Chapter-I

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1.1 INTRODUCTION

Our environment is composed of atmosphere, earth, water and space. Under normal circumstances, it remains clean and therefore, enjoyable. However, with increasing world population and with limited natural resources, the composition and complex nature of our environment has changed. Our world is beautiful, but the increasing use and improper disposal of the effluents from various industries is creating pollution in the environment. Human activities like rapidly growing industrialization, new constructions, and increase in transportation etc. lead to the generation of objectionable materials into the environment, thus making it polluted.

There are various types of pollution e.g., air pollution, water pollution, soil pollution and noise pollution. Out of all these, water pollution is one of the most dangerous for mankind, aquatic living creatures and whole environment. Water pollution occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. In almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities. Water pollution occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds.

The scientific study of the chemical and biochemical phenomena that occur in natural places is called “environmental chemistry”. It is the study of the sources, reactions, transport, effect and fate of chemical species in the air, water and soil and the effect of human activities upon these. Colored solutions containing dyes from industrial effluents may cause harmful effects on human being, animals and plants, due to photosensitization and photodynamic damage.

The effluents from dyeing, textile and printing industries pollute the water bodies. Dye effluents originating from dyes production and application industries pose a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature. This situation if not controlled timely would become malignant problem for the survival of mankind on this
planet. In world, life is not possible without water. In general, water accounts
almost 70 to 90 % of the weight of living organisms. One cannot imagine life
without clean water. No doubt, there is no raw material in the world which is
more than water. Thus, the quality of this valuable resource will directly
influence the normal life of human being.

Many chemicals undergo reactive decay or change themselves
chemically especially over long periods of time in ground water reservoirs. A
noteworthy class of such chemicals is the chlorinated hydrocarbons such
as trichloroethylene (used in industrial metal degreasing and electronics
manufacturing) and tetrachloro ethylene used in the dry cleaning industry.
Both of these chemicals, which are carcinogens themselves, undergo partial
decomposition reactions, leading to new hazardous chemicals (including
dichloro ethylene and vinyl chloride). Ground water pollution is much more
difficult to abate than surface pollution because ground water can move great
distances through unseen aquifers.

Viessman and Hammer\(^1\) reported that recycling of wastewater is
associated with the presence of suspended solids, health-threat coliforms and
soluble organic compounds and is quite expensive to treat wastewater. Gaya
and Abdullah\(^2\) studied about the conventional water treatment methods such
as sedimentation, filtration, and chemical and membrane technologies which
involve high operating costs and could generate toxic secondary pollutants
into the ecosystem. Neamtu \textit{et al.}\(^3\) reported about the physico-chemical
methods such as coagulation/flocculation, activated carbon adsorption and
reverse osmosis techniques have been developed in order to remove the
color.

Chemical oxidation processes is an alternative technology that can be
successfully applied for the degradation of broad spectrum of organic
compounds.\(^4,5\) As a result, the use of alternative treatment technologies,
aiming to mineralize or transform larger refractory molecules into small
molecules which could be further biodegraded, is a matter of great concern.
Among these, “Advanced Oxidation Processes (AOPs)” are the innovative
water treatment technologies. The rationales of these AOPs are based on the *in situ* generation of highly reactive transitory species (i.e. \( \text{H}_2\text{O}_2 \), \( ^\cdot \text{OH} \) and \( \text{O}_3 \)) for mineralization of refractory organic compounds, water pathogens and disinfection by-products.\(^6,7\)

In recent days the use of photocatalysis as an important AOP for the decontamination of wastewater from industries has attracted the attention of chemists all over the world. An important advantage of photocatalytic process is that these may be carried out at low or ambient temperature and usually leads to the complete mineralization of pollutants.\(^8\) The photocatalytic method of effluent treatment involves the exposure of polluted water to light in the presence of photocatalyst. The photocatalytic process not only enhances the rate of degradation, but also provides an oxidizing as well as reducing environment to the substances simultaneously. The photocatalytic technique has proved to be faster, economical and environment friendly than the traditional technique of treating industrial effluents with adsorbents. Now-a-days photocatalytic methods for wastewater treatment seem to be the most promising and ecofriendly process.

It is the prime objective of environmental education to make people aware about the importance of protection and conservation of our environment, because indiscriminate release of various pollutants in the environment will lead to serious health hazards in the coming generations.

### 1.2 METHODS OF WASTEWATER TREATMENT

Water treatment is the process of removing undesirable chemicals, materials and biological contaminants from raw water. Drinking water quality is defined in terms of physical, chemical, biological and radiological parameters, and limiting values are set either as national regulations within countries or as recommendations from international organizations especially as of the WHO.\(^9\) Dye waste represent one of the most problematic groups of pollutants because they can be easily identified by the human eyes and are not easily biodegradable. Treatment of dye waste includes biological treatment, catalytic oxidation, membrane filtration, sorption process, ion-
exchange and coagulation-flocculation. A brief discussion about these processes is given below.

1.2.1 Biological Treatment

Biological treatment systems use microbes which consume, and thereby destroy, organic compounds as a food source. The microbes use the organic compounds as both a source of carbon and as a source of energy. Chagas and Durrant reported the decolorization of azo dyes by *Phanerochaete chrysosporium* and *Pleurotus sajor-caju* and these microorganisms cleave the azo bond(s) of the respective azo dyes and colorless, possibly toxic, aromatic amines are formed. Martins et al. reported the biodegradation of azo dyes by the yeast *Candida zeylanoides* in batch aerated cultures.

Ramalho et al. reported the improved conditions for the aerobic reductive decolorization of azo dyes by *Candida zeylanoides*. Yang et al. reported the decolorization of an azo dye, reactive black 5 using manganese-dependent peroxidase (MnP) and *Debaryomyces polymorphus*. Ramalho et al. studied the characterization of azo reduction activity in a novel ascomycete yeast strain. Lucas et al. reported the biodegradation of the diazo dye reactive black 5 by *Candida oleophila*.

1.2.2 Membrane Filtration

The use of membranes for the water treatment has increased tremendously in the recent past. There are many types of membranes used for water treatment such as: reverse osmosis (RO), nanofiltration (NF), dialysis and electro-dialysis (ED), ultra-filtration (UF) and microfiltration (MF) membranes. Reverse osmosis is primarily used to remove salts from salty water, although it is also capable for very high rejection of synthetic organic compound. Ultra-filtration and micro-filtration are used to remove turbidity, pathogens and particles from fresh water.

Ren et al. reported the use of novel aromatic polyamide asymmetric nanofiltration membrane for the treatment of dye aqueous solutions. Han et
al.\textsuperscript{19} reported the use of copoly (phthalazinone biphenyl ether sulfone) (PPBES) ultrafiltration (UF) membrane in dye wastewater treatment at high temperature. It showed 100% rejection for congo red, sulfur black B and gentian violet.

Some benefits of water treatment through nanofiltration membrane are as follows.

- Lower operating costs
- Lower energy cost
- Lower discharge of wastewater than reverse osmosis
- Reduction of total dissolved solid (TDS) contents in slightly brackish water
- Reduction of pesticides and VOCs (organic chemicals)
- Reduction of heavy metals
- Reduction of nitrates and sulfates
- Reduction in turbidity, color and tannins
- Hard water softening

1.2.3 Sorption Process

Adsorption of a substance involves its accumulation at the interface between two phases, between liquid and solid phase or between gas and solid phase. The molecule that accumulates or adsorbs at the interface is called an adsorbate, and the solid on which adsorption occurs is called adsorbent. Adsorbents used in water treatment include activated carbon, ion exchange resins, adsorbent resins, metal oxides, hydroxides and carbonates, activated alumina, clays, and other solids that are suspended in or are in contact with water. Organic contaminants, unwanted coloring, taste and odor causing compounds can be removed through adsorption.\textsuperscript{20}
Wong et al.\textsuperscript{21} studied the ability of chitosan to act as an adsorbent produced from waste seafood shells for the removal of five acid dyes, namely, acid green 25, acid orange 10, acid orange 12, acid red 18, and acid red 7. Rosa et al.\textsuperscript{22} reported the utility of cross-linked quaternary chitosan as adsorbent for the removal of reactive orange 16 from aqueous solutions. Jalil et al.\textsuperscript{23} reported the use of batch adsorption technique for the removal of methyl orange onto calcined lapindo volcanic mud.

Nanoadsorbants show high rate of adsorption of organic compounds as compared to granular or powdered activated carbon. This is due to their large surface area and therefore, nanoadsorbants have great potential for more efficient, faster and novel decontamination processes aimed at removal of organic and inorganic pollutants like heavy metals and micropollutants.

### 1.2.4 Ion Exchange

Ion exchanger removes the unwanted ions from raw water by ion exchange process wherein ions are exchange in its frame. Natural zeolites (i.e., crystalline alumino-silicates) were the first ion exchangers used to soften water. The choice of ion exchange is mostly determined by-

- The background water quality including TDS level, competing ions, alkalinity and contaminant concentration, and

- The resin affinity for the contaminant ion in comparison with the competing ions.

Ion exchange resin consists of a cross linked polymer matrix containing covalent bonding charged functional groups. In order to complete the exchange reaction, a packed bed of ion-exchange resin beads is used. Source water is continuously passed through the bed in a down-flow or up-flow mode until the adsorbent is exhausted, as evidenced by the appearance. Resins beds containing chloride-form of anion exchange resins can be used for nitrate, arsenate, chromate, selenate, dissolved organic carbon (DOC) and uranium removal.\textsuperscript{24}
Slokar and Marechal\textsuperscript{25} studied the use of ion exchange process for the treatment of dye-containing effluents, mainly because ion exchangers cannot accommodate a wide range of dyes. Macoveanu \textit{et al.}\textsuperscript{26} reported the integration of the membrane processes with ion exchange to improve the efficiency of natural organic matter removal and to reduce the intensity of membrane blocking. Robinson \textit{et al.}\textsuperscript{27} studied that the main advantages of ion exchange are removal of soluble dyes, no loss of adsorbent at regeneration, and reclamation of solvent after use. The important disadvantages of this process is the cost, since organic solvents are expensive, and ion exchange treatment is not efficient for disperse dyes.

1.2.5 Coagulation-Flocculation

Coagulation-Flocculation is the most widely applied process for the production of potable water as well as for treating wastewater.\textsuperscript{28, 29} The process of destroying the stabilizing forces and causing aggregation of colloidal particles is called coagulation.\textsuperscript{30} The commonly used coagulants divided into two general categories are metal coagulants and polymerized metal coagulants based on Al and Fe.\textsuperscript{31} Tang\textsuperscript{32} reported that coagulation is traditionally done using aluminum (Al) or iron (Fe) salts. Inorganic polymer flocculants are also currently in use. The chemical coagulation has been successfully used for treatment of textile effluents.\textsuperscript{33,34}

Martin \textit{et al.}\textsuperscript{35} reported the feasibility of new tannin-based coagulant-flocculant (tanfloc) in surface water and textile wastewater treatment at a pilot plant level. Wang \textit{et al.}\textsuperscript{36} investigated the novel applications of red mud, a byproduct of bauxite processing of bayer process in gas cleaning and wastewater treatment. Zidane \textit{et al.}\textsuperscript{37} reported the use of red mud as a coagulant, catalyst and adsorbent for the decolourization of dyes in effluents. The red mud as a mineral coagulant was produced by electrocoagulation.

1.2.6 Catalytic Oxidation

Khataee \textit{et al.}\textsuperscript{38} reported the use of TiO\textsubscript{2} for the degradation of basic blue 3 under UV light. Damodar \textit{et al.}\textsuperscript{39} reported the use of TiO\textsubscript{2} entrapped
PVDF (PVDF/TiO₂) membrane for the degradation of reactive black 5 under UV light. Lin and Lee⁴⁰ investigated the use of TiO₂/Ag photocatalysis system for decolorizing procion red MX-5B. Ag carrier from the TiO₂/Ag catalyst has the oxidizing ability to degrade MX-5B color even in the absence of UV-A, however TiO₂ alone was ineffective.

Wu et al.⁴¹ reported that silver nanoparticles attached on the surface of amidoxime fibers for the degradation of methyl orange in the presence of sunlight. Yu and Shi⁴² investigated the catalytic oxidation of simulated wastewater containing acid chrome blue K using chlorine dioxide as oxidant. Valero et al.⁴³ investigated the use of photovoltaic (PV) cells for the degradation of remazol RB 133. Maljæi et al.⁴⁴ reported the use of an indirect electrochemical oxidation method for the decolorization of reactive yellow 3.

Zhang et al.⁴⁵ studied the degradation of acid orange by ultrasound enhanced heterogeneous Fenton-like process. Hsieh et al.⁴⁶ studied the degradation of dye wastewater by use of an ultrasound/Fenton/nanoscale iron oxidation process, the Taguchi statistical method was employed to find the optimum experimental conditions. The percent removal of dye under optimal conditions was 99.91%.

Liu et al.⁴⁷ studied the degradation of methyl orange by using microwave-assisted catalysis of H₂O₂ with chromium residue. Chromium ion residue and H₂O₂ can form Fenton-like reagent and microwave heating can enhance the rate of degradation and utilization efficiency of H₂O₂ in the catalysis process. Cristovao et al.⁴⁸ reported that the percentage removal of various reactive dyestuffs was relatively high especially reactive black 5 (above 86%) by using commercial laccase, which is a catalytic enzyme. Xu et al.⁴⁹ reported that the dye wastewater degradation efficiency was increased by using a flowing aqueous film photoelectrocatalytic (PEC) reactor.

1.3 ADVANCED OXIDATION PROCESSES

Advanced Oxidation Processes (AOPs) are promising alternatives for decontamination of waste containing dissolved recalcitrant organic
substances, which would not be efficiently removed by conventional methods. Advanced oxidation processes (AOP) are technologies characterized mainly by the generation of hydroxyl radicals, which are highly reactive and non-selective intermediates used to degrade toxic organic compounds present in a medium (such as wastewater and soil).

Hydroxyl radicals (‘OH) have highest oxidation potential (oxidation potential, $E_0$: 2.8 eV versus normal hydrogen electrode (NHE)) after fluorine radical). Fluorine, the strongest oxidant (oxidation potential, $E_0$: 3.06 eV) cannot be used for wastewater treatment because of its high toxicity. AOPs involve the two stages of oxidation-

- The formation of strong oxidants (e.g., hydroxyl radicals) and
- The reaction of these oxidants with organic contaminants in water.

1.3.1 Mechanism of Advanced Oxidation Processes

AOPs are promising methods for the remediation of wastewaters containing recalcitrant organic compounds such as pesticides, surfactants, coloring matters, pharmaceuticals, phenolic wastes and endocrine disrupting chemicals. The main mechanism of AOPs involves the generation of highly reactive free radicals. Hydroxyl radicals (‘OH) are effective in destroying organic contaminants because they are reactive electrophiles (electron preferring) that react rapidly and non-selectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.8 eV and exhibit faster rates of oxidation reactions comparing to conventional oxidants such as $\text{H}_2\text{O}_2$ or $\text{KMnO}_4$.

$$R + \cdot \text{OH} \rightarrow R\cdot \text{OH} \rightarrow \text{Products} \quad \ldots(1.1)$$

$$R + \cdot \text{OH} \rightarrow R' + \text{H}_2\text{O} \quad \ldots(1.2)$$

$$R^n + \cdot \text{OH} \rightarrow R^{n-1} + \cdot \text{OH} \quad \ldots(1.3)$$

In the above reactions, $R$ is used to describe the reacting organic compound.
1.3.2 Types of Advanced Oxidation Processes

Advanced oxidation processes are technologies based on the generation of highly reactive species, the hydroxyl radicals, used in oxidative degradation for organic compounds dissolved or dispersed in aquatic medium. The reason for the use of AOPs is due to the inability of conventional processes to treat highly contaminated toxic water. Several advanced oxidation methods are available for generating •OH radicals. These include both non-photochemical and photochemical methods:

1.3.2.1 Non-photochemical oxidation processes

Non-photochemical oxidation processes can be classified as -

a) Ozonation at elevated pH

b) Ozone/Hydrogen Peroxide (Peroxone) and Ozone/ Catalyst

c) Fenton’s Process

d) Electrochemical Oxidation

e) Supercritical water oxidation

f) Cavitaion

g) Electrical discharge-based non-thermal plasma

h) Gamma-rays

i) X-ray and

j) Electron beam.

Ozonation, ozone/hydrogen peroxide or ozone/catalyst and Fenton process are widely applied and examined processes for the treatment of textile effluent. Therefore, a brief description of these processes is given below.
(a) Ozonation at elevated pH

As the pH rises, the decomposition rate of ozone in water increases. For example, at pH 10, the half-life of ozone in water can be less than 1 min. Oxidation of organic species may occur due to a combination of reactions with molecular ozone and reactions with 'OH radicals. The reaction between hydroxide ions and ozone leads to the formation of superoxide anion radical $O_2^{-}$ and hydroperoxy radical $HO_2^\cdot$. By the reaction between ozone and the superoxide anion radical the ozonide anion radical $O_3^{-}$ is formed, which decomposes immediately giving 'OH radical. Summarizing, three ozone molecules produce two 'OH radicals in water.^[51]

$$3O_3 + H_2O \rightarrow 2'OH + 4O_2 \quad \text{...(1.4)}$$

Bicarbonate and carbonate play an important role as scavengers of 'OH radicals in natural systems. The products of a reaction between 'OH radical and carbonate or bicarbonate ions are passive carbonate or bicarbonate radicals, which do not interact further with ozone or organic compounds. Tert-butyl alcohol also suppresses the chain reaction, if present.

(b) Ozone/hydrogen peroxide (O₃/H₂O₂, Peroxone) and Ozone/Catalyst

Peroxone is an Advanced Oxidation Process (AOP) used to treat soil and groundwater contaminated with volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), polynuclear aromatic hydrocarbon (PAH), petroleum hydrocarbons, metals, and materials used in the manufacture of explosives. The Peroxone process is based on the use of ozone in conjunction with hydrogen peroxide to produce highly energetic species called hydroxyl radicals. These radicals react with and oxidize most organic contaminants in solution.

Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of 'OH radicals.^[52]

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad \text{...(1.5)}$$
\[ \text{HO}_2^- + \text{O}_3 \rightarrow \text{HO}_2^+ + \text{O}_3^{--} \] ...(1.6)

The reaction continues along the indirect pathway described above and \(^{1}\text{OH}\) radicals are produced. The combination of different reaction steps shows that two ozone molecules produce two \(^{1}\text{HO}\) radicals:

\[ 2\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2^{2}\text{OH} + 3\text{O}_2 \] ...(1.7)

Paillard et al.\(^{53}\) studied the elimination of atrazine in filtered Seine river water using combination of ozone and hydrogen peroxide. Results showed better degradation of the pesticide in water treated with ozone–hydrogen peroxide combination as compared to ozone alone. The inhibitory performance of \(\text{H}_2\text{O}_2/\text{O}_3\) process on microbial growth depended on the \(\text{H}_2\text{O}_2\) to \(\text{O}_3\) mass ratio. This ratio was ranged from 0.3 to 0.6 for different type of dyes.\(^{54}\)

Another opportunity to accelerate ozonation reactions is to use heterogeneous or homogeneous catalysts. Several metal oxides and metal ions (\(\text{Fe}_2\text{O}_3\), \(\text{Al}_2\text{O}_3\)-Me, \(\text{MnO}_2\), \(\text{Ru/Fe}_2\text{O}_3\), \(\text{TiO}_2\)-Me, \(\text{Fe}^{2+}\), \(\text{Fe}^{3+}\), \(\text{Mn}^{2+}\) etc.) have been studied and sometimes a significant acceleration in the decomposition of the target compounds has been achieved, although the reaction mechanism in most cases remained unclear.

Leitner et al.\(^{55}\) reported the catalytic ozonation of succinic acid, which is barely oxidized by ozone. Legube et al.\(^{56}\) studied the use of \(\text{Al}_2\text{O}_3\), \(\text{TiO}_2\) and clay as the support for metal catalysts in the catalytic ozonation process. Kaptijn\(^{57}\) studied the eco-clear process – oxidation of biorefractory organics in the ozonation column filled with the granulated activated carbon systems (GAC) bed by the radicals such as \(\text{O}_2^{--}\) and \(\text{O}_3^{--}\) (not by \(^{1}\text{OH}\) radicals) formed on the surface of GAC.

(c) Fenton’s Process

The Fenton reagent, a mixture of hydrogen peroxide and iron(II)salt, was discovered by Henry J. H. Fenton. He described the oxidation power of hydrogen peroxide on certain organic molecules in which \(^{1}\text{OH}\) radicals are
produced from hydrogen peroxide under the addition of Fe (II) as a catalyst. This system is considered as the most promising treatment among AOPs for remediation of highly contaminated waters.\textsuperscript{58} The mechanism of the Fenton process is reported below.\textsuperscript{59, 60}

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \cdot \text{OH} \quad \text{... (1.8)}
\]

\[
\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \cdot \text{OH} \quad \text{... (1.9)}
\]

\[
\cdot \text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^* \quad \text{... (1.10)}
\]

\[
\text{R}^* + \text{Fe}^{3+} \rightarrow \text{R}^+ + \text{Fe}^{2+} \quad \text{... (1.11)}
\]

Fenton process is cost-effective, easy to apply and effective for the degradation of a wide range of organic compounds. One of the advantages of Fenton’s reagent is that no energy input is necessary to activate hydrogen peroxide. Therefore, this method offers a cheap source of hydroxyl radicals, by using easy-to-handle reagents.\textsuperscript{61}

Furthermore, Fenton oxidation commonly requires a relatively short reaction time compared with other AOPs. Thus, Fenton’s reagent is frequently used when a high reduction of COD is required.\textsuperscript{62} Electro-Fenton methods include electrochemical reactions for the generation of the reagents used for the Fenton reaction. The generated reagents depend on solution conditions, cell potential and nature of electrodes.\textsuperscript{63} Ferrous ions may be produced by oxidative dissolution of anodes such as iron metal or by reduction of ferric ions at an inert cathode such as platinum.\textsuperscript{64} Moreover, H$_2$O$_2$ may be produced by oxygen reduction at the cathode.\textsuperscript{65}

However, the major drawback of the Fenton reaction is the production of iron sludge waste, which paved the way for the development of the photo-Fenton process, that uses UV or solar light for the reduction of Fe(III) oxalate back to Fe(II) oxalate resulting in a drastic reduction of the sludge waste.\textsuperscript{66}
1.3.2.2. Photochemical oxidation processes

Conventional methods of using ozone or hydrogen peroxide for the oxidation of organic compounds do not completely oxidize organics to CO₂ and H₂O in many cases. In some reactions, the intermediate oxidation products remaining in the solution may be as toxic as or even more toxic than the initial compounds. Completion of oxidation reactions, as well as oxidative destruction of compounds immune to ozone or H₂O₂ oxidation, can be achieved by supplementing the reaction with UV/visible radiations.

(a) Vacuum UV (VUV) photolysis

The vacuum ultraviolet range is absorbed by almost all substances including water and air. The absorption of a VUV photon causes one or more bond to break. For example, water is dissociated according to the following reactions.

\[ \text{H}_2\text{O} + \text{hv} (<190\text{ nm}) \rightarrow \text{H}^+ + \cdot\text{OH} \quad \ldots(1.12) \]

\[ \text{H}_2\text{O} + \text{hv} (<190\text{ nm}) \rightarrow \text{H}^+ + \text{e}^- + \cdot\text{OH} \quad \ldots(1.13) \]

Photochemistry in the vacuum ultraviolet spectral domain (approx. 140–200 nm) is of high applicatory interest, e.g.

- In microelectronics, where materials with surface structures of high spatial resolution provide a basis for the fast development of high computational and electronic and optical storage capacities or

- In environmental techniques, in particular for the production of ultra-pure water and for the oxidative treatment of waste gas and water.

VUV-photolysis can be achieved by the use of either a monochromatic (Xe-eximer Xe₂*) or polychromatic (mercury) radiation sources. These light sources have some limitations such as high price, wave length variations etc. Due to these reasons, applications of VUV photolysis are too limited.
(b) **Ozone/UV radiation (O$_3$/UV)**

Wagler and Malley$^{69}$ reported that due to the relatively high molar extinction coefficient of ozone, UV radiations at 254 nm wavelength can be applied to ozonated water to form highly reactive hydroxyl radicals. The use of UV irradiation to produce hydroxyl radicals with ozone occurs by the following reaction sequence.

$$O_3 + \text{hv} \rightarrow O_2 + O \left(^1\text{D}\right) \quad \ldots (1.14)$$

$$O \left(^1\text{D}\right) + H_2O \rightarrow H_2O_2 \rightarrow 2'\text{OH} \quad \ldots (1.15)$$

The photolysis of ozone generates hydrogen peroxide and, thus, O$_3$/UV involves all of the organic destruction mechanisms present in H$_2$O$_2$/O$_3$ and H$_2$O$_2$/UV AOPs. Chen *et al.*$^{70}$ reported that these mechanisms include direct reaction with ozone, direct photolysis by UV irradiation, or reaction with hydroxyl radicals.

Common low pressure mercury lamps generate over 80% of their UV energy at this wavelength. Photolysis of ozone therefore, appears only to be an expensive way to make hydrogen peroxide that is subsequently photolyzed to $'\text{OH}$ radicals. Although photochemical cleavage of H$_2$O$_2$ is conceptionally the simplest method for the production of hydroxyl radicals, the exceptionally low molecular absorptivity of H$_2$O$_2$ at 254 nm limits the $'\text{OH}$ yield in the solution. The absorptivity of H$_2$O$_2$ can be increased by using UV lamps with output at lower wavelength.

Crawford$^{71}$ reported that quartz sleeve cleaning devices are common in UV oxidation technologies, and the costs are generally included in the total costs of the system. UV lamp and sleeve failures can potentially contaminate treated water with mercury, although all lamp failures to date have resulted in aqueous Hg concentrations below drinking water standards. If water solutions contain organic compounds strongly absorbing UV light, then UV radiation usually does not give any additional effect to ozone because of the screening of ozone from the UV by optically active compounds such as phenol, 5-methylresorcinol, xylenols etc.$^{72}$ Peyton *et al.*$^{73}$ demonstrated the efficiency of
O₃/UV system for C₂Cl₄ elimination from water compared to ozonation and photolysis only.

(c) Hydrogen peroxide/UV radiation (H₂O₂/UV)

This advanced oxidation process involves the formation of hydroxyl radicals generated by the photolysis of H₂O₂ and the corresponding propagation reactions. The photolysis of hydrogen peroxide occurs when UV radiation is applied. During this process, ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and to generate the hydroxyl radicals. The reactions describing UVI H₂O₂ process are presented below.⁷⁴

\[
\begin{align*}
H₂O₂ + hv &\rightarrow 2 \cdot OH \quad \cdots (1.16) \\
H₂O₂ + \cdot OH &\rightarrow HO₂^- + H₂O \quad \cdots (1.17) \\
H₂O₂ + HO₂^- &\rightarrow \cdot OH + H₂O + O₂ \quad \cdots (1.18) \\
2 \cdot OH &\rightarrow H₂O₂ \quad \cdots (1.19) \\
2 \cdot HO₂^- &\rightarrow H₂O₂ + O₂ \quad \cdots (1.20) \\
\cdot OH + \cdot HO₂^- &\rightarrow H₂O + O₂ \quad \cdots (1.21)
\end{align*}
\]

In the above mentioned equations, Eq. 1.16 is the rate limiting reaction because the rates of the other reactions are much higher than that of Eq. 1.16. This technique requires a relatively high dose of H₂O₂ and/or a much longer UV-exposure time. The rate of photolysis of hydrogen peroxide has been found to be pH dependent and increases when more alkaline conditions are used, which decomposes more target compound because, at 254 nm, peroxide anions HO₂⁻ may form HO₂· (hydroperoxyl radicals) (Eq. 1.17), which display a higher molar absorptivity than hydrogen peroxide, 240 M⁻¹ cm⁻¹. The molar absorptivity of hydrogen peroxide at 254 nm is low, about 20 M⁻¹ cm⁻¹ and \·OH radicals are formed per incident photon absorbed.

Trapido et al.⁷⁵ reported the use of H₂O₂/UV process for the destruction of chlorophenols and other chlorinated compounds. Bischof et al.⁷⁶ studied the degradation of atrazine, desethylatrazine and simazine to carbon dioxide
within reasonable irradiation time in the presence of hydrogen peroxide. Sundström et al.\textsuperscript{77} investigated the use of H\textsubscript{2}O\textsubscript{2}/UV process for water disinfection purposes. The advantages of using the H\textsubscript{2}O\textsubscript{2}/UV process can be attributed to the fact that the reagent (H\textsubscript{2}O\textsubscript{2}) is totally soluble in water, there is no mass transfer limitation, it is an effective source of \textsuperscript{1}OH, and there is no need for a separation process after treatment.\textsuperscript{78}

Stepnowski et al.\textsuperscript{79} reported the use of H\textsubscript{2}O\textsubscript{2} in the presence and in the absence of UV radiation, in degrading an oil refinery wastewater pretreated with flotation and coagulation, analyzing total petroleum hydrocarbons (TPH), dichloromethane (DCM), 1, 2-dichloroethane (DCE) and methyl tert-butyl ether (MTBE). The application of the H\textsubscript{2}O\textsubscript{2}/UV process to purify oily wastewater from a lubricant producing unit belonging to an oil company was studied by Philippopoulos and Poulopoulos.\textsuperscript{80}

(d) Ozone/hydrogen peroxide/UV radiation (O\textsubscript{3}/ H\textsubscript{2}O\textsubscript{2}/UV)

The addition of H\textsubscript{2}O\textsubscript{2} to the O\textsubscript{3}/UV process accelerates the decomposition of ozone, which results in an increased rate of \textsuperscript{1}OH generation. In processes involving pollutants that are weak absorbers of UV radiation, it is more cost effective to add hydrogen peroxide externally at a reduced UV flux. If direct photolysis of pollutants is not a major factor, O\textsubscript{3}/ H\textsubscript{2}O\textsubscript{2} should be considered as an alternative to photooxidation processes.

\textbf{Table 1. Comparative operating costs of some AOPs}

<table>
<thead>
<tr>
<th>Process</th>
<th>Cost of oxidant</th>
<th>Cost of UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{3}/UV</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>O\textsubscript{3}/ H\textsubscript{2}O\textsubscript{2}</td>
<td>High</td>
<td>Zero</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}/UV</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Photocatalytic oxidation</td>
<td>Very low</td>
<td>Medium to high</td>
</tr>
</tbody>
</table>
(e) **Photo-Fenton Process**

Fenton’s reagent is a solution of hydrogen peroxide and ferrous ions and was discovered by the chemical engineer Henry John Horstman Fenton (1894).\(^1\) He reported that this solution in acid medium had high oxidizing power. Neyens and Baeyens\(^2\) reported the use of Fenton’s reagent in oxidation processes to destroy toxic organic compounds.

Fenton’s reagent is able to destroy toxic compounds in wastewater such as phenols and herbicides. Production of \(^\cdot\)OH radicals by Fenton reagent occurs by addition of \(\text{H}_2\text{O}_2\) to \(\text{Fe}^{2+}\) salts.

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

\(\text{(1.22)}\)

This is a very simple way of producing \(\cdot\)OH radicals neither special reactants nor special apparatus being required. This reactant is an attractive oxidative system for wastewater treatment due to the fact that iron is very abundant and non-toxic element and hydrogen peroxide is easy to handle and environmentally safe. The oxidation using Fenton’s reagent has proven a promising and attractive treatment method for the effective decolourization and degradation of dyes.\(^3\) The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants.\(^4\)

Malik and Saha\(^5\) reported the addition of UV to Fenton’s process in dye decolorization due to the direct formation of \(\cdot\)OH radicals. The rate of organic pollutant degradation could be increased by irradiation of Fenton with UV light (photo-Fenton process). UV light leads to recycling of ferrous catalyst by reduction of \(\text{Fe}^{3+}\). In this way, the concentration of \(\text{Fe}^{2+}\) is increased and the overall reaction is accelerated. Sun and Pignatello\(^6\) reported that a number of herbicides and pesticides can be completely mineralized by the \(\text{Fe}^{(III)}/\text{H}_2\text{O}_2\) process, and the mineralization of chlorophenol by the photo-Fenton process was investigated by Ruppert *et al.*\(^7\)
1.4 TITANIUM DIOXIDE AS A PHOTOCATALYST

A good photocatalyst should be photoactive, able to utilize visible and/or near UV light, biologically and chemically inert, photostable, inexpensive and non-toxic. In order for a semiconductor to be photochemically active as a sensitizer the redox potential of the photogenerated valence band hole must be sufficiently positive to generate ‘\( \cdot \)OH radicals, which can subsequently oxidize the organic pollutant. The redox potential of the photogenerated conduction band electron must be sufficiently negative to be able to reduce absorbed oxygen to superoxide. TiO\(_2\), ZnO, WO\(_3\), CdS, ZnS, SrTiO\(_3\), SnO\(_2\), WSe\(_2\), Fe\(_2\)O\(_3\), etc. can be used as photocatalysts. Titanium dioxide (TiO\(_2\)) is used as an excellent catalyst for photooxidation of a variety of organic and inorganic compounds.

TiO\(_2\) absorbs radiation at wavelengths below 400 nm which enables the use of sunlight capable of forming e\(^-\)-h\(^+\) pairs (Eq. 1.23) that may recombine also.\(^{88}\) Recombination of e\(^-\) - h\(^+\) pairs occur in the catalyst, generating heat which is adsorbed by water molecules and hydroxyl ions present in the medium. Conduction band electrons interact with surface adsorbed molecular oxygen to yield superoxide radical anions (Eq. 1.24), while valence band holes interact with water to produce hydroxyl radicals (Eq. 1.25).\(^{89}\)

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{e}^-(\text{CB}) + \text{h}^+(\text{VB}) \quad \text{...(1.23)}
\]

\[
\text{e}^-(\text{CB}) + \text{O}_2 \rightarrow \text{O}_2^{-} \quad \text{...(1.24)}
\]

\[
\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \cdot \text{OH} \quad \text{...(1.25)}
\]

Saien and Nejati\(^{90}\) reported the use of TiO\(_2\)/UV process for the degradation of the petroleum aliphatic hydrocarbons (up to C10) and the well-known aromatic compounds such as benzene, toluene and ethylbenzene in refinery wastewater.

TiO\(_2\) catalyzed UV oxidation is a process recommended for use in ultra pure water applications (e.g., semiconductor industry) and for treating waters
with low contaminant concentrations. Although this technology shows promise, it is still in the developmental stages, and additional studies are needed prior to its use in large scale remediation or drinking water treatment applications.

Kamat\textsuperscript{91} studied that due to its inertness to chemical environment and long-term photostability has made TiO\textsubscript{2} an important material in many practical applications, and, in commercial products ranging from drugs to foods, cosmetics to catalysts, paints to pharmaceuticals, and sunscreens to solar cells in which TiO\textsubscript{2} is used as a desiccant, brightener, or reactive mediator.

The photocatalysed decolorization of a dye in solution is initiated by the photoexcitation of the semiconductor, followed by the formation of electron-hole pair on the surface of catalyst (Eq 1.26). The high oxidative potential of the hole (h\textsuperscript{+}\textsubscript{VB}) in the catalyst permits the direct oxidation of the dye to reactive intermediates (Eq 1.27).

\[
(\text{MO/}\text{MO}_2) + h\nu \rightarrow (\text{MO/}\text{MO}_2) (e^{-}\text{CB} + h\textsuperscript{+}\text{VB}) \quad \text{...(1.26)}
\]

\[
\text{Metal oxide} = \text{MO/}\text{MO}_2
\]

\[
h\textsuperscript{+}\text{VB} + \text{dye} \rightarrow \text{dye}^{+} \rightarrow \text{Reactive intermediates} \rightarrow \text{oxidation products...}(1.27)
\]

The reactive intermediate responsible for the degradation is hydroxyl radical ('OH). Banat \textit{et al.}\textsuperscript{92} investigated the hydroxyl radical is an extremely strong, non-selective oxidant (E\textsubscript{0}: 2.8 eV) which leads to the partial or complete mineralization of several organic chemicals.

Zainal \textit{et al.}\textsuperscript{93} reported the photocatalytic degradation of indigo carmine. This pigment has been used for many years in industries, such as textile, paper, and plastics, as colorant. Even in very small quantity dyes can be easily recognized either in industrial products or in the wastewater.
1.5. FACTORS AFFECTING PHOTOCATALYTIC ACTIVITY OF TiO$_2$

1.5.1 Amount of the Catalyst

Catalyst concentration is to be used only till an optimum value, as using excess catalyst reduces the amount of photo-energy being transferred in the medium due to opacity offered by the catalyst particles. It should also be noted that the optimum value is dependent on the type and concentration of the pollutant, as well as the rate of generation of free radicals.

When the amount of TiO$_2$ increases above a saturation level (leading to a high turbidity state), the light photon absorption coefficient usually decreases radially. However, such a light attenuation over the radial distance could not be well correlated with the Beer Lambert Law owing to the strong absorption and scattering of light photons by the TiO$_2$ particles.$^{94}$

Therefore, any chosen photoreactor should be operated below the saturation level of TiO$_2$ photocatalyst avoid excess catalyst and ensure efficient photons absorption. In this sense, both catalyst loading and light scattering effect can be considered as a function of optical path length in the reactor. Xu and Langford$^{95}$ reported that during the dark homogenization period of the catalyst, a lower concentration of organic pollutants was observed owing to the strict adsorption of organics onto the catalysts surface.

1.5.2. Effect of pH

In heterogeneous photocatalysis water system, pH is one of the most important operating parameters that affect the charge on the catalyst particles, size of catalyst aggregates and the positions of conductance and valence bands. Any variation in the operating pH is known to affect the isoelectric point or the surface charge of the photocatalyst used. Many reports have used the point of zero charge (PZC) of TiO$_2$ to study the pH impact on the photocatalytic oxidation performance.$^{96}$ The PZC is a condition where the surface charge of TiO$_2$ is zero or neutral that lies in the pH range of 4.5-7.0, depending on the catalysts used. At PZC of TiO$_2$, the interaction between the
photocatalyst particles and water contaminants is minimal due to the absence of any electrostatic force. Stylidi et al.\textsuperscript{97} reported the degradation of acid orange 7 by TiO\textsubscript{2} in presence of light. It has been found that the dye adsorbs on TiO\textsubscript{2} and undergoes a series of oxidation steps, which lead to decolorization and formation of a number of intermediates, mainly aromatic and aliphatic acids. These molecules are further oxidized to compounds of progressively lower molecular weight and, eventually to CO\textsubscript{2} and inorganic ions, such as sulfate, nitrate and ammonium ions.

A similar electrostatic interaction enhancement for photodisinfection of microorganisms during the photocatalytic process was observed by Gogniat et al.\textsuperscript{98}. It must be stressed that appropriate pH control strategies must be implemented at every different location of a photocatalytic water treatment process for efficient photocatalytic reaction to proceed.

\textbf{1.5.3 Effect of Temperature}

Numerous studies have been conducted on the dependence of photocatalytic reaction on the reaction temperature.\textsuperscript{99} Although heat energy is inadequate to activate the TiO\textsubscript{2} surface, the understanding on such dependency could be extrapolated when operating the process under natural sunlight illumination. Most of the previous investigations stated that an increase in photocatalytic reaction temperature (>80 °C) promotes the recombination of charge carriers and disfavour the adsorption of organic compounds onto the TiO\textsubscript{2} surface. At a reaction temperature greater than 80 °C, the photocatalytic reaction is interpreted with Langmuir Hinshelwood (LeH) mechanism where the adsorption of the reactants is disfavoured resulting in KC becomes “1.

The photocatalytic activity of TiO\textsubscript{2} is drastically reduced when the reaction temperature rises. Desorption of degraded products from the TiO\textsubscript{2} surface is the rate-limiting step when temperatures rise. On the contrary, a low temperature below 80 °C actually favours adsorption which is a spontaneous exothermic phenomenon, resulting in getting KC of LeH model 1, enhancing the adsorption of final reaction products. A further reaction in
temperature down to 0 °C will cause an increase in the apparent activation energy. As a consequence, the optimum reaction temperature for photomineralization is reported to be in the range of 20-80 °C as reported by Malato et al.\textsuperscript{100}

1.5.4 Effect of Light Wavelength

The effect of light sources with different wavelength emitting ranges will have a profound consequence on the photocatalytic reaction rate, depending on the types of photocatalysts used. These may be crystalline phase, anatase-to-rutile composition and any state of photocatalyst modifications. Using commercial Degussa P-25 TiO\textsubscript{2}, which has a crystalline ratio of anatase 70/80: 20/30, a light wavelength at $\lambda < 380$ nm is sufficient for photonic activation.\textsuperscript{101}

The crystalline phase of rutile TiO\textsubscript{2} has smaller band gap energy of 3.02 eV compared to the anatase TiO\textsubscript{2} of 3.2 eV. This dictates that rutile TiO\textsubscript{2} can be activated with light wavelength up to 400 nm, depending on the band gap threshold for the type of rutile TiO\textsubscript{2} used. For UV irradiation, its corresponding electromagnetic spectrum can be classified as UV-A, UV-B and UV-C, according to its emitting wavelength. Rinco´n and Pulgarin\textsuperscript{102} reported that UV-A range has its light wavelength spans from 315 to 400 nm (3.10-3.94 eV), while UV-B has wavelength range of 280-315 nm (3.94 - 4.43 eV) and the germicidal UV-C ranges from 100 to 280 nm (4.43-12.4 eV).

In most of the previous studies, the UV-A light provides light photons sufficient for photonic activation of the catalyst.\textsuperscript{103} The mechanism of UV-C cell destruction involves the direct induction on pyrimidine and purine and pyrimidine adducts on the cell DNA. Sichel et al.\textsuperscript{104} reported the use of longer wavelength of solar irradiation ($I > 400$ nm) in solar disinfection (SODIS) studies.

1.5.5 Effect of Light Intensity

Light intensity is one of the few parameters that affect the degree of photocatalytic reaction on organic substrates. Fujishima et al.\textsuperscript{105} studied that the initiation of TiO\textsubscript{2} photocatalysis reaction is not highly dependent on light
intensity, where a few photons of energy (as low as 1 mW cm\(^{-1}\)) can sufficiently induce the surface reaction. To achieve a high photocatalytic reaction rate, particularly in water treatment, a relatively high light intensity is required to adequately provide each TiO\(_2\) surface active sites with sufficient photons energy required.

The organic conversion in the presence of UV wavelength (\(\lambda < 400\) nm) in many studies obeyed the linear proportionality correlation to the incident radiant flux. This was evidenced by scientists, where they observed that the destruction of dioxin and polychlorinated biphenyls was significantly enhanced in the presence of high intensity photons.\(^{106}\) Magrini and Webb\(^{107}\) reported that organic decomposition rate increases with the radiation intensity. Rincó’n and Pulgarin\(^{108}\) reported that the residual disinfecting ability of the photocatalyst depends on the duration of light intensity.

1.6 PHOTOCATALYSIS

The word "Photocatalysis" is of Greek origin and compose of two parts: - the prefix "photo" (phos: light) and the word "catalysis" (katalyo: break apart, decompose). The IUPAC definition of photocatalysis is “a catalytic reaction involving light absorption by substrate.” In real sense the term photocatalysis is used for those chemical reactions, which occur in the presence of light and a photocatalyst. The main difference between a conventional thermal catalyst and photocatalyst is that the former is activated by heat whereas the latter is activated by photons of appropriate energy.

The principle of photocatalysis is based on the activation of a semiconductor particulate material (CdS, TiO\(_2\), ZnO, WO\(_3\) etc.) by the action of radiation with an appropriate wavelength. Photocatalysis is used for the elimination of several pollutants (e.g., alkanes, alkenes, phenols, aromatics, pesticides) and complete mineralization of the organic compounds.\(^{109}\)

Photocatalytic reactions are of two types. These are -

1.6.1 Homogeneous Photocatalytic Reaction
1.6.2 Heterogeneous Photocatalytic Reaction

1.6.1 Homogeneous Photocatalytic Reaction

The homogenous photocatalysis processes have attracted wide interest because of its relatively low cost and high performance in generating \(^{\cdot}\)OH radicals for the decomposition of refractory organic compounds. \(^{110}\) Augugliaro et al. \(^{111}\) studied the use of ozonation for the treatment of drinking water. Garoma et al. \(^{112}\) studied the use of the ozone/UV process in removing components from gasoline, such as BTX, MTBE, tert-butyl alcohol and total petroleum hydrocarbons such as gasoline, present in contaminated ground water samples and it removes 99% of pollutants initially present in all contaminated water samples.

According to Brillas et al. \(^{113}\), electrochemical processes can produce hydroxyl radicals by two means: anodic oxidation (direct form) and mediated electrooxidation (indirect form). In anodic oxidation, the hydroxyl radical is generated at the anode (Pt, PbO\(_2\), doped with SnO\(_2\) etc.) of an electrochemical cell from water oxidation (Eq. 1.31). In mediated electrooxidation, chemical species, such as H\(_2\)O\(_2\), are continuously generated in the cathode by the reduction of two electrons of dissolved oxygen, as shown by Eq. 1.32 and reported by Brillas and Casado: \(^{114}\)

\[
\begin{align*}
H_2O & \rightarrow ^{\cdot}OH + H^+ + e^- \\
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2
\end{align*}
\]  

(1.31) 

(1.32)

Wet air oxidation (WAO) is an ecologically safe technology for treating water containing organic pollutants was investigated. \(^{115}\) This technique enables the oxidation of pollutants by oxygen dissolved in water, under high pressure conditions (100-220 bar) and high temperatures (150-370°C), leading to the formation of hydroxyl radicals. \(^{116}\) Supercritical water oxidation (SCWO) consists of submitting water to higher temperature and pressure conditions than their critical point (above 374°C and 221 bar, respectively). This technique gives rapid results, but requires high energy demand and, consequently, high operational costs.
1.6.2 Heterogeneous Photocatalytic Reaction

Marc et al.\textsuperscript{117} reported that among the AOPs, heterogeneous photocatalysis in the presence of irradiated polycrystalline semiconductors represents a viable alternative for treating contaminated gaseous and aqueous streams. For this purpose, another most successful and ecofriendly alternative is the use of heterogeneous photocatalysis processes where metal ion (particularly iron) is supported on some active carriers like zeolite, silica, carbon etc. Herney et al.\textsuperscript{118} studied the disadvantage associated with homogeneous processes and their elimination in heterogeneous processes.

Heterogeneous photocatalysis is a developing advanced oxidation technology for treatment of industrial wastewater containing non-biodegradable organic pollutants.\textsuperscript{119} Heterogeneous photocatalysis using semiconductors such as titanium dioxide is more efficient than conventional methods. This is because as the photocatalytic process gradually breaks down the contaminant molecules, no residue of the original material remains and therefore, no sludge requiring disposal to landfill is produced. The catalyst itself is unchanged during the process and no consumable chemicals are required. These results in considerable savings and a simpler operation of the equipments involved. Additionally, because the contaminant is attracted strongly to the surface of the catalyst, the process will continue to work at very low concentrations. Taken together, these advantages mean that the process results in considerable savings in water production cost and keeping the environment clean.

Yavuz and Kopara\textsuperscript{120} studied the degradation of phenol present in refinery wastewater via electrochemical oxidation, using a titanium electrode coated with titanium oxide and ruthenium oxide. The initial phenol concentration was 192.2 mg/L and the chemical oxygen demand (COD) was 590 mg/L. After treatment, a 94.5% removal of phenol and 70.1% of chemical oxygen demand (COD) was obtained, the latter because the wastewater still contained other organic and inorganic contaminants.
Santos et al.\textsuperscript{121} studied the use of dimensionally stable anodes (or DSA, a metallic base of titanium coated with titanium and ruthenium oxides) in the electroremediation of oily wastewater produced during petroleum extraction and refining and it removes 57% of initial COD from the wastewater. They attributed this reduction to the consequence of the electrodegradation of organic compounds, through the anodic oxidation of components in the DSA electrode and the electro-flotation of oil droplets in suspension that aggregate on the surface owing to the gas formed in the cathode (H\textsubscript{2}) and in the anode (O\textsubscript{2} and Cl\textsubscript{2}).

Bessa et al.\textsuperscript{122} studied the treatment of water produced from oil fields via a photocatalytic process using TiO\textsubscript{2}/UV, with the addition of H\textsubscript{2}O\textsubscript{2}. Hu et al.\textsuperscript{123} reported the degradation of a gasoline additive (methyl tert-butyl ether–MTBE). The use of Ag/TiO\textsubscript{2}/UV achieved a higher degradation rate than that obtained with TiO\textsubscript{2}/UV, reaching higher MTBE removal indices (around 80%) more rapidly. The fundamentals of photophysics and photochemistry underlying the heterogeneous photocatalysis employing the semiconductor TiO\textsubscript{2} catalyst have been intensively reported by Fujishima et al.\textsuperscript{124}

The numbers of important features of the heterogeneous photocatalysis which have extended their feasible applications in water treatment are

- Ambient operating temperature and pressure,
- Complete mineralization of parents and their intermediate compounds without secondary pollution and
- Low operating costs. The fact that the highly reactive oxygen species (ROS) generated as a result of the photo-induced charge separation on TiO\textsubscript{2} surfaces for microbial inactivation and organic mineralization without creating any secondary pollution is well-documented.

Technically, doping is the introduction of foreign elements into the parent photocatalyst without giving rise to a new crystallographic forms, phases or structures and the aims are to enhance the net separation of photogenerated charges and thereby efficiently harness the wide visible light
component of about 43% in the solar spectrum as opposed to the narrow ultraviolet component of 5\%\textsuperscript{125}. It is thus an area of increasing research activity in photocatalysis.

A dopant must increase the valence band edge; thus, reducing the band gap without lowering the conduction band and either improve or minimize electron-hole recombination, so as to avoid any loss in quantum yield. Nanosized particles possess very high surface to volume ratios because of the fine grain size and they are characterized by a very large amount of low coordination number atoms at edge and corner sites. The higher surface area of smaller particles provide a higher number of active sites on the surface of semiconductor with less recombination of electron-hole pairs, which is rate determining step in the photocatalytic degradation.

Daneshvar et al.\textsuperscript{126} reported that TiO\textsubscript{2} doped with nitrogen demonstrated superior photocatalytic activities compared to commonly used unmodified TiO\textsubscript{2} nanoparticles in both chemical compound degradation and bactericidal reactions. Kudo\textsuperscript{127} reported that doping is used to establish a barrier through equilibration between the photocatalyst and metal deposits and is governed by the difference in work function of the deposits and the electron conduction band of the photocatalyst. Young et al.\textsuperscript{128} studied the enhancement by Pt and Ag as well as other noble metals, on TiO\textsubscript{2} over a range of organic classes arising from the combination of substrate or functional group specificity and the dark catalytic oxidation effects.

Wei et al.\textsuperscript{129} synthesized Fe\textsubscript{2}O\textsubscript{3}-Pd nanoparticle photocatalyst grown by epitaxial growth of Fe\textsubscript{2}O\textsubscript{3} on Pd nanoparticles and reported to show improved photocatalytic efficiency. Xu et al.\textsuperscript{130} reported the use of triple-modified Bi\textsubscript{2}WO\textsubscript{6}/Ag/N-TiO\textsubscript{2} nanojunction film for enhanced photogenerated charges utilization for the degradation of rose bengal. Nah et al.\textsuperscript{131} reported that nitrogen doping of nanoporous WO\textsubscript{3} layers by NH\textsubscript{3} treatment for increased visible light photo response nanotechnology. Lam et al.\textsuperscript{132} reported the photocatalytic degradation of resorcinol by Pt/TiO\textsubscript{2}, and also by Ag/TiO\textsubscript{2}. But the photocatalytic degradation of resorcinol was significantly improved by
Pt/TiO$_2$, while the presence of Ag/TiO$_2$ enhanced the initial photocatalytic degradation rate of resorcinol slightly.

Teoh et al.$^{133}$ studied the degradation of oxalic acid using iron doped titanium dioxide (Fe-TiO$_2$). Serpone$^{134}$ studied that band gap of pristine TiO$_2$ is narrowed down by anion- and cation doping in second generation photocatalysts. Sun et al.$^{135}$ reported that anionic co-doping, for example involving N/F-TiO$_2$ or N/F- and C/N-ZnWO$_4$ has been used to lower charge defects.

Cationic and anionic elements have been used either as dopants or simply as deposited with TiO$_2$ to increase its photocatalytic activity under visible light region. Doping of metal in TiO$_2$ increases more crystal defects and oxygen cavities on the surface which captures electron excited from VB to CB thereby impeding the electron-hole pair recombination.$^{136}$ Anionic or nonmetal dopants, namely, carbon, sulphur, nitrogen, phosphorus and fluorine, are being investigated to extend the photocatalytic activity into the visible light region. It is said that the related impurity states are supposed to be close to the valence band maximum.$^{137}$

The non-metal ion doped catalysts are better for extending the photocatalytic activity of TiO$_2$ into visible region as compared to metal cationic species loading methods because their impurity states are near the VB edge and their roles as recombination centers may be minimized. It is expected that a combination of doping elements could result in a marked increase in the photocatalytic activity of TiO$_2$ under both UV and visible light. Transition metal species-loaded TiO$_2$ samples often suffer from thermal instability. These cause the photocatalytic activity of cationic species-loaded TiO$_2$ to often decrease because of the thermal instability or an increase in carrier recombination centers.$^{138}$

Several methods have been devoted to enhance the photoactivity, among which, non-metal doping has attracted much attention recently. It reduces substantial amount of chemical oxidation demand (COD) and total organic carbon (TOC) from industrial effluents.
1.7 APPLICATIONS OF TITANIUM DIOXIDE AS PHOTOCATALYST

1.7.1 Treatment of Polluted Water Containing Dyes

Mohamed et al.\textsuperscript{139} studied the heterogeneous photocatalysis as an alternative treatment method for decontamination of organic compounds and disinfection of microorganisms to purify potable water. An annular type fluidized bed reactor has been constructed and tested to disinfect \textit{E.coli} bacteria. They prepared specially catalyst of (TiO\textsubscript{2} + glass bead + zeolite). The efficiency of \textit{E.coli} removal was 99.99% by using the proposed technology. Peyton and Berry\textsuperscript{140} reported the use of three different semiconductors (TiO\textsubscript{2}, ZnO, and Fe\textsubscript{2}O\textsubscript{3}) to decompose pollutant compounds in wastewater by using solar energy. They concluded that Fe\textsubscript{2}O\textsubscript{3} was found to be ineffective, both ZnO and TiO\textsubscript{2} catalyzed the removal of all compounds.

Yamashita et al.\textsuperscript{141} studied the use of metal ion-implantation method to improve the electronic properties of the TiO\textsubscript{2} photocatalyst to realize the utilization of visible light. They found that TiO\textsubscript{2} exhibit an effective photocatalytic reactivity for the liquid-phase degradation of 2-propanol diluted in water at 295 K under visible light (\(\lambda >450\) nm) irradiation. Zhang et al.\textsuperscript{142} reported that nano-ZnO/TiO\textsubscript{2} film possess improved efficiency of the charge and extended range of spectrum, which showed a higher efficiency of photocatalyst than the pure nano-TiO\textsubscript{2} and nano-ZnO film. Photocatalysis aided by TiO\textsubscript{2} nanoparticles is used in removing the organic chemicals which occur as pollutants in wastewater effluents from industrial and domestic sources.

Jaafar\textsuperscript{143} reported the use of titanium dioxide and carbon nanotube TiO\textsubscript{2}/CNT composites for the degradation of methylene blue (MB) under UV and solar light irradiation. The TiO\textsubscript{2}/CNT composite showed greater photodegradation activity under UV and solar light irradiation. Agustina et al.\textsuperscript{144} reported the use of TiO\textsubscript{2} nano-particles for the degradation of the sample of synthetic dye wastewater with solar irradiation.
Chong et al.\textsuperscript{145} carried out the photocatalytic degradation of reactive black 5 dyes using TiO$_2$–zeolite nanocomposite. TiO$_2$–zeolite nanocomposite which was annealed at 600°C shows higher photoactivity than those annealed at 300°C. The higher photoactivity in TiO$_2$–zeolite nanocomposites sample annealed at 600°C is due to the formation of higher pore size and volume in the TiO$_2$–zeolite nanocomposite. Avasarala et al.\textsuperscript{146} carried out the degradation of methyl orange (MO) using magnesium doped titanium dioxide (Mg$^{+2}$-TiO$_2$) under visible light.

Pirkarami et al.\textsuperscript{147} reported the use of WO$_3$/TiO$_2$ for the degradation of azo dye (Allura Red AC) under visible light. Aminia and Ashrafia\textsuperscript{148} reported the use of ZnO and TiO$_2$ nanoparticles for the photocatalytic degradation of various dyes, i.e., rhodamine B (RbB), methylene blue (MB) and acridine orange (AO) under solar light. Jaiswal et al.\textsuperscript{149} studied about the nanocomposite thin films of TiO$_2$ doped SnO$_2$ grown on silicon and quartz matrices by electron beam evaporation deposition technique using sintered nanocomposite pellet of SnO$_2$/TiO$_2$ taken in the mass percentage ratio of 90:10.

Wang et al.\textsuperscript{150} reported the use of mesoporous ZnO/TiO$_2$ hollow microspheres for the degradation of methyl orange (MO). Li et al.\textsuperscript{151} reported the use of CdS/TiO$_2$ nanocomposites for the degradation of methyl orange (MO) under sunlight irradiation. The photocatalytic activity of the CdS/TiO$_2$ composites after 6 h was higher than those of CdS and P25. Guo et al.\textsuperscript{152} carried out the degradation of methyl orange using CdS nanoparticles (NPs) under visible light irradiation.

Lu et al.\textsuperscript{153} studied about the TiO$_2$–graphene (TiO$_2$–GE) nanocomposites. Different molar ratios of 7 wt. % Ce/Mn active component were loaded onto the composites by ultrasonic impregnation, and the resultant catalysts were found to exhibit excellent redox and electrical properties favorable for catalytic reactions. Extensive oxidation of NO into NO$_2$ caused by addition of Ce, non-stoichiometric (MnO$_x$/Mn) on the surface of the
composite catalyst promoted electron transfer and improved the redox performance of the catalyst.

In general, the main advantage of photocatalysis is that there is no further requirement for secondary disposal methods. Other treatment methods such as adsorption by activated carbon and air stripping merely concentrate the chemicals present by transferring them to the adsorbent or air and they do not convert them to non-toxic wastes. Also as compared to other oxidation technologies, expensive oxidation methods are not required as ambient oxygen is used.

1.7.2 Degradation of Organic Compounds

Hofstadler et al.\textsuperscript{154} recommended that one of the most effective approaches to resolve this problem is the mineralization of organic contaminants by using photocatalytic semiconductors (SrTiO\textsubscript{2}). They indicated that the potential is high enough to destroy most organic compounds to carbon dioxide and mineral acids. Photocatalytic degradation using ultraviolet-irradiated TiO\textsubscript{2} suspension was used for destroying both free and complex cyanide with a concurrent removal of copper metal.\textsuperscript{155}

In contrast to conventional cyanide waste treatment processes, the photocatalytic processes convert both free and complex cyanide species into carbon dioxide and nitrogen with no residual harmful chemicals remaining. Results revealed that about 78% of free cyanide (10\textsuperscript{-3} M) was removed after illumination for 4 hours in the presence of 1 g/L TiO\textsubscript{2} at pH 11. Free copper (10–20 M) was completely removed in a shorter time of 3 hours.

Pozan and Kambur\textsuperscript{156} carried out the degradation of 4-chlorophenol using ZnO–TiO\textsubscript{2} binary oxide catalyst. 20 wt% ZnO–TiO\textsubscript{2} photocatalyst exhibited much higher \textit{photocatalytic} activity than pure TiO\textsubscript{2} and ZnO in the degradation of 4-chlorophenol under low UV irradiation due to small particle size, lower band gap energy and the presence of more surface OH groups than that on the pure TiO\textsubscript{2} and ZnO photocatalyst.
Song et al.\textsuperscript{157} reported the use of CdS–TiO$_2$ for reducing CO$_2$ in cyclohexanol. The results showed that CO$_2$ absorbed in cyclohexanol was reduced to cyclohexyl formate (CF) on conduction band and the absorbent cyclohexanol was oxidized to cyclohexanone (CH) on valance band of the photocatalyst. Murgolo et al.\textsuperscript{158} reported the use of nano-sized TiO$_2$ supported on single wall carbon nanotubes (SWCNTs) for the degradation of a mixture of 22 organic pollutants like iopamidol, iopromide, diatrizoic acid, diclofenac, triclosan and sulfamethoxazole in both ultrapure water and real secondary wastewater effluent.

Pang et al.\textsuperscript{159} carried out the degradation of acrylonitrile using F doped TiO$_2$/SiO$_2$ composition oxides. Polat et al.\textsuperscript{160} reported the use of TiO$_2$/Al$_2$O$_3$ binary oxide for decreasing the toxic NO$_2$(g) emission to the atmosphere by 75% as compared to that of Degussa P25. Pan et al.\textsuperscript{161} carried out the degradation of the pharmaceutical compound, 17α-ethinylestradiol (EE2) using TiO$_2$-doped low-silica X zeolite (TiO$_2$-LSX).

1.7.3 Treatment of Wastewater Containing Oil

Oil spills in the sea and ocean is one of the major environmental disasters in the marine environment. Researchers have been trying to study the effect of photodegradation in cleaning up the marine environment. The application of TiO$_2$ photocatalysis has therefore been reported for the remediation of marine environment.\textsuperscript{162} Photodegradation remains one of the least studied related to the crude oil and petroleum products spilled into the ocean or coastal waters. In fact, all the weathering process occurred simultaneously in the environment, and it is difficult to distinguish the changes induced by photodegradation from the changes induced by other processes such as biodegradation. Furthermore, the complex composition of crude petroleum and oil fractions makes the photodegradation process complicated.

A multitude of photoinduced reactions could take place, therefore producing a multitude of photodegradation products. Polycyclic aromatic hydrocarbons (PAHs) frequently appear in oil spills, petroleum fractions and coal. The possible applications of TiO$_2$ in the cleaning up of marine oil spills
have been reported by Garcia et al. The initial photoreactivity of photocatalyst was found to depend greatly upon the aromatic fraction. PAHs are a class of persistent organic pollutants of special concern since they are carcinogenic and mutagenic. PAHs were identified as the photosensitizing species responsible for most of the initiation reactions. An aromatic rich distillate photodegrades about ten times faster than a homologue distillate with low aromatic content.

Photodegradation is as important as biodegradation, since these two processes act upon different components of oil: alkanes are biodegraded while aromatics tend to be photodegraded, and this fact leads to synergistic reactions which enhance the degradation of oil. However, the n-alkanes with 10 or more carbon atoms and the isoprenoids such as prystane and phytane are very resistant to photodegradation, while in crude oil the secondary and the tertiary alkanes are easier to photogrades. N-alkanes were easily degraded by marine bacteria, while branched and cyclic alkanes were assumed to be less biodegradable.

Photo induced toxicity of oil and PAHs has been confirmed due to the transient photodegradation intermediates which showed higher toxicity and solubility than the initial compounds, but were subsequently destroyed in the photocatalytic process. Minero et al. reported that diluted hydrocarbons disappear in pure water in the presence of TiO₂ and simulated solar radiation. The current properties of pure TiO₂ have been found to be effective only under UV irradiation and hence there are still more challenges for in-situ application of TiO₂ in open sea or water bodies.

1.7.4 Degradation of Disinfections

Fujishima et al. studied that photocatalyst does not only kill bacteria cells, but also decompose the cell itself. The TiO₂ photocatalyst has been found to be more effective than any other antibacterial agent, because the photocatalytic reaction works even when there are cells covering the surface and while the bacteria are actively propagating. The end toxic produced at the death of cell is also expected to be decomposed by photocatalytic action.
TiO$_2$ does not deteriorate and it shows a long-term anti-bacterial effect. Generally speaking, disinfection by TiO$_2$ is three times stronger than chlorine, and 1.5 times stronger than ozone. Bacteria and viruses are decomposed on the tile surface due to the strong oxidizing properties of TiO$_2$. If you cover the walls, ceiling and floor with photocatalytic tiles, bacteria floating in the air in an operating room are also killed as they come in contact with the TiO$_2$ surface.$^{172}$

1.7.5 Degradation of Herbicides and Pesticides

One of the other applications of TiO$_2$ photocatalysis is the remediation of organically contaminated soil and sludge. Both pure and composite photocatalyst has been tried for the removal of organic pollutants from soil. Xie et al.$^{173}$ investigated the enhancement of photo degradation of organics on soil surfaces using TiO$_2$ induced by UV-light. They concluded that the photodegradation rate increased with the increase of the soil pH and photon flux. Higashi and Jardim$^{174}$ reported that heterogeneous photocatalytic of TiO$_2$ to degrade pesticide (diuron) under laboratory conditions to evaluate the potential use of this technology for in situ remediation. They reported that the photocatalytic treatment combined with solar light to be very efficient in the destruction of diuron in the top 4 cm of contaminated soil, with the degradation rate markedly dependent on the irradiation intensity.

Pelizzetti et al.$^{175}$ studied the mixed contaminated soils of 2-chlorophenol; 2,7-dichlorodibenzodioxin and atrazine with a photocatalyst (TiO$_2$) in a aqueous slurry and exposed them to simulated solar radiation in the laboratory. They noticed that the organic contaminants were destroyed in relatively short time and reported that the photocatalytic processes could be effective chemical detoxification methods for contaminated soils. According to Hamerski et al.$^{176}$ the most active photocatalyst for soil purification was TiO$_2$ modified by calcium. The common challenge on the above TiO$_2$ applications is to use its photoactivity under visible light irradiation. Thus, the following sections focus on the modification of VLR TiO$_2$. 
Although a number of wastewater treatment processes are available to restore the clean and green globe, but there is a pressing demand to develop newer and ecofriendly methods of wastewater treatment. Heterogeneous photocatalysis process is an advanced oxidation process, which can be utilized for this purpose effectively with almost no or negligible side effects.