Chapter II
Review of Literature
3. REVIEW OF LITERATURE

Maria Jose Farre et al., (2005) studied the degradation of some biocalcitrant pesticides by homogenous and heterogeneous photocatalytic ozonation. They used Photo-Fenton/ozone (PhFO) and TiO$_2$ – photocatalysis/ozone (PhCo) as advanced oxidation processes for the degradation of the biocalcitrant pesticides alachlor, atrazine, chlorfenvinfos, diuron, isoproturon and pentachlorophenol. They found that the best results of pesticide mineralisation are obtained when PhFO was applied except in the case of atrazine and alachlor for which no detoxification was achieved at the experimental conditions.

Kim et al., (2005) studied the effect of ferric ion on alachlor photodegradation in the presence of TiO$_2$ and UV radiation. They found that the rate constant increased from 0.031 to 0.05 as the concentration of ferric ion increased from 0.75 to 7.5 mg Fe$^{3+}$/l in the absence of TiO$_2$. However it showed increase from 0.05 to 0.11 in the presence of both ferric ion and TiO$_2$.

Xinle Zhu et al., 2004 examined the TiO$_2$ photoassisted degradation of pesticide pyridaben in acetonitrile/water suspensions under UV light irradiation mainly at wavelength longer than 360nm. They studied the dissipation kinetics at two different UV wavelength irradiations ($\lambda \geq 300$ nm and $\lambda \geq 360$ nm). The dissipation kinetics were also studied under different conditions such as water content, pH, catalyst concentration and radiant flux. A qualitative study of the degradation products generated during the process was performed by GC-MS.
Shankar et al., (2004) studied the adsorption of monocrotophos (MCP) over HY, Hβ and H-ZSM-5 zeolites. They found that MCP followed the order Hβ > HY > H-ZSM-5 and they had chosen Hβ as the support of TiO₂. They suggested that higher activity of the supported catalyst was due to the greater adsorption of MCP on the support and capability of support to delocalize the conduction band electrons of excited titania.

Ramesh and Maheswari, (2003) studied the dissipation of alachlor in soil, plant, water and its bioaccumulation in fish. They studied the fate of alachlor in water and constructed simulated model ecosystem to which fish was introduced after one herbicide application.

Kotagi, (2002) studied the basic profiles of hydrolysis such as pH and temperature dependency for each class of pesticides together with typical reaction mechanisms. He suggested that although these hydrolytic profiles depend on the chemical nature and functional groups of a pesticide molecule, they were not always consistent within a chemical class of pesticides. Various instrument techniques were applied to chemical identification of degradates, leading to clarification of the reaction mechanism involved.

The phototransformation of a pollutant in surface water may result from light absorption by pollutant itself (direct photolysis) or may be photoinduced by the dissolved natural organic matter (NOM) or nitrate ions present in water, as these chromophores are known to photoproduce reactive species (indirect photolysis). (Thomas-Smith et al., 2001).
The hydrolysis of pesticides is an area that has received extensive study, since most compounds entering the environment will at some stage be in contact with water or be adsorbed in lipophilic media. (Wei Zheng and Weiping Liu, 1999).

Mouvet et al., (1997) investigated the stability of isocturon, terbutylazine and alachlor in groundwater, surface water, and soil water from the unsaturated zone. They found that the initial pesticide concentration plays a significant role and the lowest concentration being the least stable for all pesticides. Significant loses of alachlor were observed only after 30 days. Terbutylazine and isoproturon were found stable for 30 days, except for a slight loss of terbutylazine in soil water. Thus, they observed that the stability of the molecules was highest in the ground water and lowest in soil water.

Brown and Cottermann, (1994) studied the degradation and metabolism of sulfonylurea herbicides in soil and water and suggested that although there were quantitative differences in the degradation pathways, the most common primary degradation and metabolic pathways were the cleavage of the sulfonyl urea bridge, O- and N- dealkylation, aryl and aliphatic hydroxylation, ester hydrolysis, and conjugation reactions with glutathione and carbohydrates.

Photolysis is one of the most important pathways of pesticide degradation in water and air, and on plant and soil surfaces (Burkhard N et al., 1979)
Heterogeneous photocatalysis using TiO$_2$ is regarded as a promising method for the transformation of toxic and bioreistant compounds into harmless species. Carey et al., 1976 first reported the photocatalytic degradation of biphenyl and chlorbiphenyls in the presence of TiO$_2$. After Carey's paper various classes of potentially hazardous compounds, including organochlorine, organophosphorus and sulphonyl ureas were successfully destroyed using TiO$_2$ enhanced photocatalysis.

3.1 PHOTOCATALYSIS USING VARIOUS TECHNIQUES

Various methods have been adopted to monitor the residual level in the environmental matrices. Losito et al., (2005) used X-ray photoelectron spectroscopy (XPS) for the analytical determinations of composite titanium dioxide-poly(vinylidenefluoride) (TiO$_2$-PVDF) films developed for applications in the photocatalytic degradation of pollutants. They studied the photocatalytic degradation tests on isoproturon, a phenylurea herbicide, under solar UV irradiation the results were compared to direct photolysis to evaluate the catalytic efficiency of immobilized TiO$_2$ and the role played by the PVDF film during the degradation process.

Saha et al., (2003) developed the method for the determination of sulfosulfuron residues and its three metabolites in wheat field by utilizing HPLC photodiode array detector. They analysed the sulfosulfuron residues in soil, wheat, grain and straw. The percent recovery ranged between 74.0 to 75.2 for soil and 70.8 to 74.7 for plant samples.
Degradates of acetochlor and alachlor (etanesulfonic acids, ESAs) were analysed in both standards and in a ground water sample using high-performance liquid chromatography –time-of-flight mass spectrometry with electrospray ionization. (Thurman et al., 2002).

Bianco-Prevort et al., (2001) found the possibility for the use of flow injection (F1) to monitor the photocatalytic mineralization of dicamba (3,6-dichloro-2-methoxybenzoic acid) present at the trace level in aqueous solutions containing TiO₂ suspensions. Experiments were performed in a stirred photochemical reactor equipped with a simple F1 manifold, integrating an online filtration unit able to perform the monitoring of the UV absorbance of the irradiated solution every 4 min. The light source used was a medium pressure mercury lamp (125W). During the initial steps of the reaction the formation of UV absorbing intermediates, which completely disappear in less than 80 min, was evidenced. Additional HPLC, DOC and chloride ion measurements were carried out on manually taken samples. They suggested that the proposed on-line monitoring was particularly suitable for the control of degradation treatments where primary degradation and mineralization steps takes place after a comparable irradiation time.

Seasonal variations of pesticide residues in surface waters and ground waters of N.Greece were studied by Albanis et al., (1998) using solid phase extraction disks followed by gas chromatographic technique with flame thermionic division, electron capture detection and Mass selective detection for monitoring various pesticides and their transformation product in environmental waters.
Photosensitized Degradation has been used to remove a broad range of organic pollutants, generally with mineralization to CO₂ & other inorganic products (such as Cl⁻). TiO₂ and Fe³⁺ were photosensitized and used to accelerate the degradation of persistent organic chemicals. Gustavo and Damia Barcelo (1998) also used HPLC, GC and ion exchange methods to identify degradation products & to monitor the degradation kinetics. Other analysis techniques such as TOC analysis, UV-visible spectrophotometry, spectrofluorimetry and potentiometry were also used.

Ming-Chun Lu and Jong-Nan Chen (1997) studied the photocatalytic oxidation of toxic chemicals 2,4-D and Propoxur. Total organic carbon analyzer was used to assess the efficiency of photocatalytic mineralization. Microtox bioassay was employed in evaluating the toxicity of solutions treated by photocatalysis. They suggested that toxicity is an important criteria in assessing the pretreatment process.

Barcelo et al., (1993) studied the photodegradation of the organophosphorus pesticides fenitrothion and the chlorotriazine herbicide propazine under different light conditions. The photodegradation of propazine was carried out using a xenon lamp in the suntest apparatus whereas a high pressure mercury lamp was used for fenitrothion. Identification of sufficiently volatile photodegradation product was achieved by gas chromatography – mass spectrometry (GC-MS) with electron impact (EI) whereas for the direct characterization of the hydroxy metabolite of propazine thermospray liquid chromatography – mass chromatography (LC-MS) was used. They studied
photodegradation pathways which include dealkylation, deamination, dehalogenation, hydroxylation, isomerization & solvolysis.

A general liquid-solid extraction procedure for the isolation of pesticides from ground water and drinking water using High Performance Liquid Chromatography (HPLC) was presented by Antonio Di Corcia et al., (1991).

3.2 PHOTOCATALYSIS UNDER VARIOUS CONDITIONS

Emmanuelle Vulliet et al., (2003) studied the photocatalytic degradation of six sulfonylurea herbicides (cinosulfuron, triasulfuron, prosulfuron, metsulfuron methyl and chlorimuron ethyl) in aqueous solutions containing TiO₂ suspensions as photocatalyst, in order to assess influence of various parameters, such as adsorption, initial concentration and photon flux on the photocatalytic process.

Chemicals having strong adsorption in the near ultraviolet or visible range can be decomposed directly by sunlight. Those having negligible light adsorption can be broken down by sensitizing mechanisms. Young-Soo Keum et al., (2002) studied the kinetics of sunlight degradation of diafen thiuron in natural paddy water, the photodegradation products, any quenching effects of acetone and isopropanol, effect of humic acid and air, on the photolysis rate was compared with photolysis rate in distilled water and pure hexane.
Photocatalytic degradation of the pesticide Aldrin dissolved in water was studied by Erick Bandala et al., (2002) in one case using concentrated solar radiation and in another case, using non-concentrated solar radiation. In these experiments the effects of catalyst concentration, oxidant agent concentration, and solar irradiation were tested. In experiments without irradiation, strong adsorption of the pesticide over TiO$_2$ was observed in the first few minutes of contact in the presence of TiO$_2$. They suggested that this was due to the columbic interaction between the catalyst surface and pesticide molecules.

A kinetic study of the chemical degradation of isoxaflutole in organic buffers at different pH values was carried out using HPLC/UV detection method by Estelle Beltran et al., (2001). They calculated the values of the pseudo-first order rate constants $K_{obs}$ for the reaction and compared with those previously obtained in inorganic buffers. They concluded that in both the cases, $K_{obs}$ was found to be dependent on pH and Temperature.

Wei Zheng and Weiping Liu (1999) studied the kinetics of imidacloprid at different pH and temperature. The hydrolysis products were identified by HPLC, MS and IR and a possible pathway for imidacloprid hydrolysis was proposed.

Song Hong and Lemley (1998) developed a GC-MS Method with direct aqueous injection, to determine alachlor and its degradation products in water. The method was optimized to give the following conditions: injections with platless mode, injection port with silawized-glass reverse, cup liner filled with 0.5mm carboflit above the cup: injection temperature of 250°C & an
analytical column with a stationary phase of 5% diphenyl to 95% dimethyl polysiloxane.

Photochemical effects of humic substances on the aquatic degradation of organophosphorus pesticides were studied on the basis of photo-induced radical generation abilities of humic substances and the increased percentage of the humin sensitized photodegradation rate constants relative to those measured in the huminless system (Mamoru Kamiya and Katsura Kameyama, 1998).

Particulate suspensions of TiO$_2$ irradiated with natural solar light in a large experimental plant, catalyze the oxidation of a typical organic contaminant, Pentachlorophenol(PCP). Maloto et al., (1997) studied and found that the addition of oxidants (such as H$_2$O$_2$, peroxymonosulphate, oxone) and per oxydisulphate) whose concentration is kept constant during treatment increases the rate of photodegradation of PCP. They also suggested that per oxydisulphate was found to the best oxidant to treat pesticide effluent.

3.3 PHOTOCATALYSIS USING DIFFERENT CATALYST

Sayam Sen Gupta et al., (2002) destroyed the priority pollutant pentachloro phenol (PCP) and 2,4,6-trichloro phenol(TCP) in water using activated H$_2$O$_2$. They activated the catalyst H$_2$O$_2$ using iron complexes of tetraamido macrocyclic ligand (TAML-Fe).

Heterogeneous hydrolysis of organophosphorus pesticides in the presence and absence of three iron oxides (heamatite, goethite and
ferricydrite) and aluminium hydroxide was investigated by Andrea Dammenberg et al. (1998). They suggested that metal oxide surfaces could catalyze as well as inhibit the hydrolysis of organophosphorus insecticides and thus significantly affect the fate of these compounds in the environment.

The photocatalytic degradation of organic environmental pollutants in the presence of semiconductor such as TiO₂ or ZnO or Fe₂O₃ has been extensively studied. (Hoffmann et al., 1995, Kamat, 1993).

Hendry and Sargeson (1990) discussed the possible mode of action of metals in the catalysed reactions of phosphate derivatives. They suggested that metal ion coordination to a phosphate derivative will enhance the reactivity in two ways: to increase the positive charge on the phosphorus and to make the phosphorus center more electrophilic. They also discussed the difficulties of using labile metal ion complexes when investigating the mechanism of enhanced reactivity with phosphorus derivatives. They concluded that one of the more effective ways for a metal ion to enhance reactivity of phosphate derivatives is to provide an intramolecular nucleophile.

3.4 PHOTOCATALYSIS USING SEPARATE AND SUPPORTED TiO₂ CATALYST

The photocatalytic oxidation has been reviewed worldwide and the significance of TiO₂ photocatalyst is well recognized in the field of photochemistry. Heterogeneous photocatalysis is a good technique to destroy organic pollutants in water. Docters et al., (2004) synthesized titania
photocatalyst by the molten salts methods by reaction of a titanium precursor with three different alkali metal nitrates (LiNO₃, NaNO₃, KNO₃). The titania powders obtained have been characterized using TEM, XRD, BET and UV-Vis adsorption spectroscopy. Their photoactivities were evaluated by degrading a commercial sulfonylurea herbicide, prosulfuron. They also found that the rate constants increased in the following order: Li<Na<K. Even though the photocatalytic activities obtained did not exceed or even equal to that of Degussa P25, nevertheless - this study constitutes the first attempt to synthesise titania photocatalyst by the molten salts method.

Wenxiu Que et al., (2003) synthesized patternable TiO₂ and originally modified silane hybrid films are synthesized by the sol-gel spin-coating technique. Optical properties and patterning of the hybrid film were also studied. UV-Vis spectroscopy and Fourier transform infrared spectroscopy were used to study the optical and structural properties of the hybrid film.

Satoshi Horikoshi and Hisao Hidaka, (2003) studied the decomposition of atrazine and cyanuric acid in either supercritical water or hydrothermal water using TiO₂ under the fixed pressure of 23 Mpa at 623K or 683K in a 120 ml Hastelloy batch reactor.

Emmanuelle Vulliet et al., (2003) investigated the photocatalytic transformation of two sulfonylurea herbicides, cinosulfuron and triasulfuron in aqueous solutions containing TiO₂ suspension as photocatalyst. It was found that both sulfonylureas dissipated with different kinetic order (1 and ½ respectively) Quantum efficiency was also calculated and was found to be similar in both the case. In addition to this the intermediate products
were also identified using HPLC-UV and HPLC-MS techniques and the degradation pathway was also discussed. Some endocrine disruptors such as 2,4-dichlorophenoxy acetic acid, 2,4-dichlorophenol, nonylphenol, bisphenol A, diethyl phthalate etc which can be neither biodegraded by bacteria nor degraded thermally can be degraded by TiO₂ photocatalytic treatment.

Chantal Guillard et al., (2002) prepared a specially designed titania photocatalyst by coating Alistron non-woven paper, used as a flexible photocatalytic support with Millennium PC 500 anatase. At the same time, a new solar photoreactor (STEP) was designed by them based on the multistep cascade falling-film principle to ensure good exposure to sunlight and good oxygenation of the effluent to be treated.

Lia and Li (2002) investigated the mechanism of photosensitization and the recombination of excited electron -hole pairs affected by depositing platinum (Pt) on the surface of titanium dioxide. A new catalyst Pt-TiO₂ was prepared by a photoreduction process. Being model reactions, the photocatalytic oxidations of methylene blue (MB) and methyl orange (MO) in aqueous solutions using the Pt- TiO₂ catalyst was carried out under either UV or Vis light irradiation.

Ozer and Ferry (2001) investigated the polyoxometalate catalyzed electron transfer from the conduction band of photoexcited TiO₂ to molecular oxygen. The oxidation of 1,2-dichlorobenzene (DCB) was used as an index reaction for evaluating the photocatalyst system TiO₂− PW₁₂O₄₀(3−), TiO₂ SiW₁₂O₄₀, (4−), and TiO₂ W₁₀O₃₂(4−) in oxygenated aqueous solution. Addition
of these polyoxometalate (POM) anions to TiO$_2$ suspensions resulted in significant rate enhancement for DCB oxidation.

Heterogeneous photocatalysis using TiO$_2$ is regarded as a promising method for the transformation of toxic and bioresistant compounds in to harmless species. Adrian Zaleska et al., (2000) studied the photocatalytic degradation of lindane, $p$-$p'$- DDT and methoxychlor in aqueous solution using UV/ TiO$_2$/O$_2$ system.

Catherine Galindo et al., (2000) studied the oxidation of the aminoazobenzene dye AO52 by the UV/H$_2$O$_2$, UV/TiO$_2$ and Vis/TiO$_2$ system. They investigated the formation of by-products by means of GC/MS, HPLC and H$^1$NMR. Spectroscopy.

Maloto et al., (2000) studied the solar photocatalytic mineralization of methamidifos (O,S-dimethyl phosphoramidothioato) in aqueous solution in the presence of dispersed particles of TiO$_2$ in a pre-industrial pilot plant. They also studied the mineralization rate using peroxydisulphate along with TiO$_2$ and found that the oxidation of organics present in the formulation was enhanced 18 times by use of the electron scavenger peroxydisulphate compared to TiO$_2$ alone.

Modestov and Lev (1998) studied the photodegradation of 2,4-dichlorophenoxyacetic acid using illuminated titania particles in buffered water solutions at pH 9.2. A simple phenomenological model which enables comparison of activity of suspended and supported photocatalysis on the basis of utilization of light was proposed by them. The features of the model were
verified by studies of the photocatalytic activity of TiO$_2$ suspended and supported on flat glass plate and on floating particles.

Titanium dioxide is one of the most efficient photocatalyst for the detoxification of organically charged wastewater. However this material suffers from the drawback of poor absorption properties because of a band gap of 3.2 eV. Thus wavelength shorter than 400 nm is needed for light induced generation of electron-hole pairs. Therefore, doping with transition metal ions is interesting for inducing batho-chromic shift of the band gap. Wilke and Breuer, (1998) doped titania with Cr$^{3+}$ and Mo$^{5+}$ ions. They showed the complex interactions between variations in lifetime of charge carriers, adsorption properties and photocatalytic behavior.

Jean-Marie Herrmann et al., (1998) studied the photocatalytic detoxification of water containing the organic pollutant 2,4-D (2,4-dichlorophenoxy acetic acid) and benzofuran using a photoreactor consisted of a tank (2471) connected to compound parabolic connectors (CPCs) (1471), through which the aqueous suspension of titania (0.2g/l of TiO$_2$ Degussa) was circulated at a flow rate of 3.5m$^3$/h. Reaction rates for pollutant and TOC removal were found to be propotional to the global radiant flux propotional to both direct and diffuse UV light. They suggested that zero kinetic order of TOC disappearance enable one to envisage an easy way of controlling the overall rate of photocatalytic detoxification of large quantities of water containing a mixture of pesticides.

Malato et al., (1998) tested a new granulated version of the well known P-25 titanium dioxide (Aeropest) to determine whether its photocatalytic
efficiency was good enough for use in photo catalytic water purification and to find out if it can be separated by water more easily than it's well known homologue, powdered Degussa P-25. Further more a new commercial catalyst (PC-100 from Millennium inorganic chemicals) having a surface area and structure that are both different from Degussa P 25, was also studied. All the experiments were carried out in sunlight in the pilot compound parabolic collector (LPC) plant at the plataforma solar de Hmesia. They studied these reaction with different substrates namely dichloroacetic acid, phenol and the pesticide imidacloprid. They found that Degussa Aeropril is not a good alternative to powdered Degussa P-25 because of its spontaneous sedimentation during photocatalysis. Millenium PC-100 efficiency was found to be on par with Degussa P-25.

The pesticides carbofuran, diazino, isoproturon, metamitron, terbuthylazine, pendimethalin were irradiated with UV light of different wavelengths in water and water/soil suspensions under various conditions. Mansour et al., (1997) found that as compared to pure distilled water, photodegradation was increased in the presence of titanium dioxide, hydrogen peroxide or ozone, or by using Natural River or lake water.

In their review, Peral et al., (1997) have explained the use of photocatalysis for purification and decontamination and deodorization of air.

Nageswara Roa and Sangeetha Dube (1995) studied the degradation of 2,4-dichlorophenoxy acetic acid (2,4-D) using UV-illuminated TiO₂ suspensions (Degussa P25 TiO₂, Aldrich TiO₂, and Indian origin TiO₂, (TiO₂, SD) and TiO₂ fixed to polyester fabric (PE-PVA- TiO₂) or TiO₂ layer formed on Ti sheet by flame oxidation (Ti/ TiO₂). They also studied 5th mode of adsorption of 2,4-D over TiO₂. In their study they found that pyridine was inhibiting 2,4-D by estimating COD as a function of irradiation time.