CHAPTER 1

INTRODUCTION

From time immemorial, light has a profound influence on mankind. Hence it is not surprising that light-induced reactions still continue to attract considerable attention of chemists. The studies of light-induced electron-transfer reactions have become an active area of research. This activity has been further stimulated by the public awareness and concern for developing alternative methods to clean the environment and eventually replace the non-destructive methods. This chapter deals with the detailed introduction of the concept of photocatalysis and its utility in the removal of pollutants from the environment.

1.1 DEFINITION OF PHOTOCATALYSIS

The term photocatalysis consists of the combination of photochemistry and catalysis and implies that light and a catalyst are necessary to bring about or to accelerate chemical transformations. (Kisch 1989).

1.2 ENERGETIC CONSIDERATIONS

The energetic requirements of a photocatalytic process are compared with those of photosynthesis as shown in Figure 1.1. While it is evident that no net storage of light energy into the final products is achieved in photocatalysis, it has been shown by many authors that free radical intermediates play an important role (Duonghong et al 1982, Moser and Gratzel 1984, Bahnemann et al 1984a, 1984b, 1991a and 1991b, Serpone et al 1985, Albery et al 1985, Kamat 1985 and Gopidas and Kamat 1989).
Figure 1.1 Energetic considerations for the definition of semiconductor particles as photosensitisers or photocatalysts.
Indeed, the formation of radical species from the original compounds is generally highly endothermic and requires a considerable amount of incident photo energy (Rao and Hayon 1974, Steenken and Netal1982, Bielski et al 1985, Wayner et al 1988, Wardman 1989 and Stanbury 1989). The energetic requirements for such a free radical mechanism are illustrated in Figure 1.1. The nature of these radical intermediates, their interaction with the semiconductor surface, their lifetime and reactivity are among the most crucial factors determining the yield of photocatalytic conversions as well as product distribution and specificity.

1.3 PHOTOCATALYTIC EFFECT

In order to induce redox reactions, a photocatalyst or a photosensitiser is required because the energy of photons of sunlight is not sufficient to excite a simple molecule electronically. The role of a photocatalyst is essentially the same as the role of chlorophyll in the photosynthetic system. Many kinds of photocatalysts have been employed. They have been classified into two groups (1) dye and other photoactive molecules in homogeneous system such as Ru(bipy)$_3^{2+}$ and metal porphyrin and (2) semiconductors in a heterogeneous system.

Extensive studies with transition metal complexes containing ligands such as bipyridyl, phenanthrolines and metalloporphyrins have indicated the potential utility of these materials in photochemical conversion of solar energy (Bolton 1977, Zamareav and Parmon 1980 and Connolly 1981). These studies have shown that the main factor that limits the efficiency in homogeneous solution is the thermal reverse electron transfer between the redox products. Studies in organised molecular assemblies such as micelles, vesicles and micro emulsions show some promise in controlling to some extent the light induced charge separation process (Kalyanasundaram 1978 and Kiwi et al 1982).
An alternate approach to this problem is the utilization of semiconductor materials as light absorbing system. Photoredox reactions between a semiconductor and redox species in solution take place vectorially, unidirectionally and are, in general, not reversible. Heterogeneously dispersed semiconductor surfaces provide a fixed environment that influences the chemical reactivity of a wide variety of adsorbates. Upon photoexcitation, simultaneous oxidation and reduction reactions occur. The incident light that initiates this sequence is in the wavelength region (visible or low energy range of the ultraviolet region) absorbed by the semiconductor rather than by the substrate of interest. Thus, these reactions involve photosensitization, i.e. an indirect photoactivation of the dispersed semiconductor rather than the direct formation of an excited state of the substrate. In addition, another point of relevance is that the photocatalyst is often stable under the photolysis conditions (particularly when a metal oxide like TiO$_2$ is employed) and usually a large number of conversions per active sites on the catalyst can be realized. Initial interest in these photoinduced redox reactions was prompted by Fujishima and Honda (1972) discovery that water can be split on illuminating a TiO$_2$ single crystal to which an electrochemical bias had been applied.

1.4 BAND MODEL AND REDOX PROCESSES ON SEMICONDUCTOR POWDERS AND DISPERSIONS

The band theory of solids and electronic theory of catalysis have proved to be useful in understanding the photoprocesses that have been studied on semiconductor systems. According to the band model (Morrison 1980), the occurrence and the efficiency of various photoredox processes are intimately related to the location of valence and conduction band edges. Absorption of light of energy greater than bandgap energy of the semiconductor leads to generation of electron-hole pairs and these under the influence of an electric field move in between the conduction band and valence band respectively. The resulting non-equilibrium distribution of electrons and holes leads to reduction and oxidation processes. Often, because of the high
absorption coefficients, the incident photons are attenuated within a short distance from the surface and hence surface properties of catalysts play a dominant role.

The main advantages of particulate system are (1) work-up of the reaction mixture is easier since powders can be separated by centrifugation. (2) they are simpler, less expensive and relatively easy to fabricate and can be recycled. (3) since a very large surface area is exposed to the reactants, their efficiency may be high.

1.5 SEMICONDUCTORS AS PHOTOCATALYST

Photocatalysis on a semiconductor powder is essentially a redox reaction. During a photocatalytic reaction, the irradiated surface of the semiconductor will act as a sink for the electrons (or holes) depending upon the direction of band bending. The other charge carrier will move under the influence of the electric field into the bulk of the semiconductor or to the surface that receives the lowest intensity of incident radiation. Thus, the separation of charge carriers, namely, the electrons and holes, determines the efficiency of any photocatalytic reaction. This problem can be circumvented by metal doping or by coupling two semiconductors. These aspects are considered in the following sections.

1.5.1 Metal-Semiconductor Systems as Photocatalyst

of any electric field, but the presence of a metal with high electron affinity effectively traps the photoexcited electrons and utilizes it to perform subsequent reduction reaction. Similarly the hole can be made to participate in the oxidation reaction unidirectionally thereby increasing the overall efficiency of the process. The photocatalytic activity varies with respect to parameters like nature of the metal loaded, method of metal loading (Sakata et al. 1981), the extent of metal loading (Ichou et al. 1985) and nature of the semiconductor in use.

1.5.1.1 Nature of the loaded metal

The choice of the metal is primarily governed by the value of the electron affinity of the metal to be loaded. The electron affinity of the metal should be preferably high enough to trap the photoexcited electrons. Another important parameter is the work function. The metal should have a suitable work function to form a favourable contact with the semiconductor. Noble metals are generally employed for the design of metallised semiconductor systems. The electron affinities and reduction potential of redox couples of various noble metals are listed in Table 1.1 (CRC Handbook of Chemistry and Physics 2000).

Table 1.1
Electron affinities and reduction potentials of various metal ions/metal redox couples of noble metals

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Electron affinity (eV)</th>
<th>Reduction potential $E^0$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$^{2+}$ + 2e$^-$ ↔ Pd</td>
<td>0.557</td>
<td>0.951</td>
</tr>
<tr>
<td>Pt$^{2+}$ + 2e$^-$ ↔ Pt</td>
<td>2.128</td>
<td>1.118</td>
</tr>
<tr>
<td>Ru$^{3+}$ + 3e$^-$ ↔ Ru</td>
<td>1.050</td>
<td>0.455</td>
</tr>
<tr>
<td>Au$^+$ + e$^-$ ↔ Au</td>
<td>2.309</td>
<td>1.692</td>
</tr>
</tbody>
</table>
Extensive studies on metal loaded semiconductor systems have shown that the extent of photoactivity depends on the nature of the metal supported on the semiconductor. Pt, Pd or Rh increases the photoactivity by a factor of 2 to 100 times (Sakata et al. 1981). The greater photoactivity may be due to the catalytic effect of the metals. For instance, Fe(III) doping of TiO₂ has been shown to increase the quantum efficiency for the photoreduction of N₂ (Palmisano et al. 1988, Soria et al. 1991 and Sclafani et al. 1992) and to inhibit electron-hole pair recombination (Martin et al. 1994a and 1994b and Choi et al. 1994). While in the case of phenol degradation, Fe (III) doping was reported to have little effect on the efficiency (Palmisano et al. 1988, Sclafani et al. 1992). Enhanced photoactivity for water cleavage (Borgarello et al. 1982) and N₂ reduction (Palmisano et al. 1988) with Cr (III) doped TiO₂ has been noted. However other authors (Herrmann et al. 1984) have found the opposite effects with Cr(III) doping. Enhanced photoactivity for bleaching of lignin solution with Pt, Au and Ag doped with TiO₂ and ZnO has also been reported (Ohnishi et al. 1989). Negative effects of doping (Luo and Gao 1992) have been noted for molybdenum and vanadium in TiO₂, while Gratzel and Howe (1990) noted inhibition of electron-hole recombination with the same dopants. Karakitsou and Verykios (1993) reported that doping of TiO₂ with cations of higher valency than that of Ti(IV) resulted in enhanced photoactivity.

1.5.1.2 Method and extent of metal loading

The photocatalytic activity also depends on the method of metal loading. One of the widely employed doping technique is the impregnation of semiconductor powder from an aqueous solution containing the corresponding metallic salt. Metallic platinum can be deposited on TiO₂ powder by photocatalytic reduction of an aqueous suspension containing chloroplatinic acid or sodium chloroplatinate. Other noble metals can also be deposited in a similar manner often resulting enhanced photocatalytic effects. Numerous studies have been performed to clarify the role of

Metallisation of semiconductor surfaces offers a method for metal recovery from industrial wastes or from dilute solutions. The potential use of semiconductor photocatalysis for the recovery of Au from an alloy containing Au, Cu, Ni or Zn has been demonstrated on either UV irradiated TiO$_2$ in HCl/HNO$_3$ mixtures (pH 3-6) or WO$_3$ irradiated with visible light. The extent of metal loading influences the photocatalytic activity. For example, at low Pt loading (0.1 - 1.0 wt %) on TiO$_2$ surface, enhancement of photoactivity probably results from an optimal attraction of free electrons of titania by platinum crystallites (Pichat et al 1987). Thus the extent of loading is important in governing the net effect of metallisation with heavy metal loading induce faster electron-hole recombination (Renault et al 1986).

1.5.1.3 Nature of the semiconductor

The energy level of the lower edge of the conduction band of a semiconductor can be considered to be a measure of the reduction strength of the photoexcited electrons whereas that of the upper edge of the valence band is a measure of the oxidation strength of the holes. Band energies of various semiconductors versus the electrochemical potential of hydrogen and oxygen is depicted in Figure 1.2. The potential of these semiconductors for oxidation and reduction can be classified into four groups from the point of view of water splitting reaction (Kalyanasundaram 1983).

1. **OR** type: The oxidation and reduction power is strong enough (in principle) for the evolution of both hydrogen and oxygen. Examples are TiO$_2$, SrTiO$_3$, CdS. OR indicates strong ability for both oxidation and reduction. 2. **R** type: Only the reduction power is strong enough to reduce water. The oxidation power is too weak to oxidize water. Examples are CdTe, CdSe and Si. 3. **O** type: The oxidation power is
The redox potential of water is indicated as reference. The values are with reference to NHE at pH 7.

Figure 1.2 Bandgap energies of various semiconductors.
strong enough to oxidise water since the valence band is located at a more positive value compared to the $O_2/H_2$ level. The reduction power is not strong enough to reduce water. Examples are $WO_3$, $Fe_2O_3$ and $Bi_2O_3$. 4. $X$ type: The conduction and valence bands are located between $H^+/H_2$ and $O_2/H_2O$ levels. Therefore, both oxidation and reduction powers are weak and neither oxygen nor hydrogen can be evolved.

1.5.2 Coupled Semiconductors

An interesting approach to prevent electron-hole recombination is the coupling of two semiconductor catalysts to improve charge separation (Serpone et al 1984b, Barbeni et al 1985 and Borgarello et al 1986a). This strategy accomplishes vectorial displacement of charges on the semiconductors and reduces electron-hole recombination of the excited particles. This inter-particle electron transfer mechanism was first applied successfully to visible light-induced decomposition of $H_2S$ into $H_2$ and $S$ (Serpone et al 1984b). Coupling of CdS with TiO$_2$ followed by irradiating CdS with visible light ($\lambda > 400$ nm) induces the formation of $e_{cb}^-$ (CdS) and $h^+_{vb}$ (CdS) which subsequently recombine in competition with a transfer of $e_{cb}^-$ (CdS) onto the conduction band of TiO$_2$. Thus, mixed semiconductor systems offer potential advantages for solar energy utilization because of the possibilities presented by inter-particle electron transfer (Serpone et al 1984) and special properties (tuning of bandgap) of co-fabricated systems (Henglein and Gutierrez 1983).

1.6 CATALYST SUPPORTED SYSTEM

The finely divided catalyst can be either dispersed in the irradiated aqueous solution as a slurry, or anchored on a suitable support as a fixed or fluidized bed. According to various reports (Anderson and Bard 1995, Crittenden et al 1996 and Pozzo et al 1997), mainly from laboratory scale investigations, slurry system seems to be more efficient than those based on immobilized catalysts. However, for engineering
applications, there is an intrinsic drawback of the first option. The need for post-radiation treatment of particle-fluid separation for catalyst recycling and for the ultimate goal of obtaining clean and powder free water. Because of the small particle size of the catalyst (somewhere between 30 and 300 nm) the cost requirements for this downstream operation may even invalidate altogether the claimed energy saving for a solar induced decontaminating process.

Although phase separation process can be avoided by using fixed or fluidized bed reactors with a supported catalyst, it is not less true that mass transfer limitations might outweigh this intrinsic advantage. Also the catalyst surface availability for reactants and photons could be significantly better in a well mixed, pseudo-homogeneous small particle slurry than in any supported catalyst arrangement.

The penetration length of light in a solid-liquid medium is another important parameter which is a function of particle size, catalyst charge (slurry concentration in one case and support surface coverage in the other) and support transparency to radiation. Actually, given the complexity of the photocatalytic process and the multiplicity of variables involved it is not an easy task to carry out an effective control and to find a common ground for comparison between supported and unsupported catalyst performances. Many alternatives have been proposed in the last few years which attempted a variety of supporting materials and coating methods in different arrangements for the degradation of several organic compounds.

1.7 ROLE OF OXIDATION PROCESSES IN HAZARDOUS WASTE TREATMENT

Oxidative destruction of chemicals provide ultimate solution for the treatment of hazardous wastes. Oxidative destruction of organic pollutants can be accomplished by various means, namely, biological, chemical and physical (thermal). While there are differences in the mode of operation, the basic principle of energy
dissipation process, intrinsic to oxidative destruction of organic matters, is largely the same among these systems.

1.7.1 Biological Oxidation Process

Traditionally, attention received by biological oxidation process far exceeds that of the chemical and physical oxidation systems due to its cost effectiveness and versatility in handling a wide variety of organic pollutants. Since its introduction in the 1900s, several biological treatment systems have evolved and been adopted for the treatment of complex wastes with a good degree of success. However, the presence of toxic chemicals in the waste streams can cause unwanted operational difficulties. Much has been reported (Huang et al 1993) on the difficulties in the operation of biological oxidation systems in treating municipal wastewater let alone hazardous wastes. These difficulties are intrinsic to the process in that it is sensitive to ambient conditions as well as waste characteristics. Moreover, the generally long retention time and start-up time of the biological oxidation process make it unattractive for the treatment of toxic and refractory organic pollutants.

1.7.2 Thermal Oxidation

Thermal destruction of specific chemicals at extreme temperature (incineration) has been successfully applied to the treatment of solid wastes, sludge and gases. While simple in principle, thermal systems have suffered from many difficulties in operations. Additionally, thermal processes are rather limited in treating aqueous wastes as considerable energy is required to heat and vaporise the water before specific organic pollutants are destroyed at relatively elevated temperatures (usually greater than 850°C). To overcome this difficulty, wet-air oxidation has been developed.
1.7.3 Wet Air Oxidation

In wet air oxidation, organic compounds are decomposed in atmospheric air or pure oxygen at 150 to 370°C and 10 to 220 bar pressure. Organic substrates are first carbonised (Lohamann and Tilly 1965). The dissolved oxygen reacts catalytically on the surface of the carbon center so as to yield hydrogen peroxide which then decomposes to form oxygen and hydroxyl radicals. These radicals then react with carbon to yield carbon dioxide (autocatalytic oxidation). The following compounds can be destroyed by wet-air oxidation (Dietrich et al. 1985): aliphatic compounds including those with multiple halogen atoms, residual oxygenated compounds of low molecular weight such as alcohols, aldehydes, ketones and carboxylic acids, aromatic hydrocarbons such as toluene and pyrene, halogenated aromatics with at least one non-halogen functional groups of electron donating nature present on the ring. The substitutes include hydroxyl, amino or methyl group. Halogenated aromatics such as 1,2-dibenzene and polychlorinated biphenyls (PCBs) are resistant to degradation unless catalysts are employed.

The wet air oxidation process has greatly improved the efficiency of the incineration process as well as ease of operation. However, due to the severity of the reaction, construction materials for the system become the major cost factor. Due to its high cost, wet air oxidation process remains an operation of the preliminary treatment nature without total destruction of the organic pollutants.

1.7.4 Thermal Catalytic Oxidation Process

A specific catalytic system based on acidic solutions of bromide, nitrate and manganese ions has been developed (Miller 1981). The organics are bathed in oxygen containing water and oxidised at the surface (in particular in the internal surface) of the catalyst. Copper ions have significant catalytic effect. Mn(V) catalyst and activated chromium compounds have also been investigated (Martinetz 1986).
The major problems associated with these processes are the separation of the catalysts after the treatment.

1.8 ADVANCED OXIDATION PROCESSES (AOPs)

In light of the increasing concern over the contamination of the environment by hazardous chemicals, there is a great need to develop innovative technologies for the safe destruction of toxic pollutants. The process must be cost effective, easy to operate and capable of achieving total or near-total mineralisation. This has prompted the researchers to investigate innovative chemical oxidation technologies. This section gives an overview of recent developments in advanced oxidation processes with an emphasis for wastewater treatment.

The oxidation potential of an oxidant is related to its oxidation-reduction potential (E°). An oxidant with a high E° value is a strong oxidising agent. Table 1.2 lists the E° values (CRC Hand book of Chemistry and Physics, 2000) for a host of oxidising agents against that of molecular O₂, although it must be mentioned that kinetic factors often outweigh thermodynamic properties in controlling the oxidation reactions. Nevertheless, a stronger oxidant will generally exhibit faster oxidation reaction. Based on this simple premise, fluorine is the strongest among the list. However, fluorine, a halogen, may produce halogenated compounds during the oxidation process. Among these oxidants, ozone has received the greatest attention. However, the mechanism of ozonation was not fully understood until the late seventies when Hoigne and coworkers (1976 and 1983) first reported the mechanism of ozonation. It was thought that molecular ozone was the major oxidation species. Hoigne et al (1976 and 1983) proposed that O₃ can have two reaction modes. Direct ozonation reaction and free radical (such as hydroxyl radical) decomposition reaction. The direct O₃ reaction involves molecular O₃ which is highly selective and produce a relatively slow reaction. The typical rate constants are in the order of \(1 \times 10^3 \text{ M}^{-1}\text{sec}^{-1}\).
Table 1.2

Oxidation – Reduction Potentials of Oxidising Agents

<table>
<thead>
<tr>
<th>Redox Reaction</th>
<th>$E^0$ (volt) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2 + 2e$</td>
<td>$2F^-$</td>
</tr>
<tr>
<td>$OH^- + H^+ + e$</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>$O_3 + 2H^+ + 2e$</td>
<td>$O_2 + H_2O$</td>
</tr>
<tr>
<td>$H_2O_2 + 2H^+ + 2e$</td>
<td>$H_3O_2^+$</td>
</tr>
<tr>
<td>$MnO_4^- + 4H^+ + 3e$</td>
<td>$MnO_2^2 + 2H_2O$</td>
</tr>
<tr>
<td>$HClO_3 + 3H^+ + 4e$</td>
<td>$Cl^- + 2H_2O$</td>
</tr>
<tr>
<td>$MnO_4^- + 8H^+ + 5e$</td>
<td>$Mn^{2+} + 4H_2O$</td>
</tr>
<tr>
<td>$HOCl + H^+ + 2e$</td>
<td>$Cl^- + H_2O$</td>
</tr>
<tr>
<td>$Cl_2 + 2e$</td>
<td>$2Cl^-$</td>
</tr>
<tr>
<td>$HBrO + H^+ + 2e$</td>
<td>$Br^- + H_2O$</td>
</tr>
<tr>
<td>$O_3 + H_2O + 2e$</td>
<td>$O_2 + 2OH^-</td>
</tr>
<tr>
<td>$ClO_2(g) + e$</td>
<td>$ClO_2^-$</td>
</tr>
<tr>
<td>$Br_2 + 2e$</td>
<td>$2Br^-</td>
</tr>
<tr>
<td>$HIO + H^+ + 2e$</td>
<td>$I^- + H_2O$</td>
</tr>
<tr>
<td>$ClO_2(g) + e$</td>
<td>$ClO_2^-$</td>
</tr>
<tr>
<td>$ClO^- + 2H_2O + 2e$</td>
<td>$Cl^- + 2OH^-</td>
</tr>
<tr>
<td>$H_2O_2 + 2H^+ + 2e$</td>
<td>$2H_2O$</td>
</tr>
<tr>
<td>$ClO_2^- + 2H_2O + 4e$</td>
<td>$Cl^- + 4OH^-</td>
</tr>
<tr>
<td>$BrO^- + H_2O + 2e$</td>
<td>$Br^- + 4OH^-</td>
</tr>
<tr>
<td>$I_2 + 2e$</td>
<td>$2I^-$</td>
</tr>
<tr>
<td>$I_3 + 3e$</td>
<td>$3I^-</td>
</tr>
<tr>
<td>$IO^- + H_2O + 2e$</td>
<td>$I^- + 2OH^-</td>
</tr>
</tbody>
</table>

The $E^0$ values are with respect to normal hydrogen electrode (NHE)
As a result, there is no complete mineralisation and a variety of intermediates could be formed (Rice et al 1987). The hydroxyl radical formed during the ozone decomposition reacts much more rapidly with organic compounds than molecular O$_3$. The rate constants are usually in the order of $10^8$-10$^{10}$ M$^{-1}$sec$^{-1}$ (Farhataziz and Ross 1977). Chemically, hydroxyl radical is much less selective than molecular ozone.

The concept of Advanced Oxidation Processes (AOPs) was established by Glaze et al (1987a and 1987b). AOP was defined as the oxidation which generate hydroxyl radicals in sufficient quantities to effect water treatment (Glaze et al 1987a and 1987b). Many systems are qualified under this broad definition of AOP. Most of these systems use combination of strong oxidants, e.g. O$_3$ and H$_2$O$_2$, catalysts like transition metal ions or photocatalysts and irradiation, e.g. ultraviolet (uv), ultrasound (us), or electron beam (eb). Table 1.3 lists typical AOP currently reported in the literature (Huang et al 1993).

### 1.8.1 Hydroxyl Radical

The hydroxyl radical is one of the reactive free radicals and one of the strongest oxidants (Buettner 1985)

$$`OH + H^+ + e^` \rightarrow H_2O \quad E^0 = 2.33 \text{ V} \quad (1.2)$$

Thus, in acidic conditions, the hydroxyl radical will have higher oxidation potential. In basic solution (pH = 11) the hydroxyl radical and H$_2$O$_2$ react to give an oxide and a peroxide ion (Spinks and Woods 1990). Irradiation of water generates OH relatively independent of pH until pH 10. The reaction of OH with organic compounds can be hydroxyl addition, hydrogen abstraction or electron transfer. Organic compounds containing aromatic systems or carbon-carbon multiple bonds
# Table 1.3
## List of Typical Advanced Oxidation Processes

1. **Homogeneous System**
   - **With irradiation**
     - Ozone/Ultraviolet (UV)
     - Hydrogen peroxide/UV
     - Electron beam
     - Ultrasound (US)
     - UV/Ultrasound
   - **Without irradiation**
     - Ozone/H₂O₂
     - Ozone/OH⁻
     - H₂O₂/Fe²⁺ (Fenton’s)

2. **Heterogeneous System**
   - *With irradiation*
     - TiO₂/Oxygen/Ultraviolet
     - TiO₂/H₂O₂/ Ultraviolet
   - *Without irradiation*
     - 1 Electro-Fenton
undergo additional reaction with \( {^\cdot}OH \) due to the rich \( \pi \)-electron cloud on the aromatic ring. For example

\[
{^\cdot}OH + C_6H_6 \rightarrow C_6H_5OH \tag{1.3}
\]

Hydrogen abstraction is the usual reaction with unsaturated organic compounds.

\[
{^\cdot}OH + CH_3COCH_3 \rightarrow CH_2COCH_3 + H_2O \tag{1.4}
\]

Electron transfer is usually found in the reactions between hydroxyl radical and inorganic ions. For example

\[
Fe^{2+} + {^\cdot}OH \rightarrow OH^+ + Fe^{3+} \tag{1.5}
\]

This is important in Fenton's reagent reaction. Since \( {^\cdot}OH \) has high and indiscriminate reactivity, it can react with almost all types of organics such as ethylenic, aromatic and aliphatic, and inorganics such as anions and cations. The addition of \( {^\cdot}OH \) to benzene is found to be very fast. The process produces cyclohexadienyl radical with an unpaired electron. The dienyl radical disproportionates to a complex mixture of products including phenol, cyclohexadienes, hydrocyclohexadienes, biphenyl and hydroxylated biphenols. Oxidation by \( {^\cdot}OH \) can result in the final products such as \( CO_2, H_2O \) through a series of reaction.

\[
HOOC-C_4H_4-COOH + {^\cdot}OH \rightarrow HOOC-COOH + H_2O + CO_2 + H_2O \tag{1.6}
\]

The above reaction involves both hydroxyl addition and hydrogen abstraction for the mineralisation of benzene.
1.8.2 Homogeneous System with Irradiation

1.8.2.1 Ozone / UV system

Photolysis of aqueous ozone produces hydrogen peroxide. The deprotonated form of hydrogen peroxide (HO$_2^-$) can react with ozone to produce ozonide (O$_3^-$) ion and hydroxyl radical (Buhler et al 1984). These species initiate the chain reaction. As a result, compounds normally refractory to ozonation are rapidly converted to CO$_2$ and water. Additionally, poly-chlorinated biphenyls (PCBs) which are very stable to ozone are destroyed rapidly by the combination of ozone and UV method.

1.8.2.2 Hydrogen peroxide / UV system

UV photolysis of H$_2$O$_2$ generates hydroxyl radical.

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \]  \hspace{1cm} (1.7)

Sundstrom et al (1990) have studied the destruction of individual aliphatic and aromatic compounds by UV catalyzed oxidation with hydrogen peroxide. The results demonstrated that the system can destroy a wide variety of hazardous compounds present in water at low concentration levels. In the case of chlorinated aliphatic compounds, the organic chlorine was converted to chloride ion indicating that the chlorinated structures were effectively destroyed by this system. In the case of aromatic compounds, many intermediates were formed which could be degraded by extending the treatment time. The oxidation rate increases with increasing concentration of hydrogen peroxide and decreases with increasing organic concentration. The decomposition of H$_2$O$_2$ by UV has much lower efficiency than that of ozone due to the much lower extinction coefficient of H$_2$O$_2$ by UV photolysis. Processes such as H$_2$O$_2$/UV, O$_3$/ UV and H$_2$O$_2$/ O$_3$/ UV have been shown to be effective for groundwater decontamination and soil remediation. The activation energy
between active radicals, such as hydroxyl radicals and organics is close to zero, oxidation occurs rapidly.

1.8.2.3 Electron-beam (eb) system

Irradiation of water with high energy electrons results in the formation of reactive free radicals e\(^-\) (aq.), H\(^+\) and 'OH. These radicals are formed through the excited state molecules such as H\(_2\)O\(^*\), H\(_2\)O\(^+\) and e\(^-\). When the excited molecules and electrons interact and transfer their energy to other molecules, several secondary reactive species are formed. The relative efficiencies (G) are defined as the number of radicals, excited states or other products formed or lost in a system absorbing 100 eV of energy. According to their production abundance, the following order exists

\[
\text{'OH (2.7) = H}_2\text{O}^- (2.7) > e^- (2.6) > H_2O_2 (0.71) > H^+ (0.55)}
\]

The e\(^-\) and H\(^+\) are the reducing species. Of these radicals e\(^-\) and 'OH make up 90% of the reactive species and are the major radicals to render the organic destruction. H\(_2\)O\(_2\) is also an important species in oxidising toxic organics although it is not as abundant as the other two species. The interaction between aqueous electrons and specific organics and inorganics has been extensively studied (Cooper et al 1990). The e\(^-\) (aq.) is a powerful reducing agent with a potential (E\(^0\)) of 2.77 V as per the equation 1.8.

\[
e^- + H^+ \rightarrow ^1/2 H_2 \quad (1.8)
\]

The aqueous electrons can result in the dehalogenation of organohalogen compounds. Further reaction of the organic radicals leads to the complete destruction of these compounds. Hydrogen radicals can undergo hydrogen addition or hydrogen abstraction. These reactions are considered as minor ones due to the following extremely fast reaction between the hydrogen radical and oxygen.
\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad k = 2.1 \times 10^{10} \text{M}^{-1} \text{sec}^{-1} \quad (1.9) \]

### 1.8.2.4 Ultrasound (US) system

Ultrasound (US) can affect organic oxidation through nucleation, growth and cavitation. Cavitation, which is created by the collapse of a gas or vapour-filled bubble in a body of liquid, is the most important phenomenon. The instantaneous pressure and temperature at the center of the collapsing bubble has been estimated to be about 75,000 psi and 72000°C respectively (Suslick 1988). Due to this high local pressure and temperature, cavitation can significantly enhance the rate of chemical reactions. Next solvent will be compressed and refracted by the rapid movement of fluids caused by the variation of sonic pressure. Then a large amount of energy will be put into a small volume with little heating. The phenomenon is called microstreaming.

Ultrasound radiation is known to decompose water vapour molecules into free radicals such as hydroxyl radicals, hydrogen radicals and hydroperoxyl radicals (Mason 1990). Prasad and Sharma (1970) studied the liberation of a chloride ion in a saturated aqueous solution of chlorobenzene by ultrasound (US). More than 90% dechlorination of chlorobenzene and m-dichlorobenzene occurs in 60 and 100 min. respectively (Prasad et al 1970). It is believed that the hydroxyl radical formed by the reaction between H\(_2\) and O\(_2\) is responsible for the oxidation of chlorobenzene and m-chlorobenzene in water. Although hydrogen peroxide can be produced by application of ultrasound alone to a diluted aqueous solution, the amount may be too small to be significant. Hydrogen peroxide can be added to this process as an initiator to increase the free radical concentration in the solution.
1.8.2.5 Hydrogen peroxide / Ultrasound System

Chen et al (1990) investigated the oxidation of chloroform by H$_2$O$_2$ / ultrasound process. The optimal molar ratios of H$_2$O$_2$ to CHCl$_3$ are between 30 and 50. When the ratio of H$_2$O$_2$ to CHCl$_3$ is 50:1, the best percentage removal (94%) was achieved. The overall reaction can be presented as follows

$$\text{CHCl}_3 + 2 \cdot \text{OH} \rightarrow \text{CO}_2 + 3 \text{Cl}^- + 3 \text{H}^+ \quad (1.10)$$

The reaction is first order with a rate constant of 0.0177 min$^{-1}$. Since the concentration of hydroxyl radical generated is much higher than that of chloroform, the order of reaction with respect to the free radical is zero. However, the optimal ratio of 50:1 for H$_2$O$_2$ to chloroform is quite high for practical applications.

It appears that an excess amount of H$_2$O$_2$ would slightly retard the decomposition of chloroform. This phenomenon has been reported by Ho (1986) in the study of photooxidation of 2, 4 - dinitrotoluene in the presence of H$_2$O$_2$. This is because H$_2$O$_2$ itself is a hydroxyl radical scavenger.

1.8.2.6 Ultrasound / UV System

Ultrasound can be combined with UV to destroy toxic organics. The chemical consequence of photolysis and sonolysis of a simple haloalkane is the cleavage of carbon-halogen bond in liberating halogen ions (Suslick 1988). The principal products of water under sonolysis are H$_2$O$_2$, H$_2$, \·OH and \·H. When sonochemical decomposition of aqueous CCl$_4$ occurs, the radicals such as \·OH and \·H react with CCl$_4$ and form Cl$_2$, CO$_2$, HCl, hexachloroethane (C$_2$Cl$_6$) and HOCl (Jennings and Townsend 1961, Mason and Lomier 1988). The pH of photosonolysis is very acidic (in the range of 1). However, less acidic solutions (pH 3) were found under sonolysis and photolysis.
The order of CHCl₃ disappearance and Cl⁻ appearance is the following for oxidation of immiscible CHCl₃ in water:

$$\text{photosonolysis} \rightarrow \text{photolysis} \rightarrow \text{sonolysis}$$

For a miscible sample of CHCl₃ in water, the efficiency for different processes follows a different order:

$$\text{photosonolysis} \rightarrow \text{sonolysis} \rightarrow \text{photolysis}$$

The aqueous solutions exhibit lower vapour pressure than higher concentration of the immiscible pair. The lower vapour pressure of the liquid causes higher cavitation bubble collapse intensity. Since the temperature and pressure can reach thousands of Kelvins and atmospheres respectively, the increasing cavitation intensity is considered as the most important factor to enhance the dissociation of the covalent bonds of the organics and their extent of decomposition (Edmonds 1981 and Suslick 1988).

1.8.3 Homogeneous System without Irradiation

1.8.3.1 Ozone / Hydrogen peroxide system

Buhler et al (1984), Formi et al (1982) and Sehested et al (1982) have reported that H₂O₂ can initiate the decomposition of O₃ by single electron transfer wherein the initiating species is the hydroperoxide ion HO₂⁻:

$$\text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}^+ \quad K_a = 1.6 \times 10^{12}$$

The hydroperoxide ion reacts with ozone to produce ozonide ion, O₃⁻ and hydroperoxide radical, HO₂⁻.
These products can form \( \cdot \mathrm{OH} \) radicals through the following initiation steps.

\[
\begin{align*}
\text{HO}_2 & \rightarrow H^+ + O_2^- \quad K_a = 1.6 \times 10^{-5} \quad (1.13) \\
O_2^- + O_3 & \rightarrow O_3^- + O_2 \quad k = 1.6 \times 10^9 \text{ M}^{-1}\text{sec}^{-1} \quad (1.14) \\
O_3^- + H^+ & \rightarrow \text{HO}_3 \quad k = 5.2 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1} \quad (1.16) \\
\text{HO}_3 & \rightarrow \cdot \mathrm{OH} + O_2 \quad k = 1.1 \times 10^5 \text{ M}^{-1}\text{sec}^{-1} \quad (1.17)
\end{align*}
\]

Once the hydroxyl radical is formed, the following propagation steps generate hydroxyl radicals by autocatalytic mechanism.

\[
\begin{align*}
O_3^- + \cdot \mathrm{OH} & \rightarrow O_2 + \cdot \mathrm{HO}_2 \quad (1.18) \\
O_3^- + \cdot \mathrm{HO}_2 & \rightarrow 2O_2 + \cdot \mathrm{OH} \quad (1.19)
\end{align*}
\]

The chain mechanism generates hydroxyl radicals by consuming \( \text{H}_2\text{O}_2 \) and \( O_3 \). It is terminated by recombination of different radicals. Hydroxyl radicals abstract a hydrogen atom from saturated hydrocarbon or add to unsaturated organics to form an organic carbon centered radical in less than \( 10^{-6} \) sec. The carbon centered radicals react quickly with oxygen to yield a peroxyl radical when oxygen is present. This radical can decompose unimolecularly to produce a superoxide ion (\( O_2^- \)) and the deprotonated form of the \( \cdot \text{HO}_2 \) radical. Predominant hydrogen peroxide and minor superoxide can also be formed if the carbon centered radical decomposes bimolecularly. The latter process is considered to take place through a tetroxide structure. Superoxide reacts quickly with ozone yielding ozonide and continuing the chain reaction. When ozone is present, this reaction is much faster than superoxide disproportionate to hydrogen peroxide.
1.8.3.2 Ozone / OH\textsuperscript{−} system

From neutral to high pH, ozone decomposes into hydroxyl radicals through the following initiation steps (Hoigne and Bader 1976 and Payton 1991).

\[
\begin{align*}
    O_3 + OH^- & \rightarrow O_2^- + O_2 \quad (1.20) \\
    O_3 + H_2O & \rightarrow 2 \cdot OH + O_2 \quad (1.21)
\end{align*}
\]

The above initial steps result in the hydroxyl radicals which is the major oxidation species. This is the reason that alkaline oxidation rates by ozone are several orders of magnitude higher than those in acidic media (Games and Staubach 1980). Several investigators classified the ozonation at alkaline condition as advanced oxidation process (Haag and Hoigne 1983). The catalytic effect of a hydroxide ion has been recognised for a long time in the ozonation of organic pollutants. Niegoski (1953) reported pH of 11.8 as the optimal value. Jones (1971) indicated phenol oxidation proceeds most efficiently at pH 11.4.

1.8.3.3 H\textsubscript{2}O\textsubscript{2} / Fe\textsuperscript{2+} (Fenton’s reagent) system

The powerful oxidizing properties of a mixture of H\textsubscript{2}O\textsubscript{2} and Fe\textsuperscript{2+} salt was first observed by Fenton (Fenton 1894 and 1899). Forty years later, Haber and Weiss (1934) established the oxidising species as hydroxyl radical. In recent years, the hydroxyl radical has been observed directly by electron spin resonance spectroscopy (Weir et al 1987). Literature studies revealed that organic compounds of nearly all types could be oxidised by Fenton’s reagent.
Fenton's reaction is given by Equation 1.22 (Walling 1975):

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} - \cdot \text{OH} + \cdot \text{OH} \]  

(1.22)

The products of the reaction are ferric ion, hydroxyl radical and hydroxide ion. The rate is first order with a rate constant of \( k_1 = 76 \ \text{M}^{-1}\text{sec}^{-1} \) (Walling 1975). In the absence of added substrate, the hydroxyl radical will oxidise a second molecule of ferrous ion as shown in Equation 1.23:

\[ \text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} - \text{OH} \]  

(1.23)

The rate constant \( k_2 \) is \( 3 \times 10^8 \ \text{M}^{-1}\text{sec}^{-1} \) (Walling 1975).

The expected stoichiometry of the reaction is given in Equation (1.24). Protons have been added to show formation of water.

\[ 2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O} \]  

(1.24)

This equation indicates that Fenton’s reaction is strongly dependent on solution pH. In fact, only in acidic condition \( \cdot \text{OH} \) is the predominant reactive oxidant.

In the presence of organic compounds, organic oxidation proceeds via addition of \( \cdot \text{OH} \) or via hydrogen atom abstraction. Equation 1.25 is for \( \cdot \text{OH} \) addition:

\[ \cdot \text{OH} + \text{R} \rightarrow \text{ROH} \quad \text{hydroxylated products} \]  

(1.25)

Equation 1.26 is for hydrogen atom abstraction:

\[ \cdot \text{OH} + \text{R} \rightarrow \text{R} - \text{H}_2\text{O} \quad \text{oxidized products} \]  

(1.26)
As the pH is raised, there is some evolution of oxygen due to the reactions

\[
\text{HO-OH} = \text{HO-O}^- + \text{H}^+ \quad (1.31)
\]

The reaction arises from the nature of \( \text{H}_2\text{O}_2 \) because \( \text{H}_2\text{O}_2 \) is an extremely weak acid \((K_a = 1.55 \times 10^{-12} \text{ at } 200^\circ \text{C})\). Its hydroxyl groups generally behave like those of alcohols (Thornton et al 1991). In the presence of \( \text{Fe}^{2+} \), oxygen is evolved through the following steps:

\[
\text{Fe}^{3+} + \text{HO-O}^- \rightarrow \text{Fe}^{2+} + \cdot\text{HO-O} \quad (1.32)
\]

\[
\cdot\text{HO-O} \rightarrow \text{H}^+ + (\cdot\text{O-O})^- \quad (1.33)
\]

\[
\text{Fe}^{3+} + (\cdot\text{O-O})^- \rightarrow \text{Fe}^{2+} + \text{O}_2 \quad (1.34)
\]

\[
\text{H}_2\text{O}_2 + (\cdot\text{O-O})^- \rightarrow \cdot\text{HO} + \text{HO}^- + \text{O}_2 \quad (1.35)
\]

Superoxide can be produced through the following reaction

\[
\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{HO-O} \quad (1.36)
\]

Haber and Weiss (1934) suggest that this reaction contributed to the maintenance of a chain reaction sequence under acidic condition of their study. Under neutral pH, the sum of Equations 1.22 and 1.31 gives Equation 1.34. In this superoxide driven Fenton’s reaction, iron functions as the true catalyst as a result of recycling mechanism where iron has been cancelled after summation of Equation 1.31 and 1.22.
1.8.4 Heterogeneous System with Irradiation

1.8.4.1 Photocatalytic oxidation

Semiconductors (e.g. TiO₂, ZnO, Fe₂O₃, WO₃, SnO₂, ZrO₂, CdS and ZnS) can act as sensitizers for light-induced redox processes due to their electronic structure which is characterized by a filled valence band and an empty conduction band (Boer 1990). Absorption of a photon with an energy greater than the bandgap energy leads to the formation of an electron/hole pair. In the absence of suitable scavengers, the stored energy is dissipated within a few nanoseconds by recombination (Rothenberger et al 1985). If a suitable scavenger is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur. The valence band holes are powerful oxidants (+1.0 to +3.5 V vs NHE depending on the semiconductor and pH) while the conduction band electrons are good reductants (+0.5 to -1.5 V vs NHE) (Gratzel 1989). Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly. In bulk semiconductor electrodes only one species either the hole or electron is available for reaction due to band bending (Memming 1988). However in very small semiconductor particle suspensions both species are present on the surface. Hence both oxidative and reductive pathways are possible in semiconductor particle suspensions.

Figure 1.3 illustrates the typical photocatalytic process. It consists of a superposition of the energy bands of semiconductors and the geometrical image of a spherical particle. Photoexcitation with light of an energy greater than the bandgap energy (Eₕ) promotes an electron from the valence band to the conduction band creating an electronic vacancy or hole (h⁺) at the valence band edge. This hole can also be identified as a chemical entity. This hole can initiate further interfacial electron transfer or other chemical reactions to an adsorbate or with surface-bound OH⁻ ions can itself diffuse into the solvent bulk.
Electron-hole recombination can occur on the surface [reaction (a)] or in the bulk [reaction (b)] of the semiconductor. At the surface of the particle, photogenerated electrons can reduce an electron acceptor A [reaction (c)] and photogenerated holes can oxidise an electron donor D [reaction (d)]. The combination of reactions (c) and (d) represents the semiconductor sensitisation of the general redox reaction.

Figure 1.3 Illustration of the major processes occurring on a semiconductor particle following electron excitation
The photogenerated electron (e') usually relaxes thermally in the conduction band edge (and the hole to the valence band edge), but further deactivation is more difficult because of energetic mismatching of the energies of the electron and hole. Unlike metals, semiconductors lack a continuum of interband states to assist the recombination of electron-hole pair. This assures an electron-hole pair lifetime sufficiently long enough to allow these species to participate in interfacial electron transfer (Nosaka and Fox 1988). Thus, the act of photoexcitation usually generates an electron-hole pair poised respectively at the conduction band and valence band edges (Eqn. 1.37). The components of this activated pair, when transferred across the interface, are capable, respectively, of reducing and oxidising a surface-adsorbed substrate, forming on a common surface a singly oxidised electron donor and singly oxidized electron acceptor (Eqn. 1.38 and 1.39).

\[
\begin{align*}
\text{Semiconductor} & \rightarrow e^+ + h^+ \quad (1.37) \\
h^+ + D & \rightarrow D^+ \quad (1.38) \\
e^+ + A & \rightarrow A^- \quad (1.39)
\end{align*}
\]

If a photogenerated hole reaches the surface of the semiconductor, it can react with an adsorbed substrate by interfacial electron transfer, assuming that the adsorbate possesses a redox potential appropriate for a thermodynamically allowed reaction. Thus, an adsorbed electron donor can be oxidised by transferring an electron to a photogenerated hole on the surface, and an adsorbed acceptor can be reduced by accepting an electron from the surface. Hole trapping generates a cation radical, \(D^+\) (Eqn. 1.38) and electron trapping generates an anion radical, \(A^-\) (Eqn. 1.39). These radical ions can participate in several pathways. They may react chemically with themselves or other adsorbates. They may recombine by back electron transfer to form the excited state of one of the reactants or waste the excitation energy by a
nonradiative pathway. They may diffuse from the semiconductor surface and participate in chemical reactions in the bulk solution (Fox and Dulay 1993).

The photocatalysis is chemically productive when the electron-hole pair recombination is suppressed. This can be accomplished by trapping either the photogenerated electron or the photogenerated hole or both. The general stoichiometric-heterogeneously-photocatalysed oxidation of a general chlorinated hydrocarbon to complete mineralisation can be written as

\[ C_x H_y Cl_z + O_2 \rightarrow xCO_2 + zH^+ + zCl^- + H_2O \] (1.40)

The exact nature of the main oxidising species formed on the surface of the semiconductor particles following the absorption of a photon is yet unclear. However, significant literature survey reveals that the initial oxidation of a pollutant molecule may either occur by indirect oxidation via a surface-bound hydroxyl radical (i.e a trapped hole at the particle surface) or directly via the valence band hole before it is trapped either within the particle or at the particle surface.

In support of hydroxyl radical as the principal reactive oxidant in photocatalysis, the observation is that the intermediates detected during photocatalytic degradation of halogenated aromatic compounds are typically of hydroxylated structure (Ollis et al 1984, Yokomizo and Bell 1989 and Terzian et al 1991). These intermediates are consistent with those found when similar aromatics are reacted with a known source of hydroxyl radicals. In addition, ESR studies have verified the existence of hydroxyl and hydroperoxyl radicals in aqueous solution of illuminated TiO_2 (Jaeger and Bard 1979). Over the years, the field of photo-induced electron transfer reactions in heterogeneous systems has witnessed a number of new discoveries. Particularly the use of semiconductor particles as photocatalysts to degrade the organic hazardous pollutants in aqueous environment has been actively studied.
The particulate semiconductor photocatalysts have several interesting features. Each photocatalyst functions as a micro photoelectrode or as photochemical diode for a metal loaded semiconductor particle. They possess large surface area which is advantageous for surface reactions. They possess novel photophysical properties which depend on the quantum size effect. Their low cost and ease of fabrication makes them attractive in several practical applications. The bandgap energy of TiO$_2$ is large (> 3.0 eV) that it becomes a good photocatalyst despite its poor catalytic activity towards electron transfer reactions. Large bandgap semiconductors prove to be better photocatalyst than the low bandgap materials (Frank and Gratzel 1983). These principles have found extensive and relative applications in the field of environmental chemistry and pollution control (Ollis et al 1989). Considerable attention has been focussed on the photocatalysis for the mineralisation of toxic chemicals present in wastewater. Several reviews have recently been published discussing the underlying reaction mechanisms and illustrative examples (Kamat 1993, Fox and Dulay 1993, Lewis 1993, Bahnemann et al 1991b, Serpone and Pelizzetti 1989, Pelizzetti and Schiavello 1991, Ollis and Al-Ekabi 1993, Hoffmann et al 1995 and Mills and Hunte 1997).

1.8.5 Heterogeneous System without Irradiation

Electrolysis has a broad definition in that it includes all reactions occuring at an electrode surface. The reactions are forced to take place by an externally imposed voltage. An important development in electrochemical oxidation process is the generation of hydrogen peroxide by the reduction of oxygen at the cathode. In the presence of ferrous ions, the hydrogen peroxide so generated can form hydroxyl radicals, a well known Fenton’s reagent (Fenton 1894 and 1899).

Hydrogen peroxide can be generated at the graphite electrode in acidic conditions. In the presence of Fe$^{2+}$ ions, the oxidation reaction can take place readily through the hydroxyl radicals (Walling 1975). An electron Fenton’s reagent can be
produced by the addition of an appropriate amount of Fe$^{2+}$ ion to the catholyte. The oxygen reduction potential is a function of pH and it is found that pH 3 is the most favorable (at a cathodic potential of -0.6V vs. saturated calomel electrode). In the presence of organic compounds, the hydroxyl radicals formed will be rapidly consumed and the organic compounds of interest will be oxidised (Bishop et al 1968, Kakvoda 1970 and Matsue et al 1981).

In a recent study, Huang et al (1992) have demonstrated that a surfactant, perfluoro-octanoate can be decomposed effectively by indirect electrochemical oxidation. Results show that in 15 min, the total perfluoro-octanoate concentration was decreased from 100 ppm to 10 and from 50 ppm to 1ppm. They have also proposed reaction pathway for the oxidation of C8 by the Fenton’s reagent reaction

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \] (cathodic reduction) \hspace{1cm} (1.41)

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{Fe}^{3+} + \text{OH}^- \] \hspace{1cm} (1.42)

\[ \text{C}_7\text{F}_{15}\text{COONH}_4 = \text{C}_7\text{F}_{15}\text{COO}^- + \text{NH}_4^+ \] \hspace{1cm} (1.43)

\[ \text{C}_7\text{F}_{15}\text{COO}^- + \text{H}^+ = \text{C}_7\text{F}_{15}\text{COOH} \] \hspace{1cm} (1.44)

\[ \text{C}_7\text{F}_{15}\text{COOH} + \text{OH}^- \rightarrow \text{C}_7\text{F}_{15}^- + \text{CO}_2 + \text{H}_2\text{O} \] \hspace{1cm} (1.45)

\[ \text{C}_n\text{F}_{2n+1}\text{OH} + \text{OH}^- \rightarrow \text{C}_n\text{F}_{2n}(\text{OH})_2 \text{ or } \text{C}_n\text{F}_{2n+1}(\text{OH}) \] \hspace{1cm} (1.47)

Reaction (1.41) is the reduction of oxygen at the cathode, reaction (1.42) is the generation of a hydroxyl radical (Fenton’s reagent), reaction (1.43) is the dissociation reaction of C8, reaction (1.44) is an acid-base equilibrium reaction.
reaction (1.45) is the Kolbe reaction, reaction (1.46) is a free radical reaction with formation of perfluoroheptanol and reaction (1.47) shows the hydroxyl radicals attacking on the perfluoroheptanol to form simple perfluoro alcohols.

1.9 PRIMARY PROCESSES IN PHOTOCATALYSIS

1.9.1 TiO$_2$ Catalyst

Titanium dioxide, the material with highest photocatalytic detoxification efficiency, has wide bandgap of 3.2 eV (Gerischer 1979). Thus only light below 400 nm (i.e. 5% of the solar energy reaching the surface of the earth) is absorbed and capable of forming electron-hole pairs for the photocatalytic process.

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 (e^-_{\text{CB}} + h^+_{\text{VB}}) (1.48)
\]

Following their generation in the bulk both charge carriers diffuse rapidly to the particles surface. In an extremely fast process the valence band electron is trapped at Ti (IV) surface sites (Eqn.1.49) or by extrinsic traps (e.g. adsorbed electron acceptors, A$_{ads}$) via interfacial transfer (Eqn. 1.50)

\[
\text{Ti(IV)$_{surface}$} + e^-_{\text{CB}} \rightarrow \text{Ti(III)$_{surface}$} (1.49)
\]

\[
\text{A}_{ads} + e^-_{\text{CB}} \rightarrow \text{A}^-_{ads} (1.50)
\]

While molecular oxygen normally serves as adsorbed electron acceptor yielding the superoxide radical anion (Eqn. 1.51), metal cations or even several organic compounds can act as efficient oxidants.

\[
\text{O}_2_{ads} + e^-_{\text{CB}} \rightarrow \text{O}_2^-_{ads} (1.51)
\]
The valence band hole can either be trapped at intrinsic oxygen sites (Eqn. 1.52) and adsorbed electron donors, $D_{\text{ads}}$ at the particle's surface (Eqn. 1.53)

$$\text{Ti(IV)} - O^{2-} - \text{Ti(IV)} + h^+_{\text{VB}} \rightarrow \text{Ti(IV)} - O^- - \text{Ti(IV)} \quad (1.52)$$

$$D_{\text{ads}} + h^+_{\text{VB}} \rightarrow D^+_{\text{ads}} \quad (1.53)$$

In the case of the strongly hydrated and hydroxylated TiO$_2$ surface, hole trapping results in surface bound hydroxyl radicals (Eqn. 1.54a and 1.54b).

$$\text{Ti(IV)_{surface}} - \text{OH} + h^+_{\text{VB}} \rightarrow \text{Ti(IV)_{surface}} - \cdot{\text{OH}} \quad (1.54a)$$

$$\text{Ti(IV)_{surface}} - \text{OH}_2^+ + h^+_{\text{VB}} \rightarrow \text{Ti(IV)_{surface}} - \cdot{\text{OH}} + H^+_{\text{aq}} \quad (1.54b)$$

Commonly, it is assumed that the degradation of organic compounds is initiated by an anodic process.

$$\text{Ti(IV)_{surface}} - \cdot{\text{OH}} + D \rightarrow \text{Ti(IV)_{surface}} + D^+ - \text{OH} \quad (1.55)$$

In the presence of air the radicals thus formed react quickly with molecular oxygen leading to eventual formation of the final mineralisation products.

### 1.9.2 ZnO Catalyst

Number of studies have been reported using ZnO as catalyst (Ohnishi et al. 1989, Tennakone et al. 1992a, Richard et al. 1992, Villasenor and Mansilla 1996 and Sakthivel et al. 1999, 2000a and 2000c). Ohnishi et al. (1989) concluded that ZnO is more effective, or at least presents the same activity as TiO$_2$ in the removal of chemicals in water contaminated with lignin-related compounds.
It has been established that ZnO photcatalysed degradation of organic matter in solution is initiated by photoexcitation of the semiconductor followed by the formation of an electron-hole pair on the surface of the catalyst (Eqn. 1.56). The high oxidative potential of the holes in the catalyst permits the direct oxidation of organic matter (OM) to reactive intermediates (Eqn. 1.57). Highly reactive hydroxyl radicals can also be formed either by the decomposition of water (Eqn.1.58) or by the reaction of the hole with OH' (Eqn. 1.59). The hydroxyl radical is an extremely strong, non-selective oxidant (E° = + 3.06 V) which leads to partial or complete mineralisation of several organic compounds.

\[ \text{ZnO} + \text{hv} \rightarrow \text{ZnO} (e^- + h^+) \]  
(1.56)

\[ \text{OM} + \text{ZnO} (h^+) \rightarrow \text{OM}^* + \text{ZnO} \]  
(1.57)

\[ \text{H}_2\text{O} + \text{ZnO} (h^+) \rightarrow \text{OH}^- + \text{H}^+ + \text{ZnO} \]  
(1.58)

\[ \text{OH}^- + \text{ZnO} (h^+) \rightarrow \text{OH}^- + \text{ZnO} \]  
(1.59)

Hidaka et al (1992), using electron spin resonance (ESR) experiments, have shown that electrons in the conduction band on the catalyst surface can reduce molecular oxygen to superoxide anion (Eqn. 1.60). This radical, in the presence of organic scavengers, may form organic peroxides (Eqn. 1.61) or hydrogen peroxide (Eqn. 1.62).

\[ \text{O}_2 + \text{ZnO} (e^-) \rightarrow \text{O}_2^- \]  
(1.60)

\[ \text{O}_2^- + \text{OM} \rightarrow \text{OM}^- \text{OO}^- \]  
(1.61)

\[ \text{O}_2^- + \text{HO}_2^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  
(1.62)
The electrons in the conduction band are also responsible for the production of hydroxyl radicals, the species which have been indicated as the primary cause of organic matter mineralisation (Ollis 1991).

1.10 PHOTOCATALYTIC OXIDATION OF COMMON POLLUTANTS

Photocatalytic oxidation (PCO) of water-borne environmental contaminants by semiconductor powders irradiated with solar or UV is a comparatively novel method for the destruction of toxic chemicals in water (Legrini et al. 1993). The objective is to effectively mineralise organic contaminants into carbon dioxide, water and oxidized inorganic anions (if any heteroatoms are present). It is preferable to classify the published literature according to the class of contaminants: halohydrocarbons / hydrocarbons, phenolic compounds, nitrocompounds, pesticides, insecticides, herbicides, fungicides, cyanides, toxic metals, dyes, surfactants, oils, lignin and other organic and inorganic compounds.

1.10.1 Halohydrocarbons and Hydrocarbons

Halohydrocarbons are widely used as solvents, in pesticides, insecticides and herbicides and pose severe environmental hazard even in very low concentrations in water. The higher the number of halogen atoms in a molecule, the higher is its toxicity. These substances are not readily degraded or hydrolysed in normal aquatic environment. Titanium dioxide has been reported to photodegrade completely simple chlorinated hydrocarbons into CO₂ and HCl (Ollis et al. 1984, Pruden and Ollis 1993a and 1983b).

The chemically complicated process of water chlorination for urban water supplies leads to the formation of lower molecular weight chlorinated hydrocarbons especially trichloromethane resulting from the destruction of humic acids and other dissolved organic matter present in the water source. Pruden and Ollis (1983a)
demonstrated complete degradation of such chlorinated hydrocarbons into carbon dioxide and hydrogen chloride as shown by the recovery of all original chlorine as chloride and also as observed by the complete disappearance of the reactant and lack of other halogenated species detectable by gas chromatography. The two most pervasive halocarbons, namely, trichloroethylene and perchloroethylene are commonly used in electronic circuit fabrication and dry cleaning of clothing. Pruden and Ollis (1983b) attempted the photocatalysed destruction of these two compounds into CO$_2$ and HCl. In the presence of dissolved oxygen, 1,1-dichloroacetaldehyde intermediate species has been identified during perchloroethylene degradation based on the following sequence of mechanisms.

\[
\text{CHClCCL}_2 \to \text{CHOCCl}_2 \to \text{CO}_2 + \text{HCl} \quad (1.63)
\]

Ollis and Turchi (1990) attempted the photocatalytic degradation of perchloroethylene (PCE) and benzene. They have represented the simple stoichiometric equation for the disappearance of perchloroethylene and the carbon dioxide formation with no evidence of significant intermediates.

\[
\text{C}_2\text{Cl}_4 + 2 \text{H}_2\text{O} + \text{O}_2 \to 2 \text{CO}_2 + 4 \text{HCl} \quad (1.64)
\]

In contrast, the mineralisation of a larger and complex reactant such as benzene clearly requires the participation of many reaction intermediates in order to arrive eventually at the end product namely, carbon dioxide. Turchi and Ollis (1990) has demonstrated the simultaneous measurement of benzene disappearance and carbon dioxide formation that the consideration of kinetically important intermediates is required. Specifically in the benzene destruction, inclusion of either no or one intermediate was insufficient to fit the carbon dioxide evolution data whereas use of two reaction intermediates (I$_a$, I$_b$) (Eqn. 1.65) provided a satisfactory agreement of kinetic rate form of experimental results.
Benzene $\rightarrow$ I$_a$ $\rightarrow$ I$_b$ $\rightarrow$ carbon dioxide (1.65)

Bahnemann (1991a) have investigated the photocatalytic degradation of chloroform using TiO$_2$. Detailed mechanistic studies have been carried out to investigate the potential use of solar illumination as the source of irradiation in these photocatalytic systems. Zhang et al (1994) have also studied the photocatalytic degradation of trichloroethylene (TCE) using TiO$_2$ supported on silica. They have reported that the supported photocatalysts displayed high light efficiencies over a wide range of weather conditions with an apparent quantum yield of 40 % was obtained in a rainy late-afternoon experiment. The complete mineralization of TCE was achieved and in addition, background natural organic matter (BNOM) in a local surface water did not interfere significantly with the degradation.

Environmental protection agency (EPA) of United States has classified PCBs as extremely toxic and carcinogenic and hence imposed several controls for their uses. PCBs are widely used in electric transformers, circuit breakers, voltage regulators and capacitors because of their resistance of flammability, excellent cooling effects and extremely low electrical conductivities (Tieram et al 1982). Tunesi and Anderson (1987) have shown that the rate of destruction of 3,4 - dichlorobiphenyl on TiO$_2$ surface depends on temperature and light intensity. Menassa et al (1988) studied the photodecomposition of different PCBs by surface modified TiO$_2$ in a medium containing hexane and water mixture. Complete degradation was observed within a short period of time. In a study by Carey et al (1976) several PCBs such as 4,4'-dichlorobiphenyl, 2,2' - dichlorobiphenyl, 2-chlorobiphenyl, 3-chlorobiphenyl and 4-chlorobiphenyl were irradiated separately at 365 nm for 30 min in 25 ppb aqueous suspension of TiO$_2$. The disappearance of dichlorinated biphenyls and the production of chloride ion showed that illuminated semiconductor catalysts could provide a viable means of degradation of PCBs. Further, there was no trace of 3 or 4 - chloroisomers identified after irradiation.
Gianturco et al (1996) have studied pilot scale level of photomineralisation of dichloromethane, tetrachloroethylene and mono-, di-, and trichloroethanoic acids using photocatalytic membranes immobilised with titanium dioxide and photopromoters. Disappearance of substrates and total organic carbon (TOC) along with chloride ion estimation has confirmed the mineralisation of contaminants. They have observed that mono-, di- and trichloroethanoic acids proceeds at a much lower rate than tetrachloroethylene.

Amalric et al (1995) have investigated the photocatalytic degradation of dimethoxy benzenes UV-irradiated in the presence of TiO₂ powder. They have observed the structure of aliphatic compounds resulting from the ring opening of aromatic pollutants in water during photocatalytic treatment by GC-MS study. The aliphatic intermediates are esters or acids which were identified either by comparison with authentic compounds or by mass spectra. These identifications show the complexity of the degradation pathways. The dimethyl esters of hexadienedioic acid and butenedioic acid could result from the opening of 1,2 - or 1,4 - dimethoxy benzene respectively, before these pollutants are hydroxylated. This suggests that hydroxyl radicals are not the only oxidizing species involved. The fact that all aliphatics contain a number of carbon atoms to that in dimethoxyl benzene bears witness to the bond cleavages which lead to mineralisation.

Crittenden et al (1996) studied the photocatalytic degradation of benzene, toluene, ethyl benzene and xylene (BTEX). These compounds were found in fuel contaminated groundwater. Platinized titanium dioxide supported on silica gel is baked in tubular photoreactors and used for single pass operation. They have observed that ionic species were primarily responsible for photocatalytic fouling and destruction inhibition. They also suggested that a simple pretreatment unit may be developed for removing turbidity, adding oxidant and ionic species. By using pretreatment, the reactor system operate efficiently and no loss in catalyst photoactivity was found during the month long test.
Pichat (1997) has investigated the photocatalytic degradation of aromatic and alicyclic (1,2-dimethoxy benzene, pyridine, morpholine and lindane) using TiO₂. In his studies briefly reviewed, their intermediate products, in particular the aliphatics, were identified both to determine what the compounds are that may be left in the treated water and increase the understanding of the photocatalytic pathways. Moreover, a comparison of the primary products of quinoline revealed that the degradation may be either by photocatalysis or by the photo-fenton process suggesting that ‘OH radicals are not the only active species involved in photocatalytic degradation. From the effects of adding superoxide, it was inferred that in situ formed O₂⁻ anion radicals intervene chemically and possibly by reacting with quinoline cation radicals generated via electron transfer from quinoline to TiO₂.

1.10.2 Phenolic Compounds

Kawagushi (1984) studied the photocatalytic decomposition of phenol using TiO₂. He observed that the decomposition rate has the maximum at pH 3.3. The addition of copper with TiO₂ increased the rate of phenol decomposition. Hydroquinone and catechol were the main intermediate products detected by high performance liquid chromatography. Okamoto et al. (1985a and 1985b) have also attempted the photocatalytic degradation of phenol over TiO₂ powder. The results reported that the products at the initial stage of the reaction were hydroquinone, pyrocatechol, 1,2,4-benzenetriol, pyrogallol and 2-hydroxy 1,4-benzoquinone. These intermediates underwent further photocatalytic oxidation via acids and/or aldehydes finally into CO₂ and H₂O. The reaction scheme suggested hydroxyl radicals as real reactive species.

Matthews (1985, 1986, 1987b, 1988 and 1990) investigated the photocatalytic oxidation of a large number of organic materials (2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, chlorobenzene, nitrobenzene,
benzoic acid, methanol, ethanol, acetic acid and formic acid) using TiO$_2$ suspension. The degradation rate was monitored through CO$_2$ formation measurement by gas chromatography. The results revealed that the rate of CO$_2$ formation did not vary greatly from one compound to another. Matthews (1987a) also attempted the photocatalytic oxidation of organic impurities (salicylic acid, phenol, 2 - chlorophenol, 4- chlorophenol, benzoic acid, 2 - naphthol, naphthalene and fluorescein) in water using thin films of TiO$_2$. The results showed that the dependence of the rate of CO$_2$ formation obeyed simple Langmuir - Hinshelwood kinetics for each substance.

Theurich et al (1996) have also studied the photocatalytic degradation of 4 - chlorophenol in aerated aqueous titanium dioxide suspension. They have compared the efficiency of two different commercial catalysts. The degradation kinetics followed Langmuir - Hinshelwood expression. Stafford et al (1997) also reported the photocatalytic degradation of 4-chlorophenol and the effects of TiO$_2$ surface loading and light conditions on the photocatalysed degradation. 4-Chlorophenol in aqueous TiO$_2$ suspension was mineralised when the suspension was illuminated with longer wavelength UV light. While increased TiO$_2$ loading did not enhance the initial rate of 4-chlorophenol degradation and the rate of mineralisation of 4-chlorophenol. This was partly due to the significant adsorption of 4-chlorocatechol on the surface and the increased importance of surface oxidation reactions. The wavelength of UV light has a great effect on the quantum yield of reaction with significantly faster rates of reaction caused by 300 nm light than by light of longer wavelength.

Modestor and Lev (1998) attempted the photocatalytic oxidation of 2,4 - dichlorophenoxyacetic acid using TiO$_2$. They have compared the photocatalytic activity of TiO$_2$, both suspended and supported systems. Maurina et al (1997) have reported the photocatalytic degradation of nitrophenols and aminophenols using TiO$_2$. The results showed that at pH < 6, extensive mineralisation (more than 90%) of the substituted phenols occurs, whereas at pH 11 organic carbon is persistently observed. Photocatalysis converts 80% of the nitro group in nitrophenols into NO$_3^-$ through the
intermediate formation of NO$_2^-$ ions and the remaining 20% is transformed into NH$_4^+$ ions. Chen and Ray (1998) have also attempted the photocatalytic degradation of 4-nitrophenol using TiO$_2$. They have studied kinetic aspects and suggested that the kinetic equation can predict the concentration of 4-nitrophenol during the entire degradation process. Herrmann et al (1999a) attempted the photocatalytic degradation of 4-chlorophenol using TiO$_2$ with association of activated carbon.

1.10.3 Nitro Compounds

Muradov (1994) has reported the solar detoxification of nitroglycerine contaminated water using immobilized titania. The study involved the design and construction of a plate type photoreactor with immobilized TiO$_2$. Estimation of nitroglycerine, nitrite and nitrate have confirmed the mineralisation of contaminants. Dillert et al (1996) investigated the photocatalytic degradation of trinitrotoluene (TNT) and trinitrobenzene (TNB) using TiO$_2$ suspension and studied the influence of the addition of by varying concentration of hydrogen peroxide and pH. They have observed that in TiO$_2$ suspension, the degradation rate of TNT is enhanced significantly compared to the homogeneous solutions of H$_2$O$_2$ at all pH. TNB is degraded significantly slower than TNT in all cases.

Shivakumar and Davis (1997) have reported the photocatalytic oxidation of nitrotoluenes (2-nitrotoluene and 3-nitrotoluene) and dinitrotoluenes (2,4-DNT and 2,6-DNT) using TiO$_2$. They have observed that the photocatalytic oxidation rates of nitrotoluenes are independent of each other because these compounds do not exhibit any pH dependent specification. Langmuir - Hinshelwood rate form is used to describe the kinetics of the photocatalytic oxidation of these compounds.

Schmelling et al (1997) also attempted the photocatalytic degradation of TNT in TiO$_2$ slurries. The study was undertaken to examine the impact of pH and the presence of inorganic ions and organic acids commonly found in natural waters on the
rate of TiO₂ photocatalysed TNT transformation and mineralisation. They have observed an increase of pH slightly increase the rate of TNT transformation, but significantly reduce the rate of mineralisation due to increased electrostatic repulsion between the catalyst surface and anionic TNT intermediates. The presence of inorganic anions did not substantially hinder TNT transformation at alkaline pH, but mineralisation rates were diminished when the anion either strongly adsorbed on TiO₂ or act as an effective hydroxyl radical scavenger.

1.10.4 Pesticides

Mengyue et al (1995) studied the feasibility of photocatalytic degradation of organophosphorous pesticides using thin film of TiO₂. The results showed that dichlorvos, monocrotophos, phorate and parathion can be completely photodegraded into PO₄³⁻ within a short period of time under illumination with medium pressure mercury lamp of 375 W. The addition of a small amount of hydrogen peroxide can increase significantly the photodegradation efficiency. Possible mechanisms of photocatalytic degradation were proposed by them.

Malato et al (1996, 1999) have investigated the mineralisation of two commercial pesticides (lindane and methamidophous) utilizing both UV and sunlight in the presence of TiO₂ particles in a preindustrial pilot plant. Estimation of total organic carbon (TOC) and PO₄³⁻ analysis have confirmed the mineralisation of contaminants. They have suggested that the use of oxidants (peroxydisulphate and peroxide) is recommendable when the organic content of the water is relatively high and/or the mineralisation rate is low. These additives dissociate the pesticide into harmless by-products. O'Shea et al (1997) have attempted the photocatalytic decomposition of pesticides like dimethyl methylphosphonate (DMMP) and diethyl methylphosphonate (DEMP) using TiO₂. They have reported the kinetic models and formation of intermediate compounds during decomposition of pesticides.
Muneer et al (1999) have studied the photocatalytic degradation of the pesticide, diuron using different types of TiO$_2$ and in the presence of electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate besides molecular oxygen. The results showed that all additives indicated a beneficial effect on the degradation of diuron. In the diuron mineralisation only the addition of bromate ions leads to an enhancement while in the presence of the other additives even a slight decrease in the mineralisation rate was observed. Toxicity tests proved the formation of highly toxic intermediates during the photocatalytic reaction.

### 1.10.5 Insecticides

Lu et al (1995) have reported the photocatalytic mineralisation of both insecticides (dichlorvos, propoxur) and herbicide (2, 4-dichlorophenoxyacetic acid). Their results revealed that photocatalytic system is effective in mineralising such compounds. Kerzhentsev et al (1996) have reported the photocatalytic purification of water containing fenitrothion insecticide in TiO$_2$ suspension. The mineralisation products identified were CO$_2$, H$_2$PO$_4^-$, SO$_4^{2-}$ and NO$_3^-$. Several intermediates have been identified by HPLC and GC-MS. The mineralisation of fenitrothion is achieved in a much shorter time by photocatalysts at $\lambda > 340$ nm than direct photolysis at $\lambda > 290$ nm. The kinetics of fenitrothion disappearance followed an apparent first-order kinetics which is consistent with Langmuir-Hinshelwood mechanism.

Guillard et al (1996) have investigated the photocatalytic degradation of lindane using TiO$_2$. They have reported that lindane is a common soil insecticide. Despite its low solubility, lindane is found in natural waters as well as in rain. As it is stable and may be reasonably anticipated to be a carcinogen, it is considered as a pollutant of great concern in drinking water. The intermediate products were identified by GC-MS and the photocatalytic pathway of lindane was clearly indicated in their paper. Pramauro et al (1997) have studied the photocatalytic degradation of carbaryl insecticide in aqueous TiO$_2$ dispersion irradiated with simulated solar light. Estimation
of CO₂, NO₃⁻ and NH₄⁺ ions have confirmed the mineralisation of carbaryl. Various aromatic intermediates detected during the process were identified using HPLC and GC-MS techniques, and their kinetics were also reported exhaustively. Aguera et al (1998) reported the degradation of a commonly used insecticide, imidacloprid irradiated with TiO₂ photocatalyst. Degradation of imidacloprid mainly occurred through the formation of 6-chloronicotinic aldehyde and acid. After 450 min of oxidative reaction, the degraded products and imidacloprid concentrations were found to be practically negligible.

1.10.6 Herbicides

Pelizzetti et al (1987) investigated the complete photomineralisation of 2-chloro-4-ethy lamino-6-isopropylamino-s-triazine, a popular class of herbicide commonly used for grassy weed control in crops in an aqueous suspension of TiO₂ in the presence of artificial or actual sunlight. Continued release of chloride and ammonium ions indicate clearly the formation and decomposition of reaction intermediates. Draper and Crossby (1987) reported that the rice herbicides, molinite (s-ethyl hexahydro-lH-azepine-l-carbothioate) and thiobencarb (s-(4-chlorophenyl) methyl-N, N-diethyl carbomothioate) were degraded rapidly in sunlight irradiated suspensions of TiO₂/ZnO. Barbeni et al (1987a) attempted the photoassisted degradation of the herbicide, 2,4,5-trichlorophenoxyacetic acid on TiCb within a short period of time. Pelizzetti et al (1990a and 1990b) investigated thoroughly the photocatalytic degradation of atrazine and other s-triazine herbicide using TiO₂ as a photocatalyst under stimulated solar light. The herbicides are decomposed in a very short time below the level of 0.1 ppb. Several intermediates have been identified, and cyanuric acid has been recognised as the final product of degradation in all the investigated herbicides.

Minero et al (1996) have also studied the photocatalytic degradation of atrazine in a large solar plant reactor using TiO₂ catalyst. The results showed that the
degradation leads to complete mineralisation of the alkyl substituents of s-triazine give rise to trihydroxy-s-triazine as the final product with efficient detoxification. They have suggested that use of oxidants like peroxydisulphate is particularly advantageous when large amounts of polluted groundwater have to be treated. Torimoto (1996) has attempted the photocatalytic degradation of propyzamide herbicide using TiO₂ in association with adsorbents such as zeolite, silica and activated carbon. Propyzamide is a typical herbicide which is widely utilized for golf links and its removal from rainwater flowing into drains has become an important subject in ecomanagement. They suggested that the adsorbent support concentrates a target substrate of low solution phase concentration on its surface, providing the substrate-rich environment at the adsorbent/TiO₂ interface. This concentration effect results in an enhanced rate of propyzamide mineralisation.

Lobedank et al (1997) have thoroughly studied the sensitized photocatalytic degradation of terbutryene using tris(bipyridyl)ruthenium complexes as sensitizer and TiO₂ as semiconductor. Tris (4, 4'- dicarboxy - 2, 2' - bipyridyl) ruthenium (II) chloride is an excellent sensitizer and on exposure to sunlight complete degradation of the pollutants occurs. The adsorption of the components on the semiconductor surface, electron transfer and electron back transfer determine the efficiency of the process.

Herrmann et al (1998) reported TiO₂ based solar photocatalytic detoxification of water containing two model organic pollutants, namely, 2, 4-dichlorophenoxyacetic acid, a common herbicide and 2,3-benzofuran. The disappearance of both pollutants followed first-order kinetics, and completely mineralised in quite reasonable time. They have clearly demonstrated the results obtained at the laboratory scale with a microphotoreactor using artificial UV light could be extrapolated to pilot scale. The estimation of total organic carbon (TOC) is a convenient means for comparing the reactivity of different pollutants. The compound parabolic collector (CPC) models were utilized for this study. The detailed study of
photocatalytic degradation as well as its main intermediates (2-coumaranane and salicylaldehyde) has been reported. Modestor and Lev (1998) have also attempted the photocatalytic oxidation of 2,4-dichlorophenoxyacetic acid using TiO_2. They have compared the photocatalytic efficiency of both suspended and supported systems.

1.10.7 Fungicides

Doherty et al (1995) investigated the photocatalytic degradation of morpholine fungicide (tetrahydro-2H-1, 4-oxazine) using TiO_2 particles. The results showed that degradation rate of morpholine was greater with, than without, TiO_2 in the UV spectral range. The intermediates were identified by GC-MS and HPLC. The results have shown the formation of hydroxy and oxo derivatives of morpholine, and oxidation of five membered ring compounds have been tentatively identified.

Topalov et al (1999) have investigated the photocatalytic oxidation of the fungicide metalaxyl (N-(2,6-dimethyl phenyl)-N-(methoxy-acetyl)-D, L-alanine methyl ester, C_{15}H_{21}NO_4) dissolved in water using TiO_2. The intermediates formed during photomineralisation and reaction pathways were analysed by recording proton NMR spectra. They have also explained the Langmuir-Hinshelwood kinetic model on the basis of measurements of TOC.

1.10.8 Dyes/dye stuffs

Matthews (1991) has investigated the photocatalytic degradation of coloured organics (methylene blue, rhodamine B, methyl orange and salicylic acid) using TiO_2 coated sand in a flat bed configuration. The results showed that the disappearance of solute in each case obeys first order kinetics. Flow rate data, total organic carbon analysis and the effect of H_2O_2 were also reported. Reeves et al (1992) studied the photocatalytic destruction of several classes of organic dyes utilizing highly concentrated solar energy. The rate and extent of decomposition were
determined by UV-Vis spectroscopy and HPLC. Complete mineralisation was confirmed by TOC. This work suggested that there exists a great potential for the use of sunlight in the removal of textile dyes and biological stains from wastewater. Mills and Davis (1993) reported the results of a kinetic study of the photo-oxidative bleaching of reactive black 5 by dissolved oxygen sensitized TiO₂. The initial rate of photobleaching of reactive black 5 is dramatically reduced with increasing concentration of sodium citrate, a sacrificial electron donor present in the dye solution. The amount of CO₂ generated in the photosystem was monitored as a function of time. The delay of CO₂ evolution indicates that stable intermediates are generated in the photomineralisation of the dye.

Kiwi (1994) has reported that TiO₂ assisted degradation of anthraquinone-sulphonate dye is an effective method for destruction of dyes. The presence of oxygen promotes the degradation efficiency, and the added hydrogen peroxide enhances the degradation rate considerably. Mills et al (1994) have investigated the kinetic study of the bleaching of rhodamine 6G photosensitised by titanium dioxide. They have reported the quantum yield and overall activation energy for the semiconductor sensitised dye. Sharma et al (1995) have studied the photocatalytic reactions of xylidine ponceau azo dye using ZnO catalyst. They have proposed a tentative mechanism for the photocatalytic bleaching of xylidine ponceau. Lakshmi et al (1995) studied the photocatalytic degradation of methylene blue by TiO₂ photocatalyst. The reaction was found to confirm Langmuir adsorption isotherm. The rate versus pH profile exhibits a linear increase with pH in acidic solutions.

Vinodgopal and Kamat (1995) studied the photocatalytic degradation of acid orange 7 in slurry form and on immobilised films. A very rapid and complete decolourisation of textile azo dyes is achieved under UV irradiation. They have pointed out the enhanced rate of electrochemically assisted photocatalytic degradation of the dye in aqueous solution. Vinodgopal et al (1996a) have investigated the photosensitized degradation of a textile azo dye, acid orange 7 on TiO₂ particles using
visible light. Degradation did not occur on Al$_2$O$_3$ surface or in the absence of oxygen. Diffuse reflectance FTIR was used to make a tentative identification of reaction intermediates and products of dye degradation. Vinodgopal et al (1996b) also attempted visible light induced degradation of textile diazo dye, naphthol blue black (NBB) using TiO$_2$ nano particles. Diffuse reflectance transient absorption and FTIR technique have been used to elucidate the mechanistic details of the dye degradation. Diffuse reflectance FTIR study facilitated identification of reaction intermediates and products of dye degradation. Vinodgopal et al (1996c) have also attempted the photocatalytic degradation of textile azo dye, naphthol blue black (NBB) using SnO$_2$/TiO$_2$ nanostructured semiconductor composite films. The result showed that the degradation rate is significantly higher for SnO$_2$/TiO$_2$ composite films than the individual SnO$_2$ and TiO$_2$ films. The enhanced degradation rate of NBB using composite semiconductor films is attributed to the increased charge separation in these systems.

Freudenhammer et al (1997) investigated the solar catalytic treatment of different real wastewaters, and biologically pretreated textile wastewater successfully using non-concentrating thin film fixed bed reactor (TFFBR). They suggested that photocatalysis is a suitable technique for the final stage of purification of biologically pretreated wastewater and will offer a great opportunity for sun rich areas. Zhang et al (1997) have reported the photocatalytic degradation of dyes (erythrosine and rhodamine B) using TiO$_2$. Serrano and Lasa (1997) studied the photocatalytic degradation of methylene blue dye in a novel reactor unit using both bulk TiO$_2$ and TiO$_2$ mesh. In addition the photochemical - thermodynamic efficiency factor (PTEF) is further examined with the help of enthalpy of OH formation from water and oxygen, and based on the analysis of the light energy absorbed by the mesh.

Rao and Dube (1997a and 1997b) studied the TiO$_2$/UV assisted degradation of textile dyes, reactive orange 84 and alizarin red S in the form of both slurry and supported on titanium sheet or polyester fabric. The supported forms of the
catalyst have been used for treating larger volumes of the effluent. Direct UV irradiation of TiO₂ catalyst in aerated aqueous solution is capable of destroying azo dye in dye house effluents. The rate of degradation of alizarin red S can be accelerated in strongly alkaline medium. Rao and Dube (1997a and 1997b) also reported the photocatalytic degradation of reactive orange 84 with TiO₂ catalyst as slurry in aqueous dye solution. The results showed that the effect of flow rate on COD removal has suggested the need for upgradation of the catalyst.

Ray and Beenackers (1997) have studied the kinetics of heterogeneous photocatalytic processes on immobilized semiconductor catalysts. The true kinetic rate constants for the destruction of a textile dye were measured as a function of wavelength of light intensity and angle of incidence, catalyst layer thickness, and the effect of absorption of light by liquid film on the overall rate of photocatalytic degradation. Photocatalytic activities of two commercially available TiO₂ catalysts (Degussa P25 and Hombikat UV 100) were also compared for different light intensities and catalyst layer thickness. Ray and Beenackers (1998) have fabricated a novel photocatalytic reactor for water treatment. Complete photocatalytic degradation of special brilliant blue dye was observed in the presence of TiO₂ and UV light which is biologically not degradable. COD was measured for various virgin dye solution in order to determine the completion of degradation. COD values for the final treated liquid shows the complete mineralisation, and the present model component colorimetric analysis was justified as it was not merely measuring the decolourisation of the dye. Neppolian et al (1998, 1999a, 1999b, 2001a and 2001b) have extensively investigated the photocatalytic degradation of common textile dyes such as reactive yellow 17, reactive red 2 and reactive blue 4 using solar / UV light and TiO₂ / ZnO catalyst. They have reported the optimisation of parameters viz., concentration of dye, catalyst loading, irradiation time and pH in addition to the influence of oxidising agents such as oxygen, hydrogen peroxide and potassium persulphate and interference of sodium chloride and sodium carbonate. They observed that TiO₂ (P-25) is found to be the most efficient catalyst. The results also described disappearance of dye
molecule in each case obeys first order kinetics. The presence of oxygen promotes the
degradation efficiency and the added hydrogen peroxide and potassium persulphate
enhance dye degradation rate considerably.

Ma and Yao (1998) have also attempted the photocatalytic degradation of
rhodamine B using TiO₂ thin films. The photocatalytic properties of the sol-gel
derived films were assessed by measuring the photodegradative oxidation of
rhodamine B in aqueous solution and compared with Degussa P-25 coated films. The
results showed that sol-gel TiO₂ films has higher photoactivity than P-25 coated films
at the initial time of the reaction. Naskar et al (1998) have investigated the
photocatalytic degradation of methylene blue using TiO₂ nanoparticles immobilized
on foamed polyethylene sheet. The results showed that the rate data fit well to
classical Langmuir - Hinshelwood model. Zhang et al (1998) have studied the
photocatalytic degradation of eosin dye using TiO₂. The degradation kinetics followed
Langmuir - Hinshelwood type equation. They have observed that the degradation rate
was greater in acid medium than in neutral and alkaline media, which correlates with
adsorption behaviour of eosin on the TiO₂ surface.

Zhao et al (1998) also reported the photocatalytic degradation of cationic
dye, rhodamine B using TiO₂ with anionic surfactant dodecylbenzene sulfonate
(DBS). They have observed that rhodamine B degrades slowly in TiO₂ dispersions
without DBS which is a independent process. The surfactant, DBS, adsorbs strongly
on the TiO₂ particles and significantly accelerates rhodamine B degradation. In the
presence of DBS, rate decrease with increase in pH, an effect directly attributable to
variations in the extent of adsorption of rhodamine B with changes in the surface
charge of TiO₂ particles. The zeta potentials of TiO₂ particles in
rhodamineB/DBS/TiO₂ dispersions show that DBS significantly enhances rhodamine
B adsorption and correlates with an enhancement in the rate of photodegradation of
rhodamine B. Nanping et al (1999) investigated the influence of particle size of TiO₂
on the photocatalytic degradation of methylene blue in aqueous solution. The results
suggest that adsorption rate and adsorbility of methylene blue on suspended TiO₂ particles increase as the particle size of TiO₂ decreases. Photocatalytic activity of TiO₂ increases when the particle size is less than 30 nm.

1.10.9 Surfactants

Hidaka et al (1985, 1986) investigated TiO₂ photocatalysed conversion of anionic surfactant, sodium dodecylbenzene sulphonate (DBS) as well as degradation of the component parts such as sodium dodecyl-1-sulphonate (SDS) and sodium benzene sulphonate (BS). It was found that DBS and BS were rapidly photodegraded in aqueous aerated TiO₂ suspension. This degradation is found to be a better method in comparison to biodegradation which require long time. Hidaka et al (1989) have also shown that anionic dodecyl benzene sulphonate, cationic benzyldodecyldimethyl ammonium chloride and nonionic p-nonylphenol poly(oxy-ethylene) surfactants can be photodegraded in aqueous suspension of TiO₂ powder upon solar exposure. The aromatic moiety in the surfactants was decomposed more easily than the alkyl or ethoxylate groups.

Lea et al (1998) studied the photo-oxidative degradation of sodium dodecyl sulphonate (SDS) surfactants using TiO₂ in a bubble column reactor. They have observed that increase in solution pH enhanced the hydrolysis of SDS and hence increase in free dodecyl sulphonate species on the predominantly negatively charged titania surface at pH values higher than the isoelectric point. The empirical models devised were consistent with the proposition of a dual site (photogenerated positive and electron rich sites). Langmuir - Hinshelwood mechanism where the rate - controlling step is the surface interaction between the adsorbed dodecyl sulphonate and peroxy radicals. Highly reactive peroxy radicals were presumably formed from the protonation of surface superoxide anion, O₂⁺ produced via adsorption of oxygen on the electron - rich site.
Pelizzetti et al (1989) investigated the photocatalytic degradation of p-alkyl phenols and nonylphenol ethoxylate surfactants using TiO$_2$ particles. Complete conversion was demonstrated by liquid chromatography and from the measurements of carbon dioxide evolution, dissolved organic carbon and particulate organic carbon. The stable and toxic compound, 4-nonylphenol has been completely mineralised by this technique. Hence this method may be used to ensure final disposal of these undesirable products.

1.10.10 Lignin compounds

Villasenor et al (1996) reported the effect of temperature on the photocatalytic degradation of kraft black liquors using ZnO particle. The results showed that the mineralisation reaction exhibits a first order dependence on the dissolved oxygen concentration and a half order dependence on the concentration of the substrate. The catalysed reaction accounts for more than 95% of the CO$_2$ production at all temperatures and the uncatalysed reaction accounts for 5%.

Ohnishi et al (1989) have reported the bleaching of lignin solution by photocatalysed reaction using different semiconductors, namely, TiO$_2$, ZnO, In$_2$O$_3$, CdS, Fe$_2$O$_3$ and WO$_3$. The results showed that TiO$_2$, ZnO and CdS have high photocatalytic activities in neutral solution and TiO$_2$, ZnO and WO$_3$ also show high activities in alkaline solutions. The catalytic efficiency is improved by loading TiO$_2$ with noble metals such as Pt, Ag and Au.

1.10.11 Oils

Rosenberg et al (1992) studied the photocatalytic degradation of oil using TiO$_2$ coated hollow glass microbeads. The results showed that glass microbeads collect most of the sunlight, channelling it to the attached photocatalyst particles. Therefore, 30 - 40 % coverage of the microbeads is optimal for photodissolving oil.
slek. Grzechulska (2000) has reported the photocatalytic decomposition of oil in water using various TiO$_2$ prepared by calcination of a mixture of KOH (Ba(OH)$_2$ or Ca(OH)$_2$) and titanium dioxide slurry with a slightly crystallized structure. The most active material was prepared from a slightly crystallized titania precursor and KOH calcinated at 550°C.

1.10.12 Cyanides

Frank and Bard (1977) have used TiO$_2$ semiconductor to destroy cyanide into OCN' and H$_2$O photochemically. They have also used CdS dispersions in alkaline media in the presence of oxygen. The gold-cyanide complex is not decomposed in excess cyanide. On the other hand, photodegradation of gold-cyanide complex was found to be the most efficient under acidic conditions. Frank and Bard have compared the photocatalytic oxidation of CN' and SO$_3^{2-}$ by several semiconductor powders including TiO$_2$, ZnO, CdS, Fe$_2$O$_3$ and WO$_3$ using xenon lamps as light source. They have observed that TiO$_2$, ZnO and CdS were active photocatalysts for cyanide oxidation while oxidation was not seen with Fe$_2$O$_3$ and WO$_3$. The product of oxidation of CN' with TiO$_2$ was quantitatively determined to be OCN'. TiO$_2$, ZnO, CdS and Fe$_2$O$_3$ photocatalysed the oxidation of SO$_3^{2-}$. The order of catalytic activity was Fe$_2$O$_3$ ~ ZnO ~ CdS > TiO$_2$. The rates of the photocatalytic oxidation were greater for SO$_3^{2-}$ than for CN' in the cases of TiO$_2$, ZnO and CdS. The chemical and photochemical stabilities of the most active catalysts were determined.

Borgarello et al (1986a) reported the complete transformation of cyanide into less toxic thiocyanate. These workers used Rh-loaded CdS dispersions in the presence of waste byproducts using H$_2$S as an oxidising agent under visible light to achieve 25% conversion in the presence of air and high concentration of cyanide. In another study, Borgarello et al (1985) have demonstrated that gold can be recovered efficiently from aqueous cyanide medium via light induced process mediated by TiO$_2$ dispersion.
Reichie et al. (1979) and Curran et al. (1985) have reported the reduction of metals on TiO$_2$ particles irradiated with UV light to be an active area of investigation due to the fact that noble metals as well as others can be photoreduced and thus can be removed from the solution. Kraeutler and Bard (1978) reported that photoreduction of metals may show the possibility of preparing metal redox catalysts supported on TiO$_2$. Serpone et al. (1988) reviewed the photoreduction and photodegradation of inorganic pollutants with special reference to metals such as Au, Pt, Pd, Rh, Hg and Pb. They have shown that photocatalysis by semiconductor materials under UV/stimulated sunlight is a better way to eliminate unwanted toxic metals from pollutants. Lawless et al. (1990) have extensively studied the removal of toxic metals from wastewater under variety of conditions using irradiated platinized TiO$_2$ particles.

Fernandez et al. (1995) thoroughly studied the photocatalytic degradation of maleic acid with TiO$_2$ supported on several rigid substances. TiO$_2$ supported on quartz showed the highest catalytic activity. It has been found that titania deposited on quartz retained constant photocatalytic activity and can be reused after mere rinsing of the plate in water. This indicates that deposited titania is not deactivated during the reaction either by inhibition or loosening or poisoning of the catalyst.

Cermenati et al. (1997) reported the photocatalytic degradation of quinoline (benzo [b] pyridine) principally because of the difference in electron density over its two rings. This study was based on the identification and quantification of the primary products or principal secondary products of quinoline degradation by TiO$_2$ at pH 3 and 6. The three major products expected from the preferential electrophilic attack of OH on the electron-rich benzene moiety are 5 and 8-hydroxyquinolines and quinoline-5-8-
dione. TiO$_2$ photocatalysis did not yield this dione. These results prove that oxidative steps in TiO$_2$ photocatalysis involve not only 'OH but also the formation of superoxide in photocatalytic oxidative steps.

Mallard-Dupy et al (1994) have studied the photocatalytic degradation of pyridine in water using TiO$_2$. In the studies briefly reviewed, the intermediate products and photocatalytic pathways of pyridine are discussed. They have suggested that hydroxylation of pyridine first occurs only at position 2 and seven aliphatic intermediates with one to five carbon atoms are identified by GC-MS.

Tahiri et al (1998) attempted photocatalytic degradation of three isomers of chloro benzoic acids using TiO$_2$ catalyst. They have reported that the three pollutants disappeared from water in the following order: 3- chlorobenzoic acid < 2- chlorobenzoic acid < 4- chlorobenzoic acid, the para position being the most reactive. The zeroth kinetic order was interpreted by Langmuir - Hinshelwood mechanism involving the saturation of the adsorption sites. The chemisorption of chlorobenzoic acid molecules involves the carboxylic groups linked to the catalyst surface with the aromatic ring possibly oriented perpendicular to the surface. The initial rate of CO$_2$ formation was equivalent to that of the disappearance of chlorobenzoic acid. The mass balance could be established for all the final products. All the intermediate products formed correlate to successive hydroxylations of the corresponding chlorophenol obtained after the initial photo-Kolbe reaction. Modification of titania by doping with Cr$^{3+}$ ions or by depositing Pt was detrimental for the activity of the catalyst.

Bekbolt et al (1996) have studied the photocatalytic detoxification of highly polluted landfill effluents using TiO$_2$ in a thin - film fixed bed reactor. Here the catalyst was fixed on a glass - plate to avoid separation of the catalyst and water after the treatment. They have measured photonic efficiencies based on the amount of incident irradiation used for the experiments. Bandara et al (1997) reported that light and dark processes involving Fenton’s reagent are effective in the degradation of
orange 2 dye. The degradation time is shown to be strongly dependent on the initial pH of the solution. Orange 2 dye is transformed completely into reactive intermediates in less than an hour. Complete mineralisation is attained with the formation of carbon dioxide, water, nitrates, ammonia and sulphate.

Serpone et al (1984a, 1984b) studied the effect of CdS in the photocatalytic decomposition of H₂S in alkaline media. Irradiation with visible light helps in the production of hydrogen in mixed semiconductor dispersions such as those containing CdS suspension in the presence of RuO₂ or Pt-loaded anatase in alkaline solution containing bisulphide ions. This may possibly improve the efficiency of hydrogen generation due to electron transfer from the conduction band of CdS to that of TiO₂ particles. Pelizzetti et al (1984) in an effort to dispose H₂S and SO₂ proposed a cyclic system to convert solar energy into useful fuel (hydrogen) and chemicals (S₂O₃²⁻). The photocatalytic cleavage of H₂S in alkaline aqueous suspension of CdS containing sulphite lead to the formation of hydrogen and thiosulphate. Chen - Yu et al (1986) have shown that illumination of a suspension of silicon powder chemically modified with polypyrrole/RuO₂ system in aqueous sulphide solution resulted in the generation of hydrogen and sulphur. It is suggested that this method is compatible for the large scale disposal of wastes from process streams.

1.11 SCOPE OF THE PRESENT WORK

Wastewater from tanneries has been treated by conventional treatment methods (precipitation, primary sedimentation, biological oxidation and secondary sedimentation). Such a treatment technique is not adequate to control colour caused by the dyes in tannery wastewater. Dyes are largely non-biodegradable and highly carcinogenic. The existing techniques like dissolved air floatation, coagulation, ion - exchange, reverse osmosis, adsorption and oxidation with peroxide or ozone are usually applied for the removal of dyes in wastewater. These methods adopt two possible strategies in treating the wastewater. The first approach is to remove the dyes
from the wastewater and second option is to degrade the dyes completely. Advanced oxidation processes (AOPs) and biological treatment fall under the second category which has the advantage that no further treatment of the dyes is necessary.

Advanced oxidation processes are based on the *in situ* generation of hydroxyl radicals. These hydroxyl radicals are highly reactive and non-selective oxidant which will oxidise organic compounds present in wastewater. Photoassisted catalytic degradation of a variety of coloured organic compounds has attracted much attention among the researchers worldwide in the last one decade and encouraging results are reported in the literature. The present study focusses the application of such a process to degrade certain common leather dyes widely used in tanneries in India.

The present study emphasises the following aspects:

1. Photocatalytic degradation of common leather dyes viz., Acid green 16 and Acid brown 14 employing TiO₂/ZnO catalyst in a batch reactor.

2. Optimisation of parameters such as catalyst loading, concentration of dye, irradiation time and pH for effective degradation.

3. The influences of inorganic oxidants like H₂O₂, FeCl₃ and Fenton's reagent on the photocatalytic degradation of the dyes.

4. The effect of interferences such as sodium chloride and sodium sulphate in the photodegradation process.

5. Evaluation of the performance of the photocatalytic degradation of the dyes upon irradiation with UV source and solar light.
Evaluation of the performance of different supported systems such as thin film coated on glass plate, catalyst coated glass and alumina beads on the photocatalytic degradation of the dyes.

Evaluation of the effect of noble metal (Pt, Au, Ru and Pd) doped catalyst (TiO$_2$ / ZnO) on the photocatalytic degradation of dyes.

Evaluation of the performance of $\alpha$-Fe$_2$O$_3$, WO$_3$ and CdS loaded on TiO$_2$/ZnO catalyst on the photocatalytic degradation of the dyes.

Comparison of the performance of different commercial photocatalysts viz., TiO$_2$, (Degussa P25), ZnO, CdS, WO$_3$, $\alpha$-Fe$_2$O$_3$, SnO$_2$ and ZrO$_2$ in the decolourisation and degradation of the dyes.

Kinetic studies to evaluate the rate constants and rates of dye degradation.