Chapter 1
INTRODUCTION

Chapter Summary

This chapter gives an introduction to the role of phenolic compounds and dyes in the environment, their sources and harmful effects to human health and ecology. Advanced oxidation processes used for treatment of water contaminated with phenols and dyes are briefly reviewed in this chapter. Recent works on photocatalytic treatment of water contaminated with dyes and phenolic compounds are also discussed with special reference to use of titanium dioxide in photocatalysis.

1.1. Objectives of the present work

The present work was formulated with the following objectives:

(i) Preparation of suitable photocatalysts based on Titanium Dioxide supported on Kaolinite and Zeolite Y.
(ii) Characterization of such materials with X-Ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), scanning electron microscopy (SEM) measurements.
(iii) Measurement of the surface area and cation exchange capacity (CEC) of the materials.
(iv) Use of TiO$_2$ supported on kaolinite and TiO$_2$ supported on zeolite Y as catalysts for photocatalytic oxidation of phenol, 2-chlorophenol and 4-chlorophenol under solar radiation and to evaluate the effects of various experimental conditions such as initial concentration of the reactants, pH, amount of catalyst, reaction time etc., on the catalytic activity.
(v) Use of the catalysts in photocatalytic oxidation study of the two dyes, acid blue 25 and methylene blue, and to evaluate the influence of various reaction parameters like initial dye concentration, catalyst load, pH, reaction time etc., on the photocatalytic oxidation of the dyes.
(vi) To determine the reaction kinetics and the order of photocatalytic oxidation of the reactants.
To monitor the extent of photo-oxidation using UV-Visible spectroscopy and also by measuring COD of the product mixture.

To study the recovery and reuse of the catalysts.

1.2. Phenol and chlorophenols in water

1.2.1. Sources

The release of toxic and hazardous chemical substances from different industries leads to serious air, water and soil pollution which have adverse effects on ecosystems and humans. Groundwater contamination is considered to be the most important source of human contact with these pollutants (Hoffmann et al., 1995). Large amounts of different organic and inorganic contaminants are produced as a result of urban, industrial, and agricultural activities which are released into natural water bodies without proper treatment. Phenols and chlorophenols are persistent organic pollutants (POP) which resist natural and biological degradation. Many POPs are present at low concentrations in rivers, lakes, oceans and other natural water bodies and the pollutants can be found even in drinking water across the globe (Brillas et al., 2009). Phenols and chlorophenols, recognized as priority pollutants by US Environmental Protection Agency (US EPA, 1991), belong to the refractory group of compounds which cannot be easily biodegraded (Vaidya and Mahajani, 2002; Maugans and Akgerman, 2003; Molina et al., 2006).

Phenol is found in effluents generated by petroleum refineries, coal conversion processes, coking plants and various other industries like fertilizer, resin, impregnating resins, plasticizers, herbicides, insecticides, dyes, rubber chemicals, flavouring substances, insulating foams, binders, adhesives, laminates, varnishes, emulsifiers, detergents, etc. (Chaliha, 2008). Apart from direct entry from various industries, phenol is also generated as an intermediate product in the oxidation of aromatic hydrocarbons of high molecular weight. Phenol and phenolic compounds are also produced by some natural processes such as decay of vegetation, animal urine (Vidic et al., 1993), degradation of lignin and humic substances (Stevenson et al., 1994; Crespin et al., 1999), and the photochemical decomposition of natural substrates from plant cell walls (Michalzowicz et al., 2008) etc.
Because of the widespread use and great diversity of their origins, chlorophenols are present not only in industrial wastewaters but also in soils and surface waters and groundwaters (Benitez et al., 2000). Chlorophenols are used as raw materials in many industries, and in some manufacturing processes they are generated as reaction intermediates also. Chlorophenols could be used directly as pesticides and antiseptics as well as in the manufacturing of other pesticides, herbicides, phenolic resins, plastics, dyes, drugs, and fungicides (Bauer et al., 1999, Sabhi and Kiwi, 2011). Chlorophenols are also used for wood preservation and Olive Oil production and consequently, wastewaters generated by these industries contain chlorophenols. These toxic organics are also available in effluents discharged by pulp and paper mills, Kraft mills, paint industry, steel industry, coal gasification and liquefaction, surface runoff from coal mines, petroleum refineries, chemical and solvent manufacturing industry (Qin et al., 2001, Posada et al., 2005). Chlorophenol contamination of soil may take place as a result of accidental leakages, uncontrolled discharges and incomplete biodegradation of different aromatic compounds and pesticides (Laurenti et al., 2003).

Chlorophenols are produced by some natural processes also. Chlorophenols may be produced in the sea water by natural chlorination of humic acid (Gribble, 1995). There are reports that addition of chloroperoxidase, hydrogen peroxide and potassium chloride to the fungi Culduriomyces fumugo forms 2,4,6-trichlorophenol (Hodin et al., 1991). In another study, humic soil samples spiked with Na$^{37}$Cl solution incubated for 1 year resulted in the formation of 4-chlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol and 2,4,5-trichlorophenol containing $^{37}$Cl (Hoekstra et al., 1999). Chlorophenols are also generated as a result of natural microbial degradation of herbicides (Czaplicka, 2004).

In the disinfection process of drinking water with chlorine, lower chlorophenols may be produced as byproducts in presence of certain contaminants (Paasivirta et al., 1985; Pouloupolos et al., 2007). The most common by-products of chlorination in drinking water are 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol (WHO, 2011).
1.2.2. Toxicity and effects on environment and human health

Toxicity of a substance may be defined as its inherent ability to cause an adverse effect on human and animal health (Khanikar, 2013). Phenol and chlorophenols have extreme toxicity to aquatic life even at very low concentration of 1.0 ppm (Masende et al., 2003). Chlorinated derivatives of phenols, even in trace concentrations, are found to add taste and odour to drinking water (Viraraghavan and Alfaro, 1998). Chlorophenols may be present in the aquatic environment in dissociated or non-dissociated state and also in the adsorbed state on suspended particulate matter (Czaplicka, 2006).

Toxicity of the chlorophenols depends on the position and number of chlorine atoms in the aromatic ring. The ortho-substituted phenol is less toxic compared to meta- and para-substituted phenols because Cl in ortho-position is shielded by – OH group (Pera-Titus et al., 2004). 3,5-dichlorophenol exhibits more toxicity compared to 2,6-dichlorophenol (Saito et al., 1991). With increase in the number of Cl atoms in the aromatic ring, toxicity of chlorophenols increases.

Phenol and chlorophenols resist biodegradation and persist in the environment for a long time. Water pollution by phenolic compounds is of major concern now as it causes harm to human health as well as other living organisms. The aesthetic quality of natural water bodies like lakes and rivers are diminished by water pollution. Polluted water has a negative impact on the reproductive abilities of aquatic organisms and destroys aquatic life. Water contaminated with hazardous compounds is not suitable for drinking, agricultural and industrial activities.

Cells and vital organs of living organisms are damaged by exposure to phenol and chlorophenols (Anandan et al., 2007). Repeated or prolonged intake of these compounds causes harm to the skin, lung, liver, mucous membranes, oesophagus, urogenital tract and kidneys of experimental animals (Bruce et al., 1987; Michałowicz and Duda, 2007). Phenol and its vapour have corrosive effect on skin, muscles, eye and respiratory tract of humans. As a result of phenol poisoning, people may suffer from headaches, dryness of the throat, dyspnoea, lung edema, nausea, vomiting, diarrhea etc. (Juhl et al., 2003). Long time exposure to phenol and chlorophenols results in structural and functional changes in the man’s brain, necrosis of the liver, and emphysema (Roy et al., 1998). Central nervous system, heart, kidney and lung are also severely affected by prolonged intake of these compounds which may even lead to dysrhythmia, seizures and coma.
Moreover, phenols have cytotoxic effect on skeletal muscles, neurotoxic effect on pyramidal neurons. Phenolic compounds have mutagenic effect as they can inhibit DNA synthesis, induce gene mutations and even lead to unbinding of the DNA helix (Chaliha, 2008).

Chlorophenols can bioaccumulate (Haimi et al., 1992). 2-chlorophenol has corrosive effect on skin, mouth and cause gastrointestinal injuries. In case of animals that were exposed to high level of chlorophenols in the laboratory, liver and immune system damage and weight loss were observed. Low birth rates and low birth weight were noticed, when pregnant female rats were given drinking water contaminated with high level of chlorophenols.

There is evidence that some particular chlorophenols like 2,4,6-trichlorophenol and pentachlorophenol are carcinogenic (Exon and Koller, 1983; Chhabra et al., 1999). Chlorophenol exposure may lead to chromosomal aberrations, leukemia, malignant lymphoma and soft tissue sarcoma in humans (Exon and Koller, 1983; DeMarini et al., 1990; Zeljezic and Garaj-Vrhovac, 2001). Industrial workers exposed to phenoxy herbicides and chlorophenols are reported to have more risks of respiratory cancer, non-Hodgkin’s lymphoma and heart diseases (Hooiveld et al., 1998).

1.3. Dyes in water

Dyes represent a relatively large group of organic chemicals, which are used in each and every step of modern life. There are more than 100,000 commercial dyes with an estimated annual production of almost $7 \times 10^5$ – $1 \times 10^6$ ton (Meyer, 1981; Zollinger, 1987; Hunger, 2003; Husain, 2006; Christie, 2007). Dye molecules consist of two main components namely, chromophores and auxochromes. Chromophores produce colour and auxochromes supplement the chromophores, make the molecule soluble in water and increase the affinity to attach to the fibers.

Dyes may be classified in different ways. They may be classified as natural or synthetic. On the basis of solubility, dyes may be classified into two classes: soluble dyes (acid, mordant, metal complex, direct, basic and reactive dyes are included in this category) and insoluble dyes (azoic, sulfur, vat and disperse dyes etc. are insoluble dyes). Dyes may also be classified depending upon their chemical structure and their application to the fiber type (Hunger, 2003). On the basis of use, dyes may be classified
into several groups such that acid dyes, basic (cationic) dyes, disperse dyes, direct dyes, reactive dyes, solvent dyes, sulfur dyes and vat dyes (Hunger, 2003; Christie, 2007).

### 1.3.1. Sources

Water pollution caused by the dye effluents has become a serious environmental problem as dyes are present in industrial wastewater as well as in natural water sources like lakes and rivers. Dyes may come in contact with the aquatic environment from three major sources (Bouzaida et al., 2004):

i. from dye manufacturers
ii. from dye users (e.g. different industries like textile and paper mills, plastic industries etc.)
iii. from diffuse or domestic discharges as a result of leaching of dyes from manufactured products.

There are reports that more than $7 \times 10^5$ metric tons of dyes are produced annually across the globe (Papic et al., 2004; Lee et al., 2006; Riera-Torres et al., 2010), but only a fraction of these huge quantities of dyes are really utilized. 10 to 15% of the dyestuffs are lost during the dyeing processes (Ratanatawanate et al. 2009). The unutilised part of the dye compounds become a part of the wastewater and enter natural water bodies such as lakes, rivers and wetlands etc., as a result of which water is polluted (Young and Yu, 1997; Gupta and Suhas, 2009; Zhao et al., 2011).

Different industries like pulp and paper mills, textile, leather, cosmetics, plastic and photographic industries, etc., have become a major source of water pollution as they generate a large volume of polluted wastewater contaminated with synthetic dyes (Ali and Sreekrishnan, 2001; Pokhrel and Viraraghavan, 2004; Crini and Badot, 2008). These industries consume substantial volume of water. Different types of dyes and chemical substances are used in these industries during manufacturing and finishing processes. The effluents of the industries contain dyes as well as other toxic and hazardous compounds and pollute the receiving water if discharged untreated (Ali and Sreekrishnan, 2001). Dyes are used in chemical laboratories for analytical purposes.
and also in biomedical and biological laboratories as biological stains (Shakir et al., 2010). The wastewater from these laboratories also carries dyes of various types.

It has been estimated that more than $5.5 \times 10^6$ m$^3$ of wastewater is generated per day by the industries in India, out of which almost $6.85 \times 10^3$ m$^3$ is discharged directly into natural water bodies (rivers and streams) without prior treatment (MOWR, 2000). The industrial sector is responsible for 3% of the total water withdrawals per year in India. In most of the developing countries, the major part of the total volume of wastewater is generated by the textile sector. There are reports that the developing countries of South Asia have contributed almost 35% textile wastewaters to the total amount of industrial wastewater generated in 2001 (World Bank, 2005). India is the major manufacturer of textiles and might be the major contributor of textile wastewater among seven core countries of South Asia namely India, Pakistan, Bangladesh, Bhutan, Nepal, Sri Lanka and Maldives. There are around 83 composite mills and 2241 semi composite processing units (COINDS, 2000) in the country which are mostly concentrated around places like Surat, Mumbai, Ahmedabad, Ludhiana, Kanpur and Coimbatore (Verma et al., 2012). The natural water bodies in these places are polluted at a very high level as a result of discharge of textile wastewater without prior treatment.

There are reports that around 200 to 350 m$^3$ of wastewaters are generated per ton of finished products in textile industries (Ranganathan et al., 2007; Gozálvez-Zafrilla et al., 2008, Verma et al., 2012). This results in an average pollution of 100 kg COD per ton of fabric (Jekel, 1997). Dye compounds in wastewaters may be chemically bound to fabric fibers (ATMI, 1997). The disperse dyes have higher percentage of fixation to the fiber in comparison to acid and reactive dyes due to which dyeing and rinsing processes for disperse dyes generate less wastewater (about 91 - 129 m$^3$ per ton of product) compared to those for acid and reactive dyes (about 113 - 151 m$^3$ wastewater per ton of product) (Snowden-Swan, 1995; Karcher et al., 2002; Riera-Torres et al., 2010). Wastewater generated by finishing processes usually contains natural and synthetic polymers and many other potentially toxic substances (Snowden-Swan, 1995).

### 1.3.2. Toxicity of dyes and their effects on environment and human health

Dye contaminated water is harmful to humans as well as to the ecosystem (Georgiou et al., 2003; Merzouk et al., 2010). Dyes in water are aesthetically unacceptable even in
very dilute concentration (less than 1 mg/L). Most of the dyes are toxic and several of
them have carcinogenic and mutagenic effects on humans and aquatic biota (McKay et
al., 1985; Gregory et al., 1991). Amongst the 4000 dyes listed in an ETDA (Ecological
and Toxicological Association of the dye staff) survey, more than 90% of the dyes were
found to have LD values greater than 200 mg/kg. Generally basic and diazo direct dyes
have highest toxicity (Garg et al., 2004). The dye contaminated wastewater is
characterized by high chemical oxygen demand (COD), turbidity, fluctuating pH and
heavy load of suspended solids (Sivraj et al., 2001). Direct discharge of these
wastewaters into the water bodies depletes the dissolved oxygen level in water bodies
and endangers aquatic life. Because of their resistance to biodegradation, the toxicity of
the dye-containing wastewater persists for a long time (Pala and Tokat, 2002; Kim et
al., 2004; Gao et al., 2007).

Wastewaters generated by textile industry mostly contain reactive azo dyes. Due to
the presence the $\text{SO}_3^-$ and $\text{NR}_2^+$ groups in their structure, azo dyes are readily soluble in
water, and they give colour to water even at low concentrations. Because of the complex
aromatic structure, azo dyes are difficult to degrade and may be converted to toxic or
carcinogenic compounds as a result of incomplete degradation (Hu et al., 2003). The
azo linkages present in these dyes are responsible for the formation of amines which are
toxic. Basic dyes and anthraquinone-based dyes also resist degradation because of their
fused aromatic ring structure. These dyes are visible even at very dilute concentrations
in water and the colour persists for a long time (Robinson et al., 2001).

The chromophoric systems present in the dye absorb solar radiations, thus affecting
sunlight penetration and reducing the intensity of solar radiation reaching the bottom.
This has a negative impact on the photosynthesis activities of the submerged aquatic
plants, and as a result, survival and growth of these plants are adversely affected (Yu et
al., 2004; Yildirim et al., 2011). Many dyes and their degradation intermediates are
toxic to aquatic plants, fish, mammals and microorganisms (Georgiou et al., 2003; Kim
et al., 2004; Ustun et al., 2007).

Some synthetic dyes release aromatic amines which are suspected to be poisonous,
allergic and carcinogenic. These harmful amines can get absorbed through the skin of
human body with sweat and friction as a result of regular contact. These dyes are not
prescribed for use in coloring articles that regularly come into contact with human body.
Some countries like Germany, Netherlands and Austria have imposed ban on use of 120 to 150 dyes out of more than 3000 azo dyes. These dyes most commonly have benzenidine and diazo-benzenidine groups, which are suspected to be carcinogenic.Repeated and excessive exposure to colored effluents may severely affect respiratory, circulatory, central nervous and immune system of humans. People exposed to dye contaminated water may suffer from several disorders like allergy, eye and skin infections, autoimmune diseases, lung edema, multiple myeloma, insomnia, leukemia, vomiting, hyperventilation, diarrhea, cyanosis, jaundice, quadriplegia, tissue necrosis, etc (Anliker, 1986; Foo and Hameed, 2010; Verma et al., 2012).

Degradation of some dyes generates intermediate products which are more toxic than the parent dyes. Microbial degradation of a mutagenic dye, Methyl Red, leads to the formation of N,N-dimethyl-phenylenediamine (DMPD) (Wong and Yuen, 1998) which is also mutagenic. This toxic aromatic amine remains unchanged in nature (Ayed et al., 2011). Similarly, the products formed as a result of oxidation of indigo blue via electro-incineration, coagulation with Al$_2$(SO$_4$)$_3$ or the use of Lac are found to be more toxic than the parent dye (Solis-Oba et al., 2009). The toxicity of the dyes as well as their degradation products must be assessed in order to study the suitability of a method for dye removal (Jadhav et al., 2011).

Some structurally similar dyes may differ in toxicity. For example, the structures of three dyes namely, Acid Red 26, Acid Red 18 and Acid Red 27 are similar (structures are given below). Among them, Acid Red 26 is a carcinogenic dye but Acid Red 18 and Acid Red 27 are non carcinogenic. The presence of a methyl group and the difference in the position of sodium sulphonate in Acid Red 26 might be responsible for the carcinogenicity (Solis et al., 2012).
1.4 Methods for wastewater treatment

1.4.1. Introduction

Water pollution is becoming a severe problem with rapid industrialization, urbanization and increased agricultural activities. Improper waste disposal practices and accidental leakages of hazardous compounds have adversely affected the quality and quantity of water available in the world. The environmental regulatory requirements have become more stringent because of increased awareness of the risks associated with polluted water. Consequently, treatment of wastewaters is gaining more attention worldwide and a vast quantity of research work is being carried out throughout the world in the last few years to develop simple, effective, economical and safe technologies for the total destruction of organic and inorganic pollutants in wastewater before final disposal. Conventional processes of wastewater treatment may be classified as separation/isolation, biological treatment and destruction (Brenner, 1999). The separation technologies are based on physicochemical processes like filtration, flotation, extraction, distillation, air stripping, membrane processes (reverse osmosis and ion exchange), adsorption, flocculation and sedimentation, coagulation, etc. (Brillas et al., 2009). Though these nondegradative processes can separate some contaminants from wastewater but have limitations. They cannot alter the chemical structure of the contaminants and are not effective in removal of many toxic organics and inorganics. Most of these processes result in transformation of contaminants from one phase to another. For example, processes like coagulation and filtration are not effective for dyes because coagulation transforms dyes to another phase and in filtration, dyes having low-molar-mass can pass through the filter system.

In the biological treatment processes of wastewater treatment, contaminants are biodegraded using microorganisms under aerobic or anaerobic conditions. A large number of organic and inorganic contaminants can be removed by these low cost processes. Biological treatment can decrease biological oxygen demand (BOD) and chemical oxygen demand (COD) of wastewater (Mouzdahir et al., 2007). However, some toxic compounds including halogenated compounds and dyes have resistance to microbial attack (Adriaens and Vogel, 1995). Instead of removing contaminants, the microorganisms are toxicated by the contaminants which limit the application of biological treatment processes.
Chemical destruction process of the pollutants involves the cleavage of structural bonds in these molecules. This results in the conversion of the contaminants into several intermediates and finally to the mineralised products (CO$_2$, water, and inorganic ions). Advanced oxidation processes (AOPs), incineration, ozonation, chlorination, supercritical water oxidation, wet air oxidation, etc. are examples of destruction processes.

AOPs involving chemical, photochemical, or electrochemical water treatment processes are eco-friendly in nature and could be carried out near ambient temperature and pressure. These processes involve in-situ production of some powerful oxidizing agents such as the hydroxyl radicals (•OH) in solution, which act as the destroyer of the recalcitrant organic molecules. A few AOPs in use are briefly described below:

1.4.2. Fenton and Fenton-like processes

Fenton reaction is one of the most popular AOPs that can be used in the treatment of various persistent and toxic compounds including phenolic compounds, dyes, formaldehyde, additives used in plastic industry, pesticides, wood preservative chemicals, and rubber chemicals (Bishop et al., 1964, Barbeni et al., 1987). Fenton and Fenton-like processes are based on an electron transfer reaction between H$_2$O$_2$ and metal ions acting in homogeneous medium (Safarzadeh-Amiri et al., 1996; Lücking et al., 1998). Though Fenton pointed out the possible reactivity of this system in 1894, but its extraordinary utility remained unrecognized until a hydroxyl radical (HO•) based mechanism was proposed in 1930s (Haber and Weiss, 1934). Fenton’s processes have become one of the most widely studied and used AOPs in the mid 1960s (Barb et al., 1951; Walling, 1975; Prousek, 1995). In Fenton reaction, a mixture of an iron (II) salt (Fe$^{2+}$) and H$_2$O$_2$ is used to as the reagent. Controversy exists whether hydroxyl radical (•OH) or ferryl ion (FeO$^{2+}$) is the actual reagent in H$_2$O$_2$–Fe$^{2+}$ mixtures in aqueous solution, but hydroxyl radical is most commonly accepted to be the key intermediate (Kremer 1999).

By comparing some thermodynamic properties of hydroxyl radicals and ferryl ions, both the species were found to be almost equally active (Koppenol and Liebman, 1984). Because of the highly reactive nature of •OH and FeO$^{2+}$, the Fenton reactions are very
difficult to control at some desired point. As a result, these reactions have almost no control on the product selectivity which limits the applicability of Fenton reactions.

In Fenton-like reactions, iron (III) ion (Fe$^{3+}$) is used instead of Fe$^{2+}$. Reactivity of Fenton-like reagent is observed to be somewhat less than that of Fenton's reagent. As Fe$^{3+}$ is produced in applications of Fenton's reagent, Fenton and Fenton-like reactions often occur simultaneously and proceed via similar mechanisms.

In Fenton and Fenton-like processes, a number of oxidation mechanisms may exist simultaneously and competing with each other. The reaction conditions determine the mechanism that prevails. As the active species have very short life-spans and are elusive in nature, it is very difficult to isolate them or monitor their activities in reactions (Kremer and Stein, 1959; Walling and Weil, 1974; Costas et al., 2000; Roelfes et al., 2000).

1.4.3. Photo-Fenton process

The photo-Fenton process is considered to be another efficient method for wastewater and soil treatment (Bauer and Fallmann, 1997; Chen and Pignatello, 1997). The Fenton reaction carried out under ultraviolet (UV) light is termed as the photo-Fenton reaction. Generally, UV-A ($\lambda = 315-400$ nm), UV-B ($\lambda = 285-315$ nm), and UV-C ($\lambda = 285$ nm) radiations are used as energy source in the photo-Fenton processes. The destruction rate of contaminants depends upon the intensity and wavelength of UV radiation. Photoassistance by UV radiation had been found to enhance the oxidative power as well as the efficiency of the Fenton process. These processes are found to have high reaction rates and are much effective in treating dye contaminated wastewaters (Bandala et al., 2008).

The use of artificial UV light increases the cost of the photo-Fenton process. In order to get rid of this disadvantage, solar photo-Fenton process has been developed recently, in which sunlight ($\lambda > 300$ nm) is used as the energy source (Malato et al., 2007; Oller et al., 2007). As solar radiation is free and inexhaustible, both environmental and economic aspects are satisfied in solar photo-Fenton process. Fenton, Fenton-like and photo-Fenton methods are considered to be economical because of the use of H$_2$O$_2$ which is much cheaper in comparison to the strong oxidizing agents like persulphate. As at higher pH, Fe$^{3+}$ ion begins to precipitate as hydroxide, low pH
(normally < 4) is required in the photo-Fenton process, which is considered to be a disadvantage of this process. Another difficulty encountered in this process is to remove the added iron from the treatment system (Klibanov et al., 1980).

1.4.4. Ozonation

Ozonation is another important oxidative destruction process in wastewater treatment that is carried out at basic pH. The radicals generated as a result of the decomposition of ozone are the active species. Ozone is a stronger oxidizing agent compared to oxygen. In thermodynamic terms, ozone can oxidize all organic compounds to carbon dioxide and water. Ozonizers are widely used in drinking water treatment stations. Ozonation process, however, suffers from the difficulty in generating ozone and also from the fact that the oxidation process is highly dependent on pH (Ullmann, 1995). Some important ozonation processes are briefly discussed below:

(i) **UV/O$_3$ process.** The UV/O$_3$ process is one of the most frequently applied AOP for destruction of a wide range of toxic and refractory organic compounds, bacteria, and viruses in water. This process is also used in the decolourization of bleaching waters in the paper mill (Prat et al., 1990). The ozonation can be used in conjunction with ultraviolet radiation leading to the generation of a high concentration of hydroxyl radicals. The overall reaction that takes place is:

$$
H_2O + O_3 \xrightarrow{hv} 2OH\cdot + O_2
$$

The low solubility of ozone in water and consequent mass transfer limitations represent one of the most serious difficulties that arises in the technical development of the UV/O$_3$ process.

(ii) **H$_2$O$_2$/O$_3$ process.** The action of ozone and hydrogen peroxide are combined in this process to enhance the formation of the hydroxyl radicals. Apart from the generation of OH$\cdot$ radical, HO$_2$· radical is also produced in this process as a result of which, the organic compounds are degraded more effectively and rapidly (Adams et al., 1994). The general reaction is given below:
(iii) \( \text{H}_2\text{O}_2 / \text{UV} / \text{O}_3 \) process. In this process, a tertiary system is obtained as a result of combination of the three systems, \( \text{UV} / \text{O}_3 \), \( \text{H}_2\text{O}_2 / \text{O}_3 \) and \( \text{UV} / \text{H}_2\text{O}_2 \). This process is found to be most effective in the treatment of highly polluted effluents. A considerable reduction of the TOC and complete mineralization of the organics can be achieved by applying this process. The following reaction takes place:

\[
\text{H}_2\text{O}_2 + 2\text{O}_3 \xrightarrow{hv} 2\text{OH}^- + 3\text{O}_2
\]

1.4.5. Wet air oxidation (WAO)

Wet air oxidation (WAO) may be defined as a process of oxidizing organic compounds in aqueous medium that uses oxygen or air as an oxidant. The oxidation proceeds via a free radical mechanism initiated by the attack of oxygen on the organic substrate (Li et al., 1991). The dissolved oxygen can react with the organic compounds in this process.

\[
\text{RH} + \text{O}_2 \rightarrow \text{R}^- + \text{HO}_2^-
\]

The free radicals generated in this initiation step subsequently react with oxygen as well as other organic and inorganic compounds leading to the formation of a variety of radical species as shown below:

\[
\begin{align*}
\text{R}^- + \text{O}_2 & \rightarrow \text{ROO}' \\
\text{RH} + \text{HO}_2^- & \rightarrow \text{R}^- + \text{H}_2\text{O}_2 \\
\text{RH} + \text{ROO}^- & \rightarrow \text{R}^- + \text{ROOH} \\
\text{H}_2\text{O}_2 & \rightarrow 2\text{HO}' \\
\text{ROOH} & \rightarrow \text{RO}^- + \text{HO}^- 
\end{align*}
\]

WAO can be used for pretreatment of wastes that cannot be degraded by the conventional biological oxidation processes. Water is found to behave much like a catalyst and is an integral part of the WAO reaction (Eletzke, 1966).
WAO processes are useful in oxidation of compounds like waste liquors, sludges and slurries, where the oxygen demanding organic matter is only a few percent of the overall waste load. Bio-refractory organics are converted to simpler and easily degradable materials before their release into the environment in wet air oxidation process. Generally, low molecular weight oxygenated compounds (e.g., acetic acid, propionic acid, methanol, ethanol, acetaldehyde etc.) are generated as end products (Luck, 1999). As these compounds are resistant to further transformation to CO$_2$, complete mineralization of organics is not achieved in WAO process which is considered as the main disadvantage of this process. Another significant drawback of this process is that high temperature and pressure are required to achieve a high degree of oxidation. The WAO process is one of the simplest and most promising technologies for partial oxidation of parent organics into biodegradable intermediates. The use of catalysts (either heterogeneous or homogeneous) can improve the efficiency of WAOs. Homogeneous Cu (II) ion and Fe (III) ion, their heterogeneous counterparts, and precious metal catalysts are observed to enhance the efficiency of WAO processes (Sadana and Katzer, 1974; Ohta et al., 1980; Maugans and Akgerman, 1997; Fortuny et al., 1999).

1.4.6. Catalytic wet oxidation (CWO)

In WAO processes, only partial oxidation of organic compounds is possible at low temperature leading to the formation of low molecular weight oxygenated compounds instead of complete mineralization. High temperatures, pressures, and reaction times are necessary for complete oxidation. To overcome this drawback, a catalyst may be incorporated into the oxidation process which may help in reducing the operating temperature, pressure and to oxidize pollutants that are not degraded in non-catalytic WAO processes. But in case of homogeneous catalysis, difficulty arises in the removal of the catalyst from the effluent after treatment. Moreover, the metal ion catalysts, themselves contaminate the wastewater in the range of concentrations used. These problems may be eliminated by using appropriate heterogeneous catalysts, as these solid catalysts can be easily separated and recovered from the reaction mixture, regenerated and reused for several times (Kim and Ihm, 2011; Ovejero et al., 2012). Thus the efficiency of WAO process can be improved by incorporating a heterogeneous catalyst.
leading to the development of catalytic wet air oxidation technique (Mishra et al., 1995; Matatov-Meytal and Sheintuch, 1998; Andreozzi et al., 1999; Luck, 1999).

Intensive contact is mandatory between the catalyst surface and the pollutant in solution in the heterogeneous oxidation process. It is proposed that the oxidation occurs in five steps (Bhargava et al., 2006), namely, (i) transfer of the reactant molecules from the aqueous solution phase to the catalyst surface, (ii) adsorption of one or more of the reactants onto the catalyst surface, (iii) chemical interactions between the adsorbed species on the catalyst surface, or between one adsorbed species and another species in solution leading to conversion of the reactants into simpler products that remain adsorbed to the catalyst surface, (iv) desorption of products from the catalyst surface, and (v) diffusion of the products from the catalyst surface to the bulk solution.

The slowest of the five steps would be the rate-determining step that controls the overall reaction. In case, either (i) or (v) is the slowest step, then the reaction is controlled by the physical process of transfer or diffusion. On the other hand, if any of the steps of (ii), (iii) or (iv) is the rate-determining slowest step, the overall oxidation is chemically controlled. Selection of a suitable catalyst is an important factor in controlling the reaction rate because the catalyst surface plays the key role in adsorption and desorption. CWO process is widely used to oxidize wastewater contaminated with dyes and phenolic compounds.

1.4.7. Semiconductor Photocatalysis

Heterogeneous semiconductor photocatalysis has been studied as one of the most promising AOPs over the past decade. This process generally requires mild reaction conditions, lesser chemical input and modest reaction time, and is applicable to aqueous, gaseous as well as to some extent, solid (soil) phase treatments. The final products are usually innocuous and secondary waste generation like that of sludge is the minimum. Because of the above mentioned advantages, heterogeneous photocatalysis is considered to be more efficient compared to the conventional processes.

Some of the semiconductors examined as photocatalysts for wastewater treatment are TiO₂, ZnO, ZrO₂, CdS, MoS₂, Fe₂O₃,WO₃ and their various combinations. To be an efficient photocatalyst, a semiconductor must have suitable band-gap energies and some other characteristics such as stability under different reaction conditions,
resistance to photocorrosion, nontoxicity and low cost, etc. The constituent element with which the semiconductor is made up must have the capability to change its valence state reversibly to accommodate a hole without decomposing the semiconductor (e.g. $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ in $\text{TiO}_2$). If the element has just one stable valence state (for example, in $\text{ZnO}$ and $\text{CdS}$, zinc and cadmium have only one stable valence state, $\text{Cd}^{2+}$ and $\text{Zn}^{2+}$ respectively) formation of holes may lead to the decomposition of the semiconductor. (Hodes et al., 1976; Kabra et al., 2004).

Among different semiconductors, examined as photocatalysts, only $\text{TiO}_2$ was found to have the above mentioned characteristics to become an efficient catalyst. The reuse property of a photocatalyst is an important criterion for commercialization as this property minimises the operating costs of the process. It is reported that the same $\text{TiO}_2$ catalyst could be used for phenol degradation for 120 h without loss of activity (Yu et al., 2000). But in case of $\text{ZnO}$ catalyst, significant loss of activity was observed due to the anodic photocorrosion of $\text{ZnO}$:

$$\text{ZnO} + h^+ \rightarrow \text{Zn}^{2+} + \text{O}$$

The quantity of $\text{Zn}^{2+}$ detected in suspension was found to be almost equal to the quantity of removed phenol (Okamoto et al., 1985a). Recently, researchers have developed several methods to improve photostability of $\text{ZnO}$. Some of these are surface organic coating of $\text{ZnO}$ (Comparelli et al., 2005) and surface hybridization of $\text{ZnO}$ with carbon and fullerene, $\text{C}_{60}$ (Fu et al., 2008). These methods also have limitations as the organic compound or carbon used could be gradually oxidized by the photogenerated active oxygen species during long photocatalytic process. This affects their photostability (Li et al., 2009). The efficiency of $\text{WO}_3$ as a photocatalyst was reported to be very low though it satisfied the criterion of stability against photocorrosion (Yoneyama et al., 1979).

In heterogeneous photocatalysis, photoinduced reactions take place at the surface of the catalyst. Photocatalysis can be classified into two processes depending on where the initial excitation occurs. If the initial photoexcitation takes place in an adsorbate molecule and this photoexcited adsorbate then reacts with the ground state catalyst substrate, the process is called a catalyzed photoreaction. On the other hand, if the initial photoexcitation occurs in the catalyst substrate which then interacts with a ground state molecule, the process is called a sensitized photoreaction (Linsebigler et al., 1995).
Semiconducting solids have a void energy region called the band gap extending from the top of the filled valence band (VB) to the bottom of the vacant conduction band (CB). An electron ($e^-$) is excited from the valence band to the conduction band only if a semiconductor absorbs a photon having energy ($h\nu$) that equals or exceeds the band gap energy ($E_g$) of the semiconductor. As a result of this electron excitation, a positive charge is generated in the valence band which is called a hole ($h^+$). Generally, photocatalytic reactions on semiconductors are initiated by UV or near-UV photons by the mechanism:

$$\text{semiconductor} + h\nu \rightarrow e_{cb}^- + h_{vb}^+$$

The lifetime of an electron-hole pair thus created is a few nanoseconds only (Bussi et al., 2002). Within this short time, the pair migrates to the photocatalyst surface where it either recombines or participates in redox reactions with the molecules adsorbed on the photocatalyst surface. In presence of suitable electron and hole scavenger or surface defect states, the electron or hole is trapped and subsequent redox reactions take place in the solution or gas phase in contact with the semiconductor. If suitable electron and hole scavengers are not available, the electron-hole pair recombines and the input energy is dissipated as thermal energy.

A general mechanism has been proposed for heterogeneous photocatalysis on TiO$_2$ (Martin et al., 1994) with the help of laser flash photolysis measurements. Generally, the valence band hole interacts with water to form hydroxyl radical (OH•), which acts as the primary oxidant. The hydroxyl radical initiates a chain of reactions leading to the oxidative degradation of organic pollutants, or it can react with an electron donor species, depending on the mechanism of the photoreaction. Similarly, the conduction band electron can interact with oxygen molecule to yield superoxide radical anion, (O$_2$•$^-$). Alternately, it can be donated to a metal ion (having a redox potential more positive than the band gap energy of the photocatalyst) leading to the reduction of the metal ion to its lower valence state and deposition of the metal on the surface of the catalyst. The electron-transfer process is favoured by pre-adsorption of the species on the catalyst surface. Turchi et al., (1990) have suggested the following mechanism:

The first step is the generation of electron and hole pair after the excitation of the catalyst by photon with energy greater than the band gap:
TiO\(_2\) + \(h\nu\) \(\rightarrow\) e\(_{cb}\)\(^-\) + h\(_{vb}\)\(^+\)

The hole interacts with surface adsorbed molecular oxygen to form superoxide radical anions. The next step is the adsorption on the catalyst surface and lattice oxygen (O\(_{L_{2-}}\)):

\[
O_{L_{2-}} + >Ti^{IV} + H_2O \rightarrow O_{L^-} + >Ti^{IV}-OH^-
\]

\[
> Ti^{IV} + H_2O \rightarrow >Ti^{IV}-OH_2
\]

\[
site + R_1 \rightarrow R_{1ads}
\]

where R\(_1\) is an organic molecule, R\(_{1ads}\) is an adsorbed organic molecule. This is followed by the trapping of charge-carrier (fast process, \(~10\) ns):

\[
> Ti^{IV}-OH^- + h_{vb}^+ \rightarrow > Ti^{IV}-OH^-
\]

\[
> Ti^{IV}-OH_2 + h_{vb}^+ \rightarrow > Ti^{IV}-OH^+ + H^+
\]

\[
> Ti^{IV}-OH^+ + h_{vb}^+ \rightarrow \{> Ti^{IV}-OH^+\}^+
\]

\[
> Ti^{IV} + e_{cb}^- \rightarrow > Ti^{III}
\]

\[
> Ti^{III} + O_2 \rightarrow > Ti^{IV}-O_2^-
\]

Charge-carrier recombination process is comparatively slow (\(~100\) ns) and produces thermal energy:

\[
e_{cb}^- + h_{vb}^+ \rightarrow \text{heat}
\]

Interfacial charge transfer takes place as follows:

\[
h_{vb}^+ + \text{Red}_1 \rightarrow \text{Ox}_1
\]

\[
> Ti^{IV}-OH^+ + \text{Red} \rightarrow > Ti^{IV}-OH^- + \text{Red}^+
\]

\[
e_{tr}^- + \text{Ox} \rightarrow > Ti^{IV}-OH^- + \text{Ox}^+
\]

where e\(_{tr}\)\(^-\) is a trapped conduction-band electron, Red is an electron donor, Ox is an electron acceptor. Attack of hydroxyl radical may take place as follows:
In the first case, surface bound hydroxyl radical attacks the substrate which is in adsorbed state, in the second case substrate is in adsorbed state but hydroxyl radical is in free state, in the third case hydroxyl radical is in adsorbed state but the substrate is not pre-adsorbed and in the last case both hydroxyl radical and the substrate are in free state.

Chains of reactions involving other radicals also take place simultaneously:

\[ \text{>Ti}^{IV} - \text{O}^-_2 + 2\text{H}^+ + \text{e}_{tr}^- \rightarrow \text{>Ti}^{IV} (\text{H}_2\text{O}_2) \]
\[ \text{>Ti}^{IV} - \text{O}^-_2 + \text{H}^+ \rightarrow \text{>Ti}^{IV} (\text{HO}_2^-) \]
\[ \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \]

Conduction band electron can reduce metal ion (having redox potential more positive than band gap energy of the semiconductor) if present to its ground state:

\[ n\text{e}_{cb}^- + M^{n+} \rightarrow M^0 \]

(The reaction mechanism is adopted from Hoffmann et al. (1995) and Kabra et al. (2004).)

1.4.8. Oxidative wastewater treatment using TiO$_2$/UV process

A large number of reports and publications on the application of TiO$_2$/UV process for wastewater treatment are available in literature. Several research groups have tried to degrade a wide variety of organic and inorganic pollutants in wastewater using TiO$_2$/UV process in the past 40 years (Okatomo et al., 1985; Pelizzetti et al., 1988; Mathews, 1988; Jakob et al., 1992; Legrini et al., 1993). TiO$_2$/UV process has been found useful in complete mineralization of a variety of contaminants like chlorinated benzenes, phenols, naphthalenes, dibenzofurans, and dibenzo-p-dioxins in aqueous media...
As the band-gap energy of pure TiO$_2$ is 3.0-3.2 eV, it exhibits strong oxidation activity and hydrophilicity only under UV radiation with wavelength shorter than 390 nm (Sato et al., 2005).

The first application of this process available in literature was on the degradation of biphenyl and chlorobiphenyls (Carey et al., 1976). There are reports that by applying TiO$_2$/UV process for 90 min reaction time, phenol could be completely removed but TOC reduction was ≤ 35% (Okamoto et al., 1985a, b). Matthews (1988) examined photocatalytic degradation of different organics like acetic acid, benzoic acid, formic acid, ethanol, methanol etc. and was successful in removing 96% TOC only in just 10 min irradiation time. The experiments were done using a spiral glass tube reactor loaded with a thin layer of TiO$_2$ and a black-light fluorescent lamp (20 W) as the source of UV radiation. Complete mineralization and 95% TOC removal was reported within 50 min irradiation time as 1,2-dimethyl-3-nitrobenzene and nitro-o-xylene were degraded photocatalytically in an annular semi-batch reactor and a medium pressure Hg lamp (125 W) (Legrini et al., 1993). The effects of different parameters on TOC removal rate (such as semiconductor dispersions, initial hydrogen peroxide concentration and wavelength of UV radiation) were also examined and it was observed that addition of hydrogen peroxide enhanced TOC removal rate. D’Oliveira et al. (1990) studied photodegradation of 2-chlorophenol (2-CP) and 3-chlorophenol (3-CP) with TiO$_2$ aqueous suspensions using Philips HPK 125-W high-pressure mercury lamp as the source of UV radiation. They investigated the effects of various parameters like radiant flux, wavelength, initial concentration, and pH and identified different reaction intermediates with the help of HPLC. According to their study, para-hydroxylation was the main pathway in the degradation of both 2-CP and 3-CP and chlorohydroquinone was the main reaction intermediate. In case of 2-CP degradation, catechol formation was a minor pathway. Further hydroxylation of chlorohydroquinone and catechol yielded hydroxyhydroquinone, which decomposed to carboxylic acids and carbonyl compounds. Total mineralization required a much longer illumination time than the disappearance of all aromatic and chlorinated compounds. Al-Ekabi et al. (1989) studied photocatalytic degradation of equimolar mixture of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,5-trichlorophenol using TiO$_2$ aqueous suspensions in an annular photoreactor. Under identical conditions, percentage degradation (53-55%) were
comparable for single-component 4-chlorophenol and in the multicomponent mixture. Langmuir-Hinshelwood kinetic model was found to be applicable for the kinetics of photodegradation of phenol and different para-substituted phenols (p-methoxyphenol, p-cresol, p-fluorophenol, p-chlorophenol, p-bromophenol, p-cyanophenol, and p-iodophenol etc.) under TiO$_2$/UV system (O’Shea et al., 1994).

In the TiO$_2$-catalysed photodegradation of 4-chlorophenol, two reactions compete as the first step: substitution to form hydroquinone and hydroxylation to give 4-chlorocatechol (Al-Ekabi and Serpone, 1991; Vinodgopal et al., 1994). The ratio of the two products depends upon the experimental setup and the reaction conditions (Stafford et al., 1994). Li et al. (1999) identified different reaction intermediates and end products generated in the photodegradation of 4-chlorophenol with the help of HPLC and GCMS. They found that one-third of the chlorophenol is converted to hydroquinone; the rest is hydroxylated to yield 4-chlorocatechol. They were able to analyse most of the cyclic and acyclic intermediates (produced both in the hydroquinone and 4-chlorocatechol pathway) which finally underwent complete mineralization leading to the generation of CO$_2$ and H$_2$O and Cl$^-$ ion.

Priya and Madras (2006) observed that photocatalytic degradation rates of both chlorophenol and nitrophenol decreased in the binary mixture compared to their degradation rates in single component system. The degradation of nitrophenol was observed to be inhibited more. Interaction between the parent compounds, interaction between the intermediates and competition among them for the active sites on the catalyst might be responsible for this inhibition. They synthesized nano-TiO$_2$ as the catalyst and used high pressure mercury vapour lamp (HPML) (125 W) as the source of UV radiation. A modified Langmuir-Hinshelwood kinetic model incorporating the effects of both competitive inhibition and interaction among the components of the mixture was developed.

The efficiency of a photocatalytic process is generally expressed in terms of quantum yield or quantum efficiency. The process was controlled by experimental conditions such as wavelength and incident intensities of radiation, type and concentrations of catalyst and reactants, pH, etc. (Satuf et al., 2007).

A vast number of publications are available on photocatalytic treatment of dye contaminated wastewater with TiO$_2$/UV system. Lachheb et al. (2002) carried out
photocatalytic degradation of Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue in TiO$_2$/UV aqueous suspensions. Degussa P-25 titanium dioxide was the photocatalyst and a high pressure mercury lamp (Philips HPK-125 W) was used as the source of UV-irradiation. They found that in addition to decolorization, complete oxidation of the dyes was possible with TiO$_2$/UV process. Carbon and sulphur in the dye molecules were completely mineralized into innocuous CO$_2$ and SO$_4^{2-}$-ions respectively. Nitrogen atoms (in −3 oxidation state) were converted to NH$_4^+$-cations, which in turn, were converted into NO$_3^-$ ions. The central –N=N– group in azo dyes was found to be converted to gaseous N$_2$.

The rate of photodegradation of dyes under TiO$_2$/ UV system is influenced by various factors like wavelength and intensity of UV radiation, initial dye concentration, catalyst load, crystallinity and phase composition of TiO$_2$, agitation speed, reaction temperature, recirculation flow rate, initial dissolved oxygen concentration, pH, addition of H$_2$O$_2$ etc. (Wu and Chern ,2006). Tayade et al. (2009) used ultraviolet light emitting diodes (UV-LED) and a simple photocatalytic reactor in dispersion medium to study the photocatalytic decomposition of methylene blue. The complete mineralization of the dye (3.12 × 10$^{-5}$ M) in 6 h with use of 5 UV-LED was confirmed by chemical oxygen demand analysis. The optimum catalyst loading and pH were reported to be 1.2 g/L and 8.84 respectively.

The industrial wastewaters usually contain some amount of aromatic solvents and trace amount of metal ions (Kyung et al., 2005) which have an inhibitory effect on photodegradation. This inhibitory effects of solvents on photodegradation are attributed to the lesser solvation of excited electrons in the organic solvents compared to the aqueous solutions (Epling et al., 2002). Lesser solvation of excited electrons increases the possibility of electron-hole recombination process, leading to decrease in photodegradation rates (Konstantinou et al., 2004; Anpo, 1989).

The interfacial charge-transfer processes, which play a key role in the photodegradation mechanism, are highly influenced by the surface characteristics of the TiO$_2$ particles (Aarthi and Madras, 2007). In presence of metal ions, surface of the TiO$_2$ catalyst gets modified due to the adsorption of these ions. Chen et al. (2002) studied the effects of transition metal ions on the TiO$_2$ assisted photodegradation in detail and observed that the degradation rate of Malachite Green dye decreased in presence of
Cu$^{2+}$ and Zn$^{2+}$ metal ions. This decrease was shown to be due to the suppression of OH$^-$ radicals due to trapping of the conduction band electrons by the adsorbed metal ions.

Aarthi and Madras (2007) studied the UV irradiated photocatalytic degradation of four Rhodamine dyes with different functional group namely, Rhodamine B (C$_{28}$H$_{31}$ClN$_2$O$_3$), Rhodamine 6G (C$_{28}$H$_{31}$ClN$_2$O$_3$), Rhodamine Blue (C$_{28}$H$_{32}$N$_2$O$_3$), and Rhodamine 6G perchlorate (C$_{28}$H$_{31}$ClN$_2$O$_7$) using two catalysts: commercial TiO$_2$ (Degussa P25) and combustion-synthesized TiO$_2$. They observed that the presence of organic solvents (like ethanol, acetonitrile) and metal ions (like Cu$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, and Al$^{3+}$) decreases the rate of photocatalytic degradation of Rhodamine B and they proposed a detailed Langmuir-Hinshelwood (LH) kinetic model to explain the photocatalytic degradation in the presence of metal ions.

Wu (2007) demonstrated that dye effluents in wastewater can be easily removed by titania nanorod thin films with high specific surface area. Using rhodamine B as the model dye, titania nanorod thin films were deposited directly on Ti substrates using hydrogen peroxide solutions under a low temperature of 80 °C.

Many investigations on photodegradation of different dyes using TiO$_2$/ UV process have been carried out to understand the fundamental processes involved and to assess the effects of various reaction parameters on photodegradation rates of different dyes. However, not all the works have been reviewed here to avoid repetition.

1.4.9. Photocatalytic degradation of wastewater using TiO$_2$/ visible light

Generally, pure TiO$_2$ is inactive under visible light irradiation as band gap energy of pure TiO$_2$ is 3.0-3.2 eV (which corresponds to the energy of UV and near UV region). This limits the practical application of TiO$_2$ as a photocatalyst. There are some reports of photocatalytic activity of pure TiO$_2$ under visible radiation. Surface complex formation on pure TiO$_2$ might be responsible for the photocatalytic transformation of colourless substrates (that are unable to absorb visible radiation by themselves) under visible radiation (Kim and Choi, 2005). For example, visible-light-induced degradation of H$_2$O$_2$ on TiO$_2$ is observed due to the formation of surface complexes of H$_2$O$_2$/TiO$_2$ that absorb visible light (Li et al., 2001).

A study on visible light induced transformation of 2,4,5-trichlorophenol on TiO$_2$ demonstrated formation of a charge-transfer complex (Agrios et al., 2003; Agrios et al.,
No mineralization was achieved; only coupling products were formed in this case. The study revealed that the charge-transfer complex formation was favoured on P25 TiO$_2$ because of the presence of mixed phases of anatase and rutile in P25 TiO$_2$.

Cho et al. (2004) were able to reduce CCl$_4$ and Cr(VI) by pure TiO$_2$ in aqueous solution of a nonionic surfactant having polyoxyethylene groups (Brij) under visible radiation. A broad absorption band was observed (320-500 nm) in the Brij/TiO$_2$ solution. A complex was formed between TiO$_2$ surface and the surfactant polyoxyethylene group that weakly absorbed visible light leading to the visible-light-induced electron transfer.

TiO$_2$-catalysed degradation and mineralization of 4-chlorophenol under visible radiation ($\lambda > 420$ nm) takes place due to surface complex formation (Kim and Choi, 2005). The substrate is attached to the catalyst surface through a phenolate linkage:

$$\text{TiO}_2^- + \text{HO-Ph} \rightarrow \text{Ti-O-Ph} + \text{H}_2\text{O}$$

This kind of surface complex formation enables visible light absorption through ligand-to-metal charge transfer (LMCT) between the substrate (ligand) and the Ti(IV) site on the catalyst surface (Wang et al., 2003; Tachikawa et al., 2004). The occurrence of LMCT was supported by the diffuse reflectance UV-Vis spectra and photocurrent measurements. Similar surface complex formation has been reported between ZnO catalyst and phenolic compounds such as phenol, 4-chlorophenol and 2,4-dichlorophenol resulting in visible photocatalytic degradation. The surface complex was characterized with several techniques like FTIR, DTG, DRUV-vis, photoelectron-chemical measurements, etc. (Li et al., 2010).

The most common example of TiO$_2$-mediated photocatalysis under visible radiation is the sensitized degradation of dyes, in which the dye molecule is excited by the visible radiation rather than TiO$_2$ photocatalyst. An electron is transferred from the singlet or triplet excited state of the dye molecule into the conduction band of TiO$_2$, as a result of which the dye molecule is converted to its cationic radical. The injected electron reacts with the O$_2$ adsorbed on the TiO$_2$ surface leading to the formation of superoxide radical anions (O$_2^-$) and other reactive oxygen radicals, such as 'OH and HO$_2$'. These oxidizing species undergo a series of reactions resulting in the photodegradation of the dyes into CO$_2$ and inorganic ions (Stylidi et al., 2004). Yang et al., (2005) studied the detail mechanism of photocatalytic degradation of cationic dyes (such as rhodamine B and
malachite green) and anionic dyes (such as sulforhodamine B and alizarin red) using TiO$_2$-film electrode under visible irradiation. Other research groups have also investigated the decolorization, degradation, and mineralization of various types of dyes in aerated TiO$_2$ dispersions under visible radiation (Vinodgopal et al., 1996; Wu et al., 1999, Lucarelli et al., 2000).

1.4.10. Photocatalytic degradation of wastewater using TiO$_2$/sunlight

Photocatalytic degradation of wastewater using solar energy is a cost effective process in comparison to the degradation processes using artificial UV light, as UV-irradiated processes consume electrical power. TiO$_2$ can absorb only a very small UV part (2-3%) of solar energy reaching the earth’s surface which is not sufficient for photodegradation of organic and inorganic contaminants. Nagaveni et al. (2004) demonstrated solar photocatalytic degradation of different dyes (methylene blue, remazol brill blue R and orange G) using nano TiO$_2$. The photocatalytic activity of nano TiO$_2$ was found to be much higher compared to Degussa P-25 TiO$_2$. The crystallinity, nano-size, large amount of surface hydroxyl groups and reduced band-gap energy of might have been responsible for the enhanced solar energy absorption (Nagaveni et al., 2004).

Efficient use of solar energy for photodegradation can be achieved by coupling of two semiconductors as it leads to more efficient charge separation, an increased lifetime of the charge carriers and an enhanced interfacial charge transfer to adsorbed substrates. A composite of ZnO and TiO$_2$ was reported to exhibit higher photocatalytic efficiency compared to either pure ZnO or pure TiO$_2$ (Wang et al., 2005). The efficiency of solar photodegradation can be further enhanced by using the ZnO-TiO$_2$ composite in combination with a visible-to-ultraviolet conversion luminescence agent (a substance that is capable of transforming visible light to UV light). Solar photocatalytic degradation of different dyes (Acid red B, methyl orange, Congo red, Rhodamine B, methylene blue and azo fuchsine) were carried out by using Er$^{3+}$: YalO$_3$ / ZnO-TiO$_2$ composite and enhanced photocatalytic degradation was observed in comparison to ZnO-TiO$_2$ as well as pure TiO$_2$ catalyst (Wang et al, 2010). Er$^{3+}$ ion hosted in fluoride and oxide crystal matrices can act as a visible-to-ultraviolet conversion luminescence
agent as it can emit in the UV and visible wavelength range depending on the excitation energy, dopant concentration and properties of the host crystal (Wang et al, 2010).

1.5. Modified photocatalysts

1.5.1. TiO$_2$ doped with cations and anions

To efficiently use TiO$_2$ photocatalyst under solar and visible light, the band-gap energy of TiO$_2$ has to be lowered which can be done by several modifications of TiO$_2$ like transition metal doping (Yamashita et al., 1999; Klosek and Raftery, 2001), surface modification with a transition metal halide complex (Zang et al., 1998; Lettmann et al., 2001). Doping of quantum-sized TiO$_2$ with Fe$^{3+}$, Mo$^{5+}$, Ru$^{3+}$, Os$^{3+}$, Re$^{5+}$, V$^{4+}$, and Rh$^{3+}$ significantly increases the photoreactivity while Co$^{3+}$ and Al$^{3+}$ doping decreases the photoreactivity (Choi et al., 1994). Doping of TiO$_2$ with platinum ions or [$\text{Pt}_3(\text{CO})_6$]$_{6^2}$ clusters enhances photocatalytic activity under visible light (Kowalska et al., 2008). Cation doping into the TiO$_2$ lattice causes thermal instability and the resultant metal centres can trap electrons and act as recombination centres for electron-hole pairs, leading to a considerable decrease in photocatalytic efficiency (Choi et al., 1994; Wang et al., 2000).

Doping or modification with anionic species such as carbon (Wu et al., 2007; Sakthivel et al., 2003), nitrogen (Sakthivel et al., 2004, Gole et al., 2004) sulphur (Umebayashi et al., 2002; Ohno et al., 2003) and fluorine (Yu et al., 2004) was reported to enhance photocatalytic activity. Sato et al. (2005) demonstrated visible light sensitization of TiO$_2$ photocatalyst by wet method N-doping. As metal ion doping process requires high temperatures (>500°C), particle size of TiO$_2$ increases due to sintering effect. Wet method N-doping of TiO$_2$ catalyst is done at temperature less than 500°C, so sintering effect is not significant. Photocatalytic activity of TiO$_2$ is favoured by small particle size; hence wet method N-doping of TiO$_2$ is more effective for visible light induced photoactivity. TiO$_2$ powders treated with low-temperature H$_2$ plasma show photocatalytic activity under visible radiation probably due to the formation of oxygen vacancies in the TiO$_2$ (Ihara et al., 2001).

Ohno et al. (2004) reported strong visible light absorption by S-doped TiO$_2$ photocatalyst (which was prepared by incorporation of S atoms as S$^{4+}$ cations into the
bulk phase of TiO$_2$). Visible light induced photocatalytic activity was demonstrated by degradation of methylene blue, 2-propanol in water and partial oxidation of adamantane.

Recently, more attention has been given to co-doping of TiO$_2$. Nitrogen and fluorine codoping of TiO$_2$ show better visible light absorption and photocatalytic activity than pure TiO$_2$ or TiO$_2$ singly doped with either dopant (Li et al., 2005). In N,F-codoped TiO$_2$, a complex interaction takes place between a p-type (N) and an n-type (F) dopant that generate a charge compensation through an internal charge transfer from the high lying Ti$^{3+}$ 3d to the low lying N states. This reduces the overall energy for the doping process and the amount of oxygen defects in the bulk leading to increased photostability and photocatalytic activity (Di Valentin et al., 2008). Li and Shang (2009) observed that self-organized nitrogen and fluorine co-doped TiO$_2$ nanotube arrays have enhanced visible light absorption capability and photodegradation efficiency on methylene blue under visible radiation. Different researchers have reported enhanced photoactivity of TiO$_2$ codoped with different elements such that Boron and Nitrogen codoped TiO$_2$ (Liu et al., 2008), C and S codoped TiO$_2$ (Sun et al., 2006), Silver and Indium codoped TiO$_2$ (Yang et al., 2008), Bismuth and Sulfur codoped TiO$_2$ (Wang et al., 2008), N and Fe codoped TiO$_2$ (Cong et al., 2007), Iodine and Platinum codoped TiO$_2$ (He et al., 2010).

Naik and Parida (2010) reported enhanced photodegradation of phenol with a mesoporous Fe$_x$Ti$_{1-x}$O$_2$-$y$N$_y$ nanophotocatalyst under direct sunlight. The synergistic effect of iron and nitrogen upon TiO$_2$ is responsible for the enhanced photoactivity. Codoping by N and Fe results in narrowing of band gap of TiO$_2$ as a result of which absorption band edge shifts to the visible region. The surface charge transfer process is facilitated by the presence of Fe. Visible light absorption by N-Ti-O and Ti-O-Fe-O environments as well as the effective inhibition of electron-hole recombination process is responsible for enhanced photoactivity (Naik and Parida, 2010). Yin et al. (2010) investigated the decomposition mechanism of pentachlorophenol by Ti-doped β-Bi$_2$O$_3$ under visible light ($\lambda > 420$ nm) and established (by identifying intermediate products and free radicals) that the decomposition took place through reduction.

**1.5.2. Supported catalysts**

To develop a practical heterogeneous photocatalytic treatment system, many operating parameters must be considered, such as type and geometry of photoreactor,
the best possible use of energy, and wavelengths of radiation. The most important part in the designing of a commercial treatment unit is the irradiation field in a scattering and absorbing heterogeneous medium (Legrini et al., 1993). The designing of a photoreactor is more complex compared to the conventional reactors because in addition to mass, momentum, and heat transfers, radiation transfer must also be considered (Li et al., 2010). Catalysts can be used either in suspended or immobilized form in liquid-phase photocatalysis. Suspended systems are observed to exhibit more efficiency than immobilized systems (Pozzo et al., 1997; Bideau et al., 1995). The majority of experiments, reported in the literature, have used TiO₂ particles suspended in aqueous medium. After treatment, the suspended catalyst must be separated from the bulk fluid phase. This separation and recovery of the used TiO₂ photocatalyst, which is carried out by using processes like filtration, ultracentrifugation, coagulation or flocculation, becomes sometimes difficult. Moreover, these steps bring complexity to the overall treatment process and increase the cost of the treatment process (Hoffmann et al., 1995). Moreover, it is not possible to achieve uniform incident light intensity on every catalyst particle because of simultaneous existence of absorption and scattering effects. This brings complexity to kinetic modelling in suspended systems.

In order to eliminate these problems, fixed bed reactor, in which semiconductor remains in immobilized form may be used. In typical fixed-bed photoreactors, the photocatalyst may be coated on the walls of the reactor or around the casing of the light source, or on a solid-supported matrix (Hoffmann et al., 1995). In fixed bed reactors, after photocatalytic treatment, recovery processes like filtration or centrifugation are not needed for separation and regeneration of catalyst. But efficiencies of these reactors are considerably less due to low surface area-to-volume ratio and simultaneous absorption and scattering of light by the reaction medium. When TiO₂ nanoparticles are immobilized on outer surface of the photoreactor, the rate of photocatalytic degradation depends upon the light intensity on the surface, the quantum efficiency of the catalyst, the adsorption properties of the reactants, and mass transfer from the bulk of the solution to the catalyst surface (Khataee et al., 2010).

An inert material is used as support of the catalyst in some fixed-bed systems. Metal fibers, fiber glass beads, glass fibre, steel mesh; steel plates, aluminium and many types of plastics and ceramics (such as alumina, silicon carbide, silica), quartz sand, activated
carbon, clays and zeolites are important among different materials investigated as supports (Kabra et al., 2004). A material will be suitable as a support if it has certain characteristics (Tasbihi et al., 2007) such as transparency to UV (or visible) radiation, strong surface chemical and physical bonding capability with the TiO$_2$ particles without inhibiting their photoactivity, good adsorption capability for the compounds to be degraded, high specific surface area, chemical inertness, etc. The support should be in a physical configuration that is favorable for the final liquid-solid phase separation and should allow a reactor design that favours the mass transfer processes. Moreover, the supported photocatalysts should be recyclable and reusable as this is an essential criterion for the cost effectiveness and practical application of a photocatalytic process. (Pozzo et al., 2000).

The photocatalytic oxidation of Rhodamine B, methylene blue, methyl orange, and salicylic acid was conducted with immobilized TiO$_2$ coated on sand in a flat-bed system (Matthews, 1991). Decrease in the catalytic activity on repeated use was reported only in case of photo-oxidation of methyl orange dye. Though TiO$_2$ dispersed in slurry reactor is considered to be more effective, enhanced photocatalytic degradation of trichloroethylene was reported using TiO$_2$ on three silica-based supports (Choi et al., 2000). Due to large surface area and uniform pore size distribution (that helps organic molecules to diffuse to the internal active sites), mesoporous materials can be used as supports. Immobilization of TiO$_2$ on mesoporous silica may increase the adsorption and inhibit agglomeration (Li et al., 2005; Yang et al., 2005). Wang et al. (2007) synthesised TiO$_2$/mesoporous SBA-15 composite through a novel ethyldiamine-assisted route which showed excellent photocatalytic activity for the removal of phenol in aqueous medium under both UV and visible radiation. Visible light activity may be attributed to partial substitution of oxygen atoms in TiO$_2$ by nitrogen atoms from ethylenediamine. The photocatalytic removal of Basic Blue 3 using TiO$_2$ nanoparticles supported on nonwoven paper was investigated in a flat-plate photoreactor (Khataee et al., 2010). Tasbihi et al. (2007) carried out photocatalytic degradation of phenol solution with TiO$_2$ supported on quartz sand, glass beads and silica gel in a batch reactor under UV radiation ($\lambda = 254$ nm). Degradation achieved with TiO$_2$ / quartz sand, TiO$_2$ /glass beads and TiO$_2$ /silica gel in 6 h reaction time was 90, 86 and 74 % respectively. Photocatalytic activity of TiO$_2$/glass bead catalyst was reported to increase after
regeneration while TiO$_2$/quartz sand and TiO$_2$/silica gel showed only a slight decrease in activity after four times of repeated use.

Different clays such as kaolinite, montmorillonite, rectorite etc. have been studied by different research groups as support for photocatalysts (Kaneko et al., 2001; Guo and Al-Dahhan, 2003; Albertazzi et al., 2005). Clays are nontoxic, easily extractable and inexpensive. In addition to immobilizing photocatalyst in its interlayer, clays can act as adsorbent due to their layered and porous structure, large surface area, and a high cation exchange capacity. Clays can adsorb different types of cations, anions and organic substances either on their external surfaces or within their interlaminar space by interaction or substitution (Miao et al., 2006). Enrichment of reactants by adsorption enhances photocatalytic degradation (Ooka et al., 2004). The nanosized TiO$_2$ particles which are located as pillars between the silicate layers of clays and large specific surface area of TiO$_2$ pillared clays might be responsible for enhanced photocatalytic activity (Ooka et al., 2004; Sun et al., 2006). Tang et al. (2006) reported photocatalytic decomposition of Rhodamine B dye using Ti-pillared bentonite. Zhang et al. (2008) demonstrated UV irradiated photocatalytic degradation of Acid red G dye with TiO$_2$-pillared montmorillonite that was prepared by hydrolyzing TiO$_2$ sol into the interlayers of montmorillonite clay at low temperatures. According to them, TiO$_2$ pillared montmorillonite synthesized at 70°C temperature showed highest photocatalytic activity due to synergetic effects of the adsorption ability of montmorillonite and the photocatalytic activity of TiO$_2$.

TiO$_2$ pillared clays can be synthesized by exchanging charge-compensating cations between the clay layers with larger inorganic hydroxyl cations (precursors). (Hutson et al., 1999; Binitha et al., 2006). Precursors of TiO$_2$ are positively charged sol particles of titanium hydrate, $[\text{TiO(OH)}_x]_{m}^{n+}$ and can be synthesized by sol-gel method (Ooka et al., 2004) or by hydrolysis of TiCl$_4$ (Long et al., 1999) or TiOSO$_4$ (Binitha et al., 2006). These precursors are 1-2 nm in size and can be readily exchanged with sodium ions present in the interlayer of clays, as a result of which intercalated structures are formed (Sterte, 1986; Yamanaka et al., 1987).

TiO$_2$ pillared clays are microporous solids having moderate porosity and most titanium dioxide in TiO$_2$ pillared clays are amorphous in nature (Ding et al., 1999). Crystallinity plays an important role in catalytic activity but the TiO$_2$ pillars are too
small to form a crystal phase. Moreover, pillar size or the pore structure of the pillared clays cannot be altered easily. These properties bring limitations to the applications of pillared clays (Yoneyama et al., 1989).

Zhu et al. (2002) reported superior photocatalytic activity of a mesoporous composite nanostructured TiO$_2$ (anatase) and silicate nanoparticles for degradation of Rhodamine 6G dye in aqueous solution. The composite nanostructures were synthesized from Laponite clay (a synthetic layered smectite clay) and a sol of titanium hydrate in the presence of poly(ethylene oxide) (PEO) surfactant.

Zeolites are used as supports in semiconductor photocatalysis because of their large surface areas, uniform pore size and suitable channel size. Zeolites are transparent to UV-visible radiation (of wavelength $>$240 nm), photochemically stable and chemically and thermally inert. Moreover, they can act as adsorbent for organic compounds and zeolite framework can actively take part in electron transfer processes. There are reports of enhanced photocatalytic activity of TiO$_2$ supported on different zeolites like HZSM-5 (Durgakumari et al., 2002), NaY and HY zeolite (Tayade et al., 2007), silver metal ion exchanged NaY zeolite (Tayade et al., 2008), MCM41, Zeolite X, and Zeolite Y (Xu and Langford, 1997), zeolite-Y, ZSM-5, and MCM-41 (Senthilkumar et al., 2010), etc.