

# CHAPTER ONE

## Introduction and Basic Concepts

### 1.1 Introduction:

The global environment pollution is becoming a matter of great concern. The major causes of environment pollution are industrialization and human activities. The industrial wastes, some of them are highly toxic chemicals, are discarded into the atmosphere, hydrosphere and lithosphere, become health hazard directly or indirectly to human beings and animals (A. Dwivedi, U. Pande, 2011).

The halo-organic compounds have wide industrial and agricultural applications. The halogenated organic compound is a general term used for the organic chemicals containing a carbon directly linked with the halogen atom. The halogenated hydrocarbons and their substituted derivatives are stable compounds and show markedly low chemical reactivity. These properties make them long lasting. These compounds are also non-biodegradable. Manufacturing of halogenated compounds leave a large residue in the soil and atmosphere, which is washed by rain and finds its way into the water bodies. These compounds are passed on to the aquatic plants and animals, which are consumed as food by human beings and other animals and become a part of food chain (A. Dwivedi, U. Pande, 2011).

Water is considered polluted if some substances or condition is present to such a degree that the water cannot be used for a specific purpose. Water pollution is generally induced by humans. It results from actions of humans carried on to better self. These could be treated under the various activities that man engages in, that lead to pollution. The growth of human population, industrial and agricultural practices is the major causes of pollution (F. Owa, 2014).

## **1.2 Justification and aim of the work:**

Chloroform may be released to the air as a result of its formation of drinking water, wastewater and swimming pools. Other sources include pulp and paper mills, hazardous waste sites, and sanitary landfills. The major effect from acute (short-term) inhalation exposure to chloroform is central nervous system depression. Chronic (long-term) exposure to chloroform by inhalation in humans has resulted in effect on the liver, including hepatitis and jaundice, and central nervous system effects, such as depression and irritability. Chloroform has been shown to be carcinogenic in animals after oral exposure, resulting in an increase in kidney and liver tumors.

Human exposure to chloroform may occur through drinking water, where chloroform is formed as a result of the chlorination of naturally occurring organic materials found in raw water supplies. Measurements of chloroform in drinking water during the 1970s and 1980s ranged from 0.022 to 0.068 part per million (ppm). Chloroform may also be found in some foods and beverages, largely from the use of tap water during production processes. (www.ox.ac.uk, 2015).

The aims of this work are:

- To study the effect of  $\text{Fe}_2\text{O}_3$  on the process of photodegradation of chloroform in waste water.
- To study the effect of the exposure time of UV light on the process of photodegradation of chloroform in waste water.

## **1.3 Structure of the thesis:**

This thesis contains three chapters, chapter one contains introduction of research (aim of the work ,definition and mechanism of photocatalysis,

fundamental concepts of semiconductors and literature review), chapter two describe experimental part, finally chapter three contains the results and then discuss this results, conclusions and then finished by references.

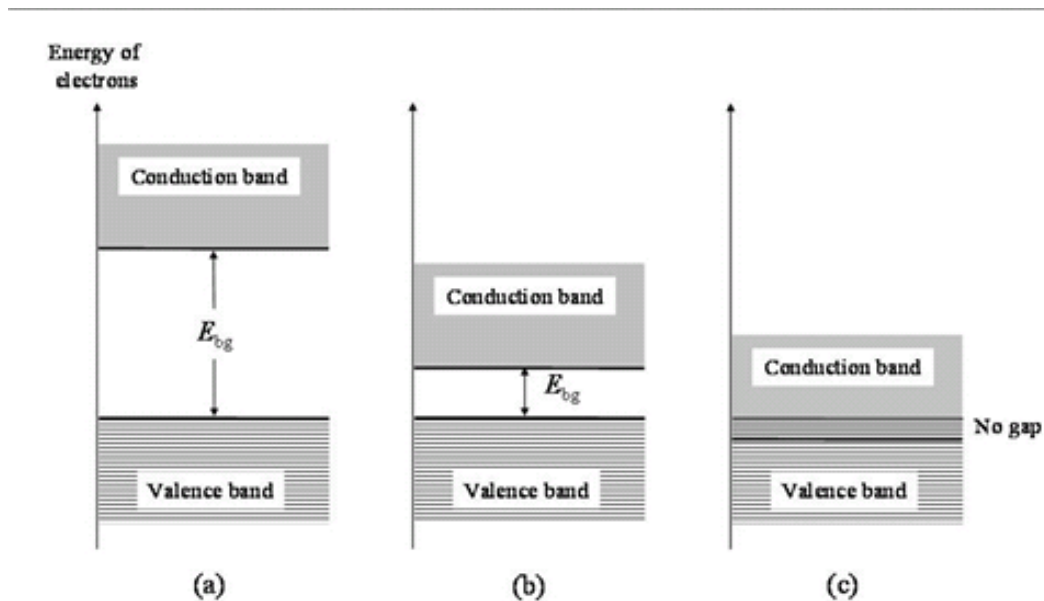
### **1.4 Fundamental Concepts of Semiconductors:**

The electronic characteristics of conductors, semiconductors, and insulators can be described according to the band theory (see figure (1.1)). Because of the very large number of atoms that interact in a solid material, the corresponding energy levels are so closely spaced that they form bands. Each band has a different energy, and the electrons fill these bands from the lowest energy to the highest, similar to the way that electrons occupy the orbitals in a single atom(K. Dimitirs, 2006).

The highest energy filled band, which is analogous to the highest occupied molecular orbital (HOMO) in a molecule, is called the valence band (VB). The next higher band, which is analogous to the lowest unoccupied molecular orbital (LUMO) in a molecule, is called the conduction band (CB). The VB and CB are separated by an energy gap, the bandgab ( $E_{bg}$ ) (K. Dimitirs, 2006).

The filling of bands in a solid and the size of the bandgab determine if a material is a conductor, a semiconductor, or an insulator. In general, for electrons to flow in a solid under the application of an a partially filled band or have access to a nearby empty band. In an electrical insulator, there is no possibility for electron flow, because the valence band is completely filled with electrons, and the conduction band is too far away in energy to be accessed by these electrons. In conductor like metals the valence band overlaps the conduction band. Thus, the electrons can access empty areas within the valence band and move freely across all atoms that make up the solid. Finally a semiconductor is a special case in which the band gab is small enough ( generally less small than 4eV) that it can be bridged by either heat or light,

because these stimuli promote electrons from the valence band to the conduction band (D. Beydoun, R. Amal, et al, 1999).



**Figure (1.1) Energy bands in solids: a) Insulator. b) semiconductor. c)conductor.**

Semiconductors are mainly classified into two categories: intrinsic and extrinsic. An intrinsic semiconductor is one, which is pure enough that impurities do not appreciably affect its electrical behaviour. Elemental ( e.g. Si, Ge ) and compound ( e.g. InSb, GaAs, SiC ) semiconductors can be intrinsic semiconductors and possess poor conductivity. At a temperature of absolute zero (0 K) there are no charge carriers in an intrinsic semiconductor and therefore the material behaves as an insulator. In energy band terms the CB is completely empty of electrons and the VB is fully occupied by the valence electrons. At a finite temperature, a valence band electron (e-) may be thermally excited into the CB, leaving behind an unoccupied state in the valence band. This unoccupied state, which can be thought of as a second carrier of positive

charge, is called a hole ( $h^+$ ). Electrons in the presence of an electric field contribute to current in the same direction since they are oppositely charged. Hole and electrons created in this way are known as intrinsic charge carriers. In intrinsic semiconductors, for each and every electron in CB, there exists a corresponding hole ( the empty state ) in VB. Therefore, the electron concentration and is equal to the hole concentration is called the intrinsic carrier concentration, denoted as  $n_i$ (K. Dimitirs, 2006).

An extrinsic semiconductor can be formed by addition of impurity atoms into the crystal of an intrinsic semiconductor, in a process known as doping. Doping results in a change of the relative concentrations of electrons and holes in the material in a manner, which depends on the kind of the dopant atom. It should be noted that, although the number of free electron or hole concentration changes, a doped semiconductor is electrically neutral. Chemical impurities that contribute to conduction electrons are called donor impurities or donors. Semiconductors doped with donors are called n-type semiconductors (n stands for negative ). For example silicon, which belong to group IV of the periodic table, has four valence electrons. When elements belonging to group V ( e.g. As, P, Sb ) are incorporated into a Si crystal, each dopant atom contributes an additional electron to the crystal thereby increasing its ability to conduct electricity (O. Crap, L. Huisman, et al, 2004).

Impurity atoms that take away an electron from the semiconductor are called acceptor impurities or acceptors and result in the formation of p-type semiconductors (P stands for positive ). For instance, when a group III element ( e.g. B, Al, Ga ) is incorporated into the crystal structure of silicon, the dopant atom has an insufficient number of bonds to share with the surrounding Si atoms. One of the silicon atoms has a vacancy for an electron and a hole is created, which contributes to the conduction process at all temperatures. In an n-type semiconductors, electrons are the majority carries and the electron concentration  $n$ , is equal to the donor impurity concentration. Holes are

minority carries in n-type semiconductors. The opposite is true for p-type semiconductor, where holes are the majority carriers and their concentration,  $P$ , is equal to the acceptor impurity concentration. Electrons are minority carriers in P-type semiconductors(R. Malato, G. Blanco, et al, 2004).

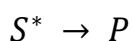
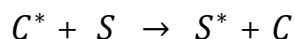
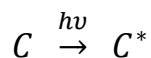
### **1.5 Definition and mechanism of Photocatalysis:**

A substance can be thought to be a catalyst when it accelerates a chemical reaction without being consumed as a reactant; that is to say, it appears in the rate expression describing a thermal reaction without appearing in the stoichiometric equation. A catalyst is a compound that lowers the free activation enthalpy of the reaction. Then, photocatalysis can be defined as the acceleration of a photoreaction by the presence of a catalyst, includes photosensitization, a process by which a photochemical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called the photosensitizer, but it excludes the photoacceleration of a stoichiometric thermal reaction irrespective of whether it occurs in homogeneous solution or at the surface of an illuminated electrode. Otherwise, any photoreaction would be catalytic (M. Castellote and N. Bengtsson, 2011 ).

Depending on the specific photoreaction, the catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct. Depending on the specific photoreaction, the catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct (M. Castellote and N. Bengtsson, 2011 ).

When the light is absorbed by the catalyst  $C$ , the system represents a sensitised photoreaction which may occur through two different ways:

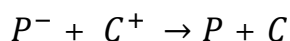
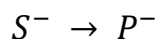
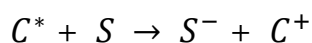
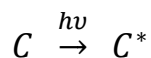
1. via energy transfer, by forming an activated state of the reactant of interest, S, which is more easily oxidized than their ground state:



Where:

S is the substance and P is the product.

2. via electron transfer, by acting either as an electron donor or acceptor.



In the case of energy transfer, the product P is formed from the activated substrate along the potential energy curve, while a new reaction path is opened when the photosensitizer transfers an electron to the substrate. In considering excited-state redox reactivity, particularly that involved in organic photocatalysis, the direct occurrence of electron transfer will be of greater concern than involving energy transfer (M. Castellote and N. Bengtsson, 2011).

Due to the fact that the difference between a sensitised and a catalysed photoreaction is somewhat arbitrary, due to the different and complex mechanisms involved (static and dynamic sensitisation, interaction with a photoproduct, photoinduced reactions, ...), the term, photocatalysis has therefore been defined as broad as possible without the specific implication of any special mechanism, and refers then to the reaction of a substance whose function is activated by the absorption of a photon. A photocatalyst can be described as one involved in the quantum yield expression for a photochemical reaction without its stoichiometric involvement; or more precisely, it appears in the quantum yield expression for reaction from a particular excited state to a power greater than its coefficient in the stoichiometric equation (M. Castellote and N. Bengtsson, 2011).

The main difference between a conventional thermal catalyst and photocatalyst is that the former is activated by heat whereas the latter is activated by photons of appropriate energy. Photocatalytic reactions may occur homogeneously or heterogeneously, but heterogeneous photocatalysis is by far more intensively studied in recent years because of its potential use in a variety of environmental and energy-related applications as well as in organic syntheses. In heterogeneous photocatalysis, the reaction scheme implies the previous formation of an interface between a solid photocatalyst (metal or semiconductor) and a fluid containing the reactants and products of the reaction. Processes involving illuminated absorbate-metal interface are generally categorized in the branch of photochemistry. Therefore, term "heterogeneous photocatalysis" is mainly used in case where a light-absorbing semiconductor photocatalyst is utilized, which is in contact with either a liquid or a gas phase. Here, we will restrict our attention to the description of semiconductor-mediated photocatalysis (M. Gratzel, 1983).



Semiconductors are particularly useful as photocatalysts because of a favourable combination of electronic structure, light absorption properties, charge transport characteristic and excited-state lifetimes(K. Dimitirs, 2006).

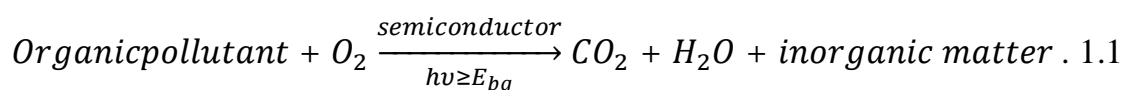
Semiconductor, by definition, is nonconductive in its un doped ground state because an energy gap, the bandgap, exists between the top of the filled valence band and the bottom of the vacant conduction band. Thus, electron transport between these bands must occur only with appreciable energy change. In semiconductor photocatalysis, excitation of an electron from the valence band to the conduction band is accomplished by absorption of a photon of energy equal to or higher than the bandgap energy of the semiconductor. This light-induced generation of an electron-hole pair is a prerequisite step in all semiconductor-mediated photocatalytic processes(M. Herrman, 2005).

Photogenerated species tend to recombine and dissipate energy as heat of photons, because the kinetic barrier for the electron-hole recombination process is low. However conduction band electrons and valence band holes can be separated efficient in the presence of an electric field, such as the one formed spontaneous in the space charge layer of a semiconductor-fluid or a semiconductor-metal interface. Thus the lifetime of Photogenerated carriers increase and the possibility is offered to these species to exchange with substrate adsorbed on the photocatalyst surface and initiate chemical reactions (M. Schiavello, 1997).

Interfacial electron transfer, i.e, transfer of an electron to or from a substrate adsorbed onto the light-activated semiconductor is probably the most critical step in photocatalytic processes, and its efficiency determines to a large extent the ability of the semiconductor to serve as a photocatalyst for a given redox reaction. The efficiency of electron transfer reactions is, in turn, a function of the position of semiconductor's conduction and valence band edges relative to the redox potentials of the adsorbed substrates. For a desired electron transfer to occur, the potentials of the electron acceptor species should be located below

(more positive than) the conduction band of the semiconductor, whereas the potential of the electron donor species should be located above (more negative than) the valence band of the semiconductor. Interfacial electron transfer processes are then initiating subsequent (dark) redox reactions to yield the ultimate products. The latter catalytic reaction steps are not different from thermal catalysis, and similar principles will apply for a photocatalytic reaction as for a thermal catalytic reaction (M. Serpone, E. Pelizzetti, 1989).

The reaction describing the process for the implementation of semiconductor photocatalysis on the degradation of organic pollutants is given by the following equation (C. Philippoulos and M. Nikolaki, 2010):



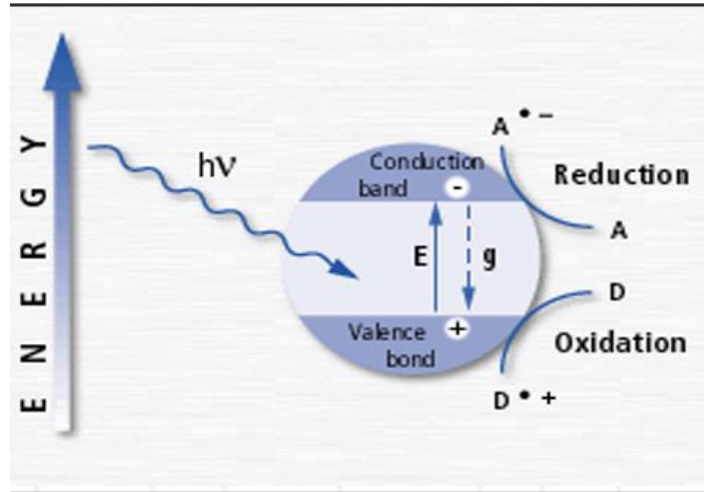
The potential energy required for the chemical transformation to occur is overcome by the large amounts of “free energy” supplied with the ultraviolet or visible light quanta. Thus, in contrast to conventional thermal catalytic reactions, which usually rely on the application of high temperature and/or pressure, photocatalysis under relatively mild (usually ambient) conditions with lower energy input. This is particularly true when the photocatalytic reaction is activated by solar light (M. Gratzel, 1983).

An important characteristic of photocatalysts is that, in contrast to thermal catalysts, they can drive thermodynamically “uphill” reactions, i.e., reactions which involve transformations of substrates to products of higher potential energy. In this respect, a distinction is often made between “photocatalytic” and “photosynthetic” reactions, depending on whether the sign of the change in Gibbs free energy ( $\Delta G^o$ ) of reaction (1.1) is negative or positive, respectively. Examples of spontaneous, exergonic reactions ( $\Delta G^o < 0$ ) include oxidation of organic pollutants present in the gas or liquid phase, whereas

endergonic reaction ( $\Delta G^o > 0$ ) is the photocatalytic cleavage of a water toward hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) (D. Bahnemann, P. Robertson, et al, 2005).

The large variety of semiconducting materials, mainly metal oxides and chalcogenides, have been investigated with respect to their photocatalytic properties, but only few of them are considered to be effective photocatalysts. In general, wide-bandgap semiconductors, such as titanium dioxide ( $TiO_2$ ), prove to be better photocatalysts than low-bandgap materials, such as cadmium sulphide (CdS), mainly due to the higher free energy of Photogenerated charge carriers of the former and the inherently low chemical and photochemical stability of the latter. However, low bandgap semiconductors are better adapted to the solar spectrum, thereby offering the significant advantage of potential utilization of a continuous and readily available power supply, the sun. A considerable amount of effort has been made in recent years for the development of more efficient photo-catalysts characterized by increased quantum efficiency and improve response to the visible spectral region. Promising results in this direction have been obtained with the use of several methods aiming at the modification of electronic and/or optical properties of semiconductors, including metal deposition, dye sensitization, doping with transition metals or non-metallic elements, use of composite semiconductors photocatalyst , etc(K. Demeestere, J. Dewolf, et al, 2007).

It must be noted that the process of electron transport ( or equally for holes ) is more effective, if the electron acceptors (or donors) are adsorbed on the particle surface and that can be shown in figure (1.2). Their transport rate depends upon the relative positions of the conduction and valence bands, as well as upon the redox potential of the adsorbed species(C. Philippoulos and M. Nikolaki, 2010).



**Figure (1.2) Photocatalysis on a semiconductor.**

The efficiency of a photocatalytic process is measured by quantum yield, which is the ratio of the stimulation incidents per absorbed photon (C. Philippoulos and M. Nikolaki, 2010).

In the heterogeneous processes, however, there is a difficulty in measuring the exact amount of the absorbed radiation, because a part of it is scattered by the semiconductor's surface. Therefore, it is assumed that all the incident radiation is absorbed and an apparent quantum yield is calculated instead (C. Philippoulos and M. Nikolaki, 2010).

An alternative definition for the efficiency (based on the reaction kinetics) is that the efficiency is equal to the ratio of the photocatalytic reaction rate ( $\text{mols}^{-1}$ ) to the absorbed radiation flux ( $\text{photon s}^{-1}$ ). In order to calculate the process quantum yield, all possible interaction phenomena between electrons and holes must be taken into account. Therefore the quantum yield is defined as:

$$\Phi \propto \frac{K_{M\Phi}}{K_{M\Phi} + K_{EP}}$$

Where  $K_{M\Phi}$  and  $K_{EP}$  the charge transfer rate (electrons or holes) and the recombination rate respectively. It is obvious that if it were not for charge

recombination, the quantum yield of the process would be equal to unity (C. Philippoulos and M. Nikolaki, 2010).

In this case, the transfer rate would depend solely upon electron and hole diffusion to the surface. This is however an ideal case, because in fact recombination takes place and the electron and hole concentration on the surface of the semiconductor is not uniform (C. Philippoulos and M. Nikolaki, 2010).

In order to reduce the electron-hole recombination rate and to increase the efficiency of the photocatalytic process, researchers are trying to modify the semiconductor surface with various ways, such as metal addition, in combination with other semiconductors and so on (C. Philippoulos and M. Nikolaki, 2010).

## **1.6 Heterogeneous Semiconductor Photocatalysis:**

The most important among the advanced oxidation processes is heterogeneous photocatalytic oxidation, often referred to as photocatalysis. This method deals with the oxidation mostly of organic molecules, with the use of a solid catalyst, which is activated by the incidence of radiation of an appropriate wavelength. It can take place both in the aqueous phase as well as in the gas phase. In 2009 it is gaining considerable interest in comparison to homogeneous catalysis due to disadvantages of the latter. The most important are the separation process of the products that may be implicated, and that in most cases is economically and/or technically impracticable, as well as the in appropriate, from an environmental point of view, use of some homogeneous catalysts, such as metal salts. This disadvantages have given a boost to the development of heterogeneous catalytic processes, despite the fact that controlling such a process difficult, since it comprises of five stages:

1. the transfer of the reactants from the liquid phase on to the catalytic surface,

2. the adsorption of at least one of the reactants,
3. the reaction in the adsorbed phase,
4. the desorption of the products away from the diphasic area.

The photocatalytic reaction takes place in the adsorbed phase (stage 3). The different form classic catalysis is that instead of the thermal activation of the catalyst, we have a photonic activation from the incident radiation.

In photocatalytic reactions in the aqueous media the most commonly used process of organic pollutants in the presence of a semiconducting solid catalyst (R. Huang, W. Ting, et al, 2001).

### **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 importante methods used to remove the carcinogen materials like phenol, chlorothalonil, methylene blue and Rohdamine 6G from water. It was found that the photocatalysis is efficient process.

A.Rajat, V.Jitendra, et al, studied the use of semiconducting iron(III) oxide in photocatalytic bleaching of some dyes in 2006. The photocatalytic bleaching was carried out on cationic dyes (methylene blue, crystal violet, malachite green) in the presence of semiconducting iron(III) oxide and was observed spectrophotometrically. The effects of the PH, concentration of dyes, amount of semiconductor, light intensity, particle size, stirring, etc. The efficiency of the reaction were observed (A.Rajat, V.Jitendra, et al, 2006).

In 2007, B. Snejana, S. Vaclav, et al, studied the Photocatalytic efficiency of iron oxides: on Degradation of 4-chlorophenol. The photocatalytic activity of ferrihydrite  $\text{Fe}_5\text{O}_7(\text{OH}) \times 4\text{H}_2\text{O}$  synthesized by homogeneous precipitation with

urea and products obtained by calcinations of as-precipitated ferrihydrite at different temperatures (200° –1000° C) was studied. They have found that hematite  $\text{Fe}_2\text{O}_3$  obtained at 1000° C exhibited satisfied photocatalytic efficiency on the degradation of 4-CP ( B.Snejana, S. Vaclav, et al, 2007).

In 2010, W. Abu Bakar, R. Ali and M. Othman studied Photocatalytic Degradation and reaction pathway of Chlorinated Hydrocarbons in gaseous phase.  $\text{TiO}_2$  was doped with various types of first row transition metals towards the degradation of dichloromethane, chloroform, carbon tetrachloride and a mixture of carbon tetrachloride and chloroform.

$\text{Zn}^{2+}/\text{Fe}_3^+/\text{TiO}_2$  photocatalyst with the ratio of 0.0005: 0.0005: 1 was revealed as the best catalyst in this study. 41.05% of dichloromethane, 49.45% of chloroform and 37.84% of carbon tetrachloride were degraded by this catalyst in the presence of UV light (6 W, 354 nm), irradiated for 90 minutes (W. Abu Bakar, R. Ali and M. Othman, 2010).

In 2012, G. Minghui, S. Vasile, et al, studied Iron oxide nanoparticle synthesis in aqueous and membrane systems for oxidative degradation of trichloroethylene from water. Trichloroethylene (TCE) was selected as the model contaminant because of its environmental importance. Degradations of TCE and  $\text{H}_2\text{O}_2$  by NP( iron oxide) surface generated  $\text{OH}^\bullet$  were investigated. Depending on the ratio of iron and  $\text{H}_2\text{O}_2$ , TCE conversions as high as 100 % (with about 91% dechlorination) were obtained. TCE dechlorination was also achieved in real groundwater samples with the reactive membranes. (G. Minghui, S. Vasile, et al, 2012).

In 2014, M. Mohamed, studied Photodegradation of Rhodamine 6G molecules using  $\text{TiO}_2$  photocatalyst. The absorption spectra of Rhodamine 6G with different amounts of catalyst, were recorded and compared before and after

irradiation by UV light. The results showed that, the efficiency of the photodegradation process was increased with the amount of semiconductor ( $\text{TiO}_2$ ) and irradiation time as well. The lower percentage of Rhodamine 6G degradation from waste water was 16% when 100mg of  $\text{TiO}_2$  was added and irradiated for 10min, while the highest percentage of Rhodamine 6G degradation was 82% when 600mg of  $\text{TiO}_2$  was added and irradiated for 30min. The study concluded that the degradation of Rhodamine 6G is increased with increasing the amount of  $\text{TiO}_2$  as well as with increasing the irradiation time (M. Mohamed, 2015).