some common semiconductor (C.chao,2013).

Table (1-1) Bandgap energies for some common semiconductor

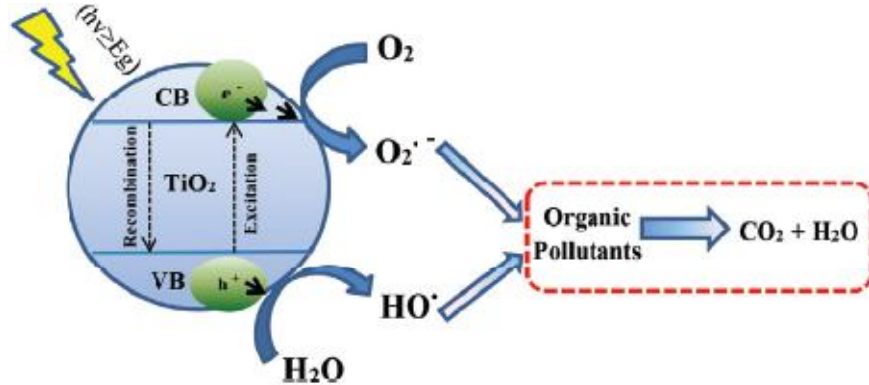
Semiconductors	Bandgap energy (eV)
Cu ₂ O	2.172
ZnS	3.6
TiO ₂	3.03
SnO ₂	3.54
Fe ₂ O ₃	2.3
CuO	1.2

1.7 Mechanism and fundamentals of photocatalytic reactions:

Environmental pollution is growing year by year, and quality of life is decreasing. Although there are several pollutant agents affecting the environment, water contamination and atmospheric pollution have been received more attention in order to increase quality of life.

in order to increase quality of life. Conventional technologies (biological, biochemical, physical process, and chemical processes) have been used to face water and atmospheric contamination, but they are not totally efficient to solve the environmental pollution problem. photocatalysis, are necessary to decrease environmental pollution more efficiently. Photocatalysis process is one of most important methods used to remove the carcinogen materials like phenol, chlorothalonil and malachite green from pollutant water. Generation of excited high energy states of electron and hole pairs occurs when wide band gap semiconductors are irradiated. If the electron (and hole) migrate to the semiconductor without recombination, they can participate in various oxidation and reduction reaction with absorbed 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. Figure (1-2) shows the mechanism of photocatalysis (C. chao, 2013).

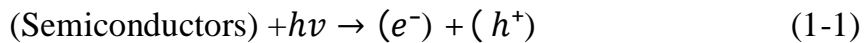


Figure(1-2): The mechanism of photocatalysis

1.8 Photocatalytic Process:

The photocatalytic process is quite complicated because the reactions occur in the photocatalysts and on the interface of the photocatalysts and reactants solution. A simple arbitrary description of the photocatalytic process is as following:

- **Photon absorption:** semiconductors absorb photons and generate electrons and holes:

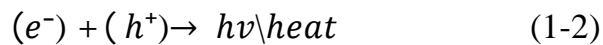


Semiconductors (e.g., TiO₂, ZnO, Fe₂O₃, WO₃, AgPO₄, CdS, and ZnS) can act as photocatalysts for light-induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band with a suitable gap between them. When a photon with energy of hv matches or exceeds the bandgap energy, E_g , of the semiconductor, an

electron, e^- , is transferred from the valence band, VB, to the conduction band, CB, leaving a hole, h^+ , in VB.

➤ **Relaxation:** electrons and holes release energy (heat) and move to the conductive band minimum position and valence band maximum position, respectively.

➤ **Recombination:**



Excited-state conduction-band electrons and valence-band holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. In the absence of suitable electron and hole separation forces, the stored energy is dissipated within a few nanoseconds in the recombination process. If a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is prevented/reduced and subsequent redox reactions may occur.

➤ **Water absorption on the surface:**

➤ **Formation of free radicals:**

a). Electrons transfer from the water molecule to the photocatalyst (holes attract electrons in water):



b). Electrons transfer from photocatalyst to oxygen solved in water:



➤ **Degeneration\disinfection of contaminations:**

Formation of free radicals and resulting decomposition of organic compounds in water have received increasing attention in the research and development of

wastewater treatment and water splitting technologies in the last three decades. The efficacy of photocatalysis depends on the concentration of reactive free radicals, the most important of which is the hydroxyl radical (OH^*). Free radical species are atoms or molecules that are capable of independent existence and possess one or more unpaired electrons such as superoxide radical (O_2^-), hydroperoxy radical (HOO^*), and hydroxyl radical (OH^*). Among these various radicals, the hydroxyl radical is thought to play a central role in photocatalysis for wastewater treatment (W.X.Li, 2013).

1.9 Radiation sources for photocatalysis:

Radiation sources play a pivotal role in the performance of photocatalytic reaction. Normally, the selection of particular lamp is made on the basis of the reaction energy requirement of particular catalyst. There are six types of radiation sources: arc lamps, fluorescent lamps, incandescent lamps, lasers, light-emitting diodes (LEDs) and solar irradiation. In general, arc lamps are the most common used source of UV and visible irradiations for photocatalytic process. In arc lamps, the emission is obtained by the activation of a gas by collisions with e^- accelerated by an electric discharge between two electrodes, typically made of tungsten. The activated gases are usually mercury and/or xenon vapor. For mercury lamps based on the pressure of Hg, these lamps can be divided into low pressure Hg lamps (pressure up to 0.1 pa, emission mainly at 253.7 nm and 184.9 nm), medium-pressure Hg lamps (pressure ranging from 100 to several hundred pa, emission from 300 nm to 1000 nm) and high-pressure Hg lamps (pressure up to Mpa or higher, emission from 200 nm to 1000 nm). Generally, arc lamps are high power and need to be cooled by air or circulating liquid around them. Moreover, a large proportion of light energy is also not useful for the photocatalytic process as they can be converted to thermal energy.

On the other hand, fluorescent lamps (FLs), which 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 vapour and argon (or xenon). The inner surface of the lamp is coated with fluorescent coating made of varying blending of metallic and rare-earth phosphor salts. When the light is turned on, the tungsten cathode is heated to produce e^- and this e^- will collide with the gases to emit light. Fluorescent 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 wavelengths to emit visible light. Therefore if the intensity of light available from ordinary FLs would be sufficient to degrade organic pollutants, they can also provide the opportunities for the application of photocatalytic process in the indoor environments (S. Lam, 2014).

1.10 Effect of Light Source on Photocatalytic Degradation:

The percentage degradation of dyes in waste water improved with increasing exposed light intensity. Under the elevated intensity of light irradiation, the enhancement was significantly higher since the electron–hole formation is predominant at high irradiation intensity and, therefore, electron–hole recombination probability is insignificant. However, when irradiated light intensity becomes very poor, separation of electron–hole pair competes with recombination which consecutively decreases the formation of free radicals, thus, causing less result on the percentage degradation of the waste water(M. Kunal &S. Ashutosh, 2002).

1.11 Effect of Temperature:

That decolorization of real textile industrial wastewater with time increases with increasing temperature for all types of catalysts. This results confirm that higher temperature is significantly helpful to decompose the pollutants in wastewater. This is probably due to the fact that the activation energy gets increased with increasing operating temperature (M. Kunal & S. Ashutosh, 2002).

1.12 Effect of pollutant Concentration:

The lowering in pollutant concentration reduces the time of decomposition of the wastewater. This performance could be described as: when the concentration of real industrial wastewater is very less than of the original concentration then the catalysts active sites probably be completely exposed by pollutant ions. The further increase in pollutant concentration may also be responsible for screening the exposed light so the light intensity will be reduced (M. Kunal & S. Ashutosh, 2002).

1.13 Photocatalytic treatment of organic compounds:

The presence of wide variety of organic compounds, which are toxic and stable to natural decomposition in water supplies and industrial effluents, is an ever increasing problem for the global concern. Nowadays, high concentrations of these compounds are introduced into the water system from various agricultural activities and industrial wastewater discharges such as coal gasification, resin manufacturing, oil refining, coking plants, chemical synthesis, dyes, plastics, textiles, pharmaceuticals, paper mill, herbicides and fungicides production. Conventional water treatment technologies such as solvent extraction, activated carbon adsorption, and chemical treatment process such as oxidation by ozone (O_3) often produce hazardous by-products and generate large amounts of solid wastes, which require costly disposal or regeneration method. Biological

treatment is often not convenient for treatment of phenolic wastewater as its toxicity may cause the phototoxic effect on the active microorganisms. Due to these reasons, considerable attention has been focused on complete oxidation of organic compounds to harmless products such as CO₂ and H₂O by the advanced oxidation process (AOP) that appears to be the most emerging technology recently. Photocatalytic of such organic pollutants with TiO₂ semiconductor has been proved to be the most efficient and popular method because it is a stable and low-cost photosensitized material (F. Elham, 2011).

1.14 Dyes:

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. About 1–20 % of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. Some dyes are toxic and even at very low concentrations may significantly affect aquatic life. Some other dyes may cause allergy, skin irritation and cancer to humans. In most countries researchers are looking for appropriate treatments in order to remove pollutants, impurities and to obtain the decolourization of dye house effluents. In recent years as an alternative to conventional methods (AOPs) based on the generation of very reactive species such as hydroxyl radicals have been proposed to oxidize quickly and non selectively a broad range of organic pollutants including several dyes. Photodegradation of various classes of dyes has been often investigated (F. Elham, 2011).

Malachite green (MG) is one of an organic compound that used as a dyestuff industry and emerged as a controversial agent in aquaculture. It is the chloride salt, is known as a colored cation. The intensity of this green color of the cationic dye has a strong absorption band at 616 nm and its min dye content of 90%. However, the name of malachite green dye comes from the similarity of

its color rather than the mineral malachite molecules. Malachite green is one of the triphenylmethane, which has been used as a dye for silk, jute, leather, wool, cotton and paper. It is also used as disinfectant, anti-helminthic, as well as, in aquaculture as and antiseptic. However, malachite green is environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals. Several studies have shown that MG is highly lethal to fresh water fish, in both acute and chronic exposures. It causes serious public health hazards and also poses potential environmental problems. It decreases food intake, growth and fertility rates; causes damage to liver, spleen, kidney and heart; inflicts lesions on skin, eyes, lungs and bones and produces teratogenic effects. Therefore, it might be concluded that malachite green caused carcinogenic symptoms (H. Haile, 2012).

1.15 Literature review:

In 2004 Chakrabharti and Dutta, studied the potential of a common semiconductor, ZnO as an effective catalyst for the photodegradation of two model dyes: Methylene Blue and Eosin Y. The effect of parameter like catalyst loading, initial dye concentration, air flow rate, UV irradiation intensity and pH on the extent of photodegradation were investigated (R. Chhotu, 2008).

In 2004, Konstantinou and Albanis, studied the photocatalytic degradation of azo dyes containing different functionalities using TiO_2 as photo catalyst in different functionalities using TiO_2 as under solar and UV irradiation and stated that the mechanism of the photodegradation depends on the irradiation used. Charge injection mechanism takes place under visible irradiation whereas charge separation occurred under UV light irradiation (R. Chhotu, 2008).

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 (M.A. Gondal, 2005).

In 2009 Yasmeen Hafiz, studied the photocatalytic degradation of toxic phenol in water, using different weights from semiconductors (Iron Oxide and Zinc Oxide), and using coherent and incoherent light sources. The study shows that the phenol degradation is increased with increasing the weight of the semiconductor and the exposure time. The best result was attained at 30 minutes exposure times, 600 mg of the Fe_2O_3 (H. Yasmeen, 2009).

In 2010, M. H. Ehrampoush, et.al, studied photocatalytic degradation of methylene using 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 (125 mL/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 dye concentration resulted in decreased efficiency and thus, as more samples passed through quartz tube, removal efficiency increased. Methylene blue with concentration of 15 mg/L and after 7 rotations in the reactor 56 min (M.H. Ehrampoush, 2010).

In 2010, Umar Ibrahim 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, Under these experimental conditions, 2,4-dichlorophenol was achieved in 180 min (I. Umar, 2010).

In 2012, Falah H. Hussein and Ahmed F. Halbus studied the photocatalytic decolorization of cobalamin in aqueous solution with different types of catalysts including ZnO, TiO₂ using UV light source. Their results showed that the activity of different types of catalysts was achieved in less than thirty minutes (H. Ahmed & H. Falah, 2012).

In 2013, Salam K.AL-Dawery studied the photocatalyst degradation of Tartrazine compound in wastewater using TiO₂ and UV light. Significant enhancement of the photo-catalytic activity was observed in the system using the photocatalyst irradiated by UV light. The concentration of photo-catalyst greatly influences the degradation rate, The results showed that the maximum rate of degradation is in a solution of 500 mg/L titanium dioxide (A. Salam, 2013).

In 2014, Mohamed Ahmed studied the photodegradation of Rhodamine 6G, using TiO_2 photocatalys. In this research different amounts of semiconductor (TiO_2) were added to Rhodamine 6G and the mixture was irradiated by UV light with wavelengths of (270 -280) and spot size of 4cm^2 . The results showed that the efficiency of the photodegradation process was increased with increasing the amount of semiconductor and irradiation time. The highest percentage of Rhodamine 6G degradation was 82% when 600mg of TiO_2 was added and irradiated for 30 min (A.Mohamed, 2014).