CHAPTER - I  
PREAMBLE  

1.1 Introduction  

Water is one of the most critical resources on the planet, with less than one percent of the total water on the planet available for human use [1]. Recent shortages in fresh water around the world have highlighted the need for greater re-use and recycling of water resources. However, re-using water including storm water, treated industrial discharge, treated sewage effluent and household waste water has been neglected. Developing methods for recycling and re-use of effluent water / wastewater has become an important and urgent issue. Despite this, treatment technologies are required to meet the demands of consumers, water companies and regulators, without compromising public health and safety. The removal of organic contaminants from the industry effluents / waste water, before it can be used is of major importance. 

The textile industry produces large quantities of highly coloured effluents. These aqueous effluents are generally toxic and resistant to destruction by biological treatment methods such as using micro organisms, which was used to decompose the sludge into smaller compounds. Azo dyes, such as methylene blue or basic blue 24, are widely used in the textile industry [2]. The worldwide annual production of these dyes is over $7 \times 10^5$ tonnes [3]. Among these dyes, azo dyes constitute the largest and the most important class of commercial dyes. Over 50% of all dyes used in industry are azo dyes. The color of azo dyes was determined by the azo bonds and their associated chromophores and auxochromes [4]. The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of the biological process. 

Generally, after the elimination of particles in suspension by filtration and flocculation, the contaminant treatment is performed [5]. Many techniques have been developed to remove and / or destroy the contaminants from waste water. These include: filtration, chlorination, bromination, sonication, ozonation and irradiation [6]. Chlorination is by far the most widely used technique and has been used to protect public health against water borne diseases since the early 1900’s [7]. While this method is
inexpensive and efficient, recently issues with this process have become apparent. The chlorination of organic compounds present within source water can lead to the formation of undesirable byproducts. A number of alternative methods are commercially available for microbiological pollutants and some chemical contaminants from water sources. Membrane filtration systems are in use, but generally on a small scale to target specific problems. These include micro-filtration, ultra-filtration, nano-filtration and reverse osmosis [8, 9]. Generally overall costs are greater for filtration processes compared with chlorination, with increasing costs inversely proportional to the contaminant size to be removed [10].

It was first demonstrated in 1877 that sunlight is capable of killing micro-organisms [11]. By using a series of filters, it was established that actinic rays (encompassing the ultraviolet region) were responsible for this lethal effect. Since then, the use of UV irradiation for the disinfection of waters has been accepted as an effective and economical alternative to chlorine use [12]. As a consequence, the number of treatment plants installing the process is growing. Conventionally, the UV spectrum is divided into three discrete sections: UV-A (320-400nm), UV-B (280-320nm) and UV-C (less than 280nm). Radiation at UV-B and UV-C wavelengths has genotoxic properties and is invariably harmful to living cells and even it can lead to cell death.

Exposure to UV light can result in the formation of range of photoproducts whose distribution and relative yields depend on the wavelength and intensity of the incident radiation [12]. The photo reactivity is a function of its absorption spectrum. Photons in UV-C region are strongly absorbed and create excited-state species that undergo intra molecular photochemical reactions. The photons with wavelengths in UV-A region damage the organic contaminants through the use of photo sensitizer molecules, whereby the photo sensitizer absorbs the UV-A radiation and initiates the process. Photons in the UV-B range are only weakly absorbed and can damage by either or both mechanisms depending on the experimental conditions. This disinfection of secondary waste water / industry effluents treatment by UV requires light intensity (50-60 mW cm$^{-2}$) due to higher concentration of contaminants.
As a result, Advanced Oxidation Processes (AOPs) have been considered as an effective technology in treating organic chemicals including dyes in wastewater [13]. Advanced Oxidation Processes include photo catalysis systems such as a combination of a semiconductor (TiO$_2$, ZnO, Al$_2$O$_3$, WO$_3$, etc.) and UV light. ZnO appears to be a suitable alternative to TiO$_2$ since its photo degradation mechanism has been proven to be similar to TiO$_2$ [14]. Zinc oxide is an n-type semiconductor with many attractive features. Zinc oxide with a wide band gap of 3.3 eV as compared to TiO$_2$ ($E_{bg\text{anatase}}$ = 3.2 eV), is capable to generate hydroxyl radicals in sufficient quantity and it is transparent to most of the solar spectrum. The synthesized ZnO was also shown to absorb more UV light than any other powders. This means that the high UV absorption efficiency leads to the generation of more electrons and holes. These electrons and holes are considered the main species involved in the photo degradation process. The general scheme of the photo catalytic destruction of an organic compounds begin with its excitation by suprabandgap photons, and continues through redox reactions where •OH radicals formed on the photo catalyst surface play a major role.

1.2 Some conventional water treatment methods

Heat treatment

Heating water to its boiling temperature is one of the oldest purification methods [15]. If the process time is increased, water can be treated at temperatures below the boiling point, as in the famous Pasteurization process. Heat treatment is a guaranteed way to remove all pathogens without any addition of chemicals. The drawback of this technology is the high energy demand.

Filtration

Filtration is a physical process which is used to separate suspended solids from water through a permeable or porous interface. The mechanisms of filtration are mechanical interception, diffusion and adsorption. Sometimes coagulating agents must be added to enhance the filter efficiency. With ultra-filtration, i.e. filtration with very low permeabilities, also microorganisms may be removed. Though filtration seems to be an
energy saving and chemical free method for removing pollutants, the contaminants are just transferred from one medium to another. The pollutant attached to the filter still needs further treatment for the filter regeneration.

**Chlorination**

Chlorination is a chemical oxidation method in which organic components and pathogens are oxidized by the chlorine agent. Since the first application in USA, the history of chlorination for drinking water treatment is almost 100 years, and it has gained huge success and saved millions of people’s life. Chlorination is also used to sanitize swimming pool water and as a disinfection stage in sewage treatment. Recently, concern about the formation of potentially carcinogenic disinfection by-products (DBP) from chlorination has arisen. Higher levels of organic content in the raw water make this problem even worse.

**Biological oxidation**

Biological oxidation is a natural process in which organic substances are catalytically oxidized by means of enzymes in micro-organisms. Biological water treatment takes advantage of the metabolism of the bacteria to digest the organic pollutant and in this process the waste water is purified. Since the biological oxidation is performed at room temperature, low energy consumption makes this process superior to ordinary chemical oxidation for the destruction of organic compounds. However, biological processes are, in general, time consuming, and many organic pollutants cannot be sufficiently degraded by biological oxidation. Its application to the treatment of effluents with highly toxic and persistent organic substances is restricted.

1.3 Advanced oxidation technology

The advances in chemical water treatment have led to the development of a range of technologies termed as advanced oxidation technology (AOT). AOT is an oxidation treatment method characterized by the production of highly oxidative hydroxyl radicals (·OH) at ambient temperature. It can lead to the degradation of an extensive variety of organic pollutants and biological contaminants. The relative strength of oxidants is
expressed by their reduction potential relative to the standard hydrogen electrode. Table 1.1 lists the reduction potentials of \( \cdot \text{OH} \) and some typical oxidants applied in water treatment.

**Table 1.1 Standard reduction potentials of typical chemical agents used in water treatment [16]**

<table>
<thead>
<tr>
<th>Species</th>
<th>Reactions</th>
<th>One electron reduction potential (V vs. SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl radical</td>
<td>( \cdot \text{OH} + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} )</td>
<td>+2.7</td>
</tr>
<tr>
<td>Ozone</td>
<td>( \text{O}_3 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} + \text{O}_2 )</td>
<td>+2.1</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>( \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} )</td>
<td>+1.8</td>
</tr>
<tr>
<td>Chlorine</td>
<td>( \text{Cl}_2(\text{gas}) + 2e^- \rightarrow 2\text{Cl}^- )</td>
<td>+1.4</td>
</tr>
</tbody>
</table>

Comparison of reaction rate constants for ozone and \( \cdot \text{OH} \) with different classes of organic compounds is provided in table 1.2. The reactivity of \( \cdot \text{OH} \) radical is dramatically higher for all the substrates listed.

**Table 1.2 Comparison of rate constants for ozone and \( \cdot \text{OH} \) with organic compounds in water [17]**

<table>
<thead>
<tr>
<th>Organic compounds</th>
<th>Rate constant (M(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{O}_3 )</td>
</tr>
<tr>
<td>Alkanes</td>
<td>0.01</td>
</tr>
<tr>
<td>Alcohols</td>
<td>0.01-1</td>
</tr>
<tr>
<td>Haloalkanes</td>
<td>0.1-1000</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>10</td>
</tr>
<tr>
<td>Ketones</td>
<td>1</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>0.001-0.01</td>
</tr>
<tr>
<td>Alkenes</td>
<td>1000-100000</td>
</tr>
<tr>
<td>Simple aromatics</td>
<td>0.01-1</td>
</tr>
<tr>
<td>Phenols</td>
<td>1-100</td>
</tr>
<tr>
<td>Amines</td>
<td>1-100</td>
</tr>
</tbody>
</table>

The reactions of hydroxyl radicals with organic substrates involve electron and hydrogen transfer, as given below:

\[
\text{Hydrogen transfer} \quad \text{RH} + \cdot \text{OH} \rightarrow \text{R}^+ + \text{H}_2\text{O}
\]
Electron transfer \[ R + \cdot \text{OH} \rightarrow R^{+\cdot} + \text{OH}^{-} \]

The free radicals produced in these reactions can trigger chain reactions under suitable conditions. The unselective high reaction rate and chain reaction inducing ability of \( \cdot \text{OH} \) make AOT more powerful than conventional chemical oxidation methods.

1.3.1 Advanced oxidation processes

Advanced oxidation processes have been defined as water treatment processes that involve an input of energy (either chemical, electrical or radiative) into the water matrix to produce highly reactive radical intermediates, which then attack and destroy the target compound(s). Most advanced oxidation processes for water and wastewater treatment are based on generation of hydroxyl radicals to initiate oxidations. Subsequently, a concise description is presented for major advanced oxidation processes [18-22].

1.3.2 Ultraviolet photolysis

A direct photo oxidation of organic compounds with ultraviolet light upon electronic excitation of the organic substrate (Equation 1.1) imply in most cases an electron transfer from the excited-state (C*) to ground state molecular oxygen (Equation 1.2), with subsequent recombination of the radical ions or hydrolysis of the radical cation, or homolysis of a carbon halogen bond (Equation 1.3) to form radicals, which then react with oxygen [23].

\[
\begin{align*}
R + h\nu &\rightarrow R^* \quad (1.1) \\
R^* + O_2 &\rightarrow R^{+\cdot} + O_2^{-\cdot} \quad (1.2) \\
R-X + h\nu &\rightarrow R^{\cdot} + X^{\cdot} \quad (1.3)
\end{align*}
\]

It should be noted that the most common use of UV radiation in water treatment is rather as a primary disinfectant to inactivate pathogens [24]. The use of ultraviolet radiation for the direct photo oxidation of organic compounds in aqueous solutions is very limited since target organics must efficiently absorb the light required for photo dissociation in competition with other absorbers, especially with water that absorbs significantly in the vacuum UV region. However, ultraviolet photolysis of pollutants may be important in
cases where hydroxyl radical reactions are known to be slow, e.g. highly fluorinated or chlorinated saturated aliphatic compounds may be efficiently eliminated upon primary homolysis of a carbon-halogen bond.

1.3.3 Ozone oxidation

Ozone is a powerful oxidant, second only to the hydroxyl radical. Therefore, it can oxidize organic matter in water either directly or through the hydroxyl radicals produced during the decomposition of ozone. The direct oxidation with molecular ozone is of primary importance under acidic conditions. However, it is relatively slow compared to the hydroxyl free radical oxidation [25-28]. In neutral and basic solutions, ozone is unstable and decomposes via a series of chain reactions to produce hydroxyl radicals (Equation 1.4) [29].

\[
2O_3 + H_2O \xrightarrow{OH^-} OH\cdot + O_2 + HO_2\cdot \quad (1.4)
\]

The added hydrogen peroxide or ultraviolet radiation accelerates the decomposition of ozone and increases the hydroxyl radical concentration. Also presence of suspensions of activated carbon might be able to stimulate the production of OH· radicals from ozone. For the photolysis of ozone in the 200-280 nm region a two step process has been proposed involving the light induced homolysis of ozone and subsequent production of OH· radicals by the reaction of excited oxygen form (O(1D)) with water (Equations 1.5 and 1.6) [30].

\[
\begin{align*}
O_3 + hv & \rightarrow O_2 + O(1D) \\
O(1D) + H_2O & \rightarrow 2 OH\cdot
\end{align*} \quad (1.5) \quad (1.6)
\]

The chemistry involved in the generation of OH· radicals by the O₃/H₂O₂ process (Peroxone) is assumed to be mainly in decomposition of ozone by conjugate base of hydrogen peroxide (HO₂⁻) to produce ozonate radical (O₃\cdot⁻) that gives hydroxyl radical by rapid reaction with water [31]:

\[
\begin{align*}
O_3 + HO_2^- & \rightarrow HO_2\cdot + O_3\cdot^- \\
O_3\cdot^- + H_2O & \rightarrow OH\cdot + OH^- + O_2
\end{align*} \quad (1.7) \quad (1.8)
\]
This process is further enhanced by the photochemical generation of hydroxyl radicals in the O3/H2O2/UV process.

1.3.4 Hydrogen peroxide oxidation

The most commonly used ways to generate hydroxyl radicals from hydrogen peroxide are through the photolysis of H2O2 and Fenton’s reaction. The primary process of H2O2 photolysis in the 200 - 300 nm region is dissociation of H2O2 to hydroxyl radicals with a quantum yield of two OH· radicals formed per quantum of radiation absorbed [32-34]:

\[ \text{H}_2\text{O}_2 + h\nu \rightarrow 2 \text{OH}\cdot \]  
(1.9)

The OH· radicals thus formed enter a radical chain mechanism in which the propagation cycle gives a high quantum yield of the photolysis of H2O2:

\[ \text{OH}\cdot + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2\cdot \]  
(1.10)

\[ \text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{OH}\cdot \]  
(1.11)

Fenton-type catalyzed generation of hydroxyl radicals is based on the decomposition of hydrogen peroxide by ferrous ions [40]:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}\cdot \]  
(1.12)

This method is very effective for generating hydroxyl radicals but involves consumption of one molecule of Fe²⁺ for each hydroxyl radical produced. The decomposition of hydrogen peroxide is also catalyzed by ferric ions. In this process, H2O2 is decomposed to H2O and O2 and a steady-state concentration of ferrous ions is maintained during peroxide decomposition [35, 36].

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightleftharpoons \text{Fe(OOH)}^{2+} \rightleftharpoons \text{Fe}^{2+} + \text{HO}_2\cdot \]  
(1.13)

\[ \text{Fe}^{3+} + \text{HO}_2\cdot \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \]  
(1.14)

Ferric system, known as the Fenton-like reagent, is attractive because degradation of organics can be catalytic in iron. However, the initial rate of destruction of organic pollutants by the Fe(III)/ H2O2 is much slower than that of the Fe(II)/ H2O2 due to the lower reactivity of ferric ion toward hydrogen peroxide. The oxidizing power of the
Fenton-type systems can be greatly enhanced by irradiation with UV or UV-visible light due to the photo reduction of hydroxylated ferric ion in aqueous solution [35].

\[
\begin{align*}
\text{Fe}^{3+} + \text{OH}^- & \rightleftharpoons \text{Fe(OH)}^{2+} \tag{1.15} \\
\text{Fe(OH)}^{2+} + h\nu & \rightarrow \text{Fe}^{2+} + \text{OH}^- \tag{1.16}
\end{align*}
\]

The combined process (Equations 1.12, 1.15 and 1.16), known as the photo-Fenton reaction, results in increased production of OH· radicals and more importantly, iron is cycled between the +2 and +3 oxidation states, so Fe(II) is not depleted, and OH· production is limited only by availability of light and H₂O₂.

### 1.3.5 ZnO photocatalysis

Photocatalytic activity of semiconductors is utilized for photo degradation of organic pollutants in water. These materials can act as sentizers for light induced redox processes due to their electronic structure consisting of a valence band filled molecular orbitals and a conduction band with empty molecular orbitals [37, 38]. Of the entire different semiconductor photo catalysts studied (e.g. TiO₂, ZnO, SnO₂, CdS, ZnS, CdSe, etc.), mostly TiO₂ in anatase form and ZnO were used due to the highest photocatalytic activity (Ebg = 3.2 eV to 3.37eV) [39, 40]. However, among these semiconductors ZnO has proven to be most suitable for widespread environmental applications. Compared with other semiconductors, ZnO is relatively inexpensive. It is chemically and biologically inert. It is stable with respect to photo-corrosions and can be used over prolonged periods of time. Irradiation with photons, which have their energy greater than the bandgap energy, generally leads to the formation of an electron/hole pair in the semiconductor particle [39]:

\[
\text{ZnO} \xrightarrow{h\nu} h_{vb}^+ + e_{cb}^- \tag{1.17}
\]

Valence band holes (h_{vb}^+) have been shown to be powerful oxidants, whereas conduction band electrons (e_{cb}^-) can act as reductants. The holes in the valence band can react with surface-bound water and hydroxide groups to give hydroxyl radical:

\[
\text{H}_2\text{O} + h_{vb}^+ \rightarrow \text{OH}^- + \text{H}^+ \tag{1.18}
\]
\[ h_{\text{vb}}^{\oplus} + \text{OH}^{-} \rightarrow \text{OH}^{\cdot} \]  

(1.19)

1.3.6 Electrochemical oxidation

The mechanism of the electrochemical treatment process is generally viewed as a direct anodic oxidation of organic compound that involves the direct transfer of one electron from the organic molecule to the electrode to form a radical cation that readily deprotonates (Equation 1.20). Subsequent reactions include further oxidation of organic compound.

\[ \text{RH} \xrightarrow{\text{electrolysis}} \text{R}^{\cdot} + \text{H}^{\oplus} + e^{-} \]  

(1.20)

However, radical recombination are also common as well as the inactivation of the anode by the deposition of formed oxidation by-products, which decreases the efficiency of the process. To overcome this problem various types of electrodes are used (e.g. Pt/IrO\textsubscript{2}, Ti/Pt, SnO\textsubscript{2}/Ti, etc.) [41-43]. Another application of electrolysis to chemical oxidation process is generation of electro generated Fenton’s reagent [44].

1.3.7 Wet oxidation

In wet oxidation, water with dissolved oxygen at elevated temperatures and pressures is used to oxidize the target compound. The process can be operated either at temperatures between 175 and 325°C and pressures between 4 and 20 MPa, known as the wet air oxidation process; or at conditions that exceed both the critical temperature and pressure of water 374.2°C and 22.1 MPa, respectively, known as the supercritical water oxidation process. In the case of the wet air oxidation, occurring in a heterogeneous gas liquid system, these conditions increase mass transfer of oxygen from the gas phase to the liquid phase and the rate of reaction between dissolved oxygen and organic compounds in water. Metal ions can be added to catalyze the oxidation, reducing the temperature and pressure requirements. Under supercritical conditions water acts as a dense gas, with the solvation characteristics of a nonpolar organic solvent. Thus, organic compounds and molecular oxygen become completely miscible with supercritical water. This leads to a
homogenous reaction mixture in which organics, water, and oxygen can exist in a single phase, in which oxidation of the organics raises the mixture temperature to 550 - 650°C, where waste destruction proceeds rapidly. In both cases, the elevated temperatures can lead to the formation of hydroxyl and hydrogen radicals from the dissociation and oxidation of water and atomic oxygen from dissociation of dissolved oxygen, which in turn can react with water and oxygen to form hydrogen peroxide and ozone. Thus, OH·, H·, HO2·, O·, O2, O3 and H2O2 are all capable of participating in the oxidation of organics (Equation 1.21) [45, 46]. However, supercritical water and products of oxidation are very aggressive. Therefore, special materials have to be used for reactor construction.

\[ \text{H}_2\text{O} \xrightarrow{e_{\alpha/T/p}} \text{OH}^\cdot, \text{H}^\cdot, \text{O}^\cdot, \text{HO}_2^\cdot, \text{O}_2, \text{O}_3, \text{H}_2\text{O}_2 \]  \hspace{1cm} (1.21)

\subsection*{1.3.8 Ultrasonic irradiation}

Free radicals such as hydrogen atoms and hydroxyl radicals are generated upon the action of ultrasonic waves on aqueous solution. The applied frequency range is from 15 kHz up to 1 MHz. The sonochemical effects are due to the electro hydraulic cavitations in liquid that causes the formation of cavitations bubbles, which can grow and implode under the periodic variations of the pressure field of the ultrasonic waves. The rapid implosion of the eventually instable gas bubbles causes adiabatic heating of the bubble vapor phase. In this way, localized and transient high temperatures of several 1000 Kelvin and pressures of some 10 MPa exist in the final stage of the compression phase of the oscillating or collapsing cavitation bubbles. In the case of water saturated with air, these conditions give rise to cleavage of water and the dioxygen molecule with the production of H· and OH· radicals (Equation 1.22) and oxygen atoms (Equation 1.23), respectively, and direct destruction of solute [47-50].

\[ \text{H}_2\text{O} \xrightarrow{\text{ultrasound}} \text{H}^\cdot + \text{OH}^\cdot \]  \hspace{1cm} (1.22)

\[ \text{O}_2 \xrightarrow{\text{ultrasound}} 2 \text{O}^\cdot \]  \hspace{1cm} (1.23)
1.3.9 Radiolysis of water

Irradiation of water by high energy ionizing radiation (in the keV or MeV range) causes excitation and ionization of water molecules which leads to the production of various radicals and molecular species. The types of radiation may be differentiated to those produced by:

- The decay of radioactive nuclei (α-, β-, and γ-radiation),
- Beams of accelerated charged particles (electrons, protons, deuterons, helium nuclei, and heavier nuclei),
- Short-wavelength electromagnetic radiation (X rays) [51].

Currently, the most widely used radiation sources for radiation-induced decomposition of organic compounds in water are cobalt-60 (γ-radiation) and electron accelerators (electron beams) [52]. The decomposition process is based on the attack of the primary water radiolytic products on the dissolved organics. Radiolysis of water produces H-atoms, solvated electrons (eaq -), OH· radicals, H₂, hydrogen peroxide, H₃O⁺ and OH⁻ [53]:

1.4 UV radiation driven AOTs

The public concern about the potential carcinogenic DBP production from the conventional chlorination disinfection methods makes ultraviolet (UV) radiation disinfection an attractive process. Besides the application in disinfection, direct UV photolysis is also used in the remedy of groundwater pollutants. However, the typically low UV photo absorption of target pollutants and, in general, the low efficiency of photodissociation limits the industrial application of direct UV photolysis.

Various techniques have been developed to enhance the performance of UV photolysis. By introducing UV absorbent oxidants like hydrogen peroxide, ozone, or semiconductors like Titanium dioxide (TiO₂) and Zinc Oxide (ZnO) into the UV system, the formed hydroxyl radicals resulting from the photo excited oxidants or semiconductors can substantially improve the organic pollutant treating efficiency and make the so called UV driven AOTs great successes in water purification applications.
Compared with the UV/ozone and UV/H$_2$O$_2$ technologies, the chemical free and solar light utilizable semiconductor photocatalysis has gained increasing attention [54]. Examples of such applications are: purification of contaminated waste water [55], protection of potable water for human consumption [56], and screening of invasive non-indigenous micro-organism in shipping ballast water [57].

1.5 Semiconductor photocatalysis fundamentals

The available energies for electrons in solid materials form bands. The valence band is the highest range of energies where electrons are normally present. The conduction band is the range of electron energy, sufficient to make the electrons occupied there free to accelerate under the influence of an applied electric field and thus constitute an electric current. The electronic structure of a semi-conductor is compromised by energy separated valence band and conduction band and the energy difference is called energy band gap (Ebg). When semiconductors are exposed to UV radiation with photon energy exceeding Ebg, pairs of electrons and positive holes are produced. The electrons will thus occupy the conduction band and leaving holes behind in the valence band. In the absence of suitable electron and hole scavengers, the stored energy is dissipated within a few nanoseconds by recombination. Otherwise, if suitable scavenger or surface defects are available to trap the electrons or holes, recombination is prevented and subsequent redox reactions may occur as shown in fig 1.1. If the semiconductor remains intact and the charge transfer to the adsorbed species is continuous and exothermic the process is termed as heterogeneous photocatalysis.

To undergo electron transfer, the standard reduction potential of electron donor is thermodynamically required to be more negative than the valence band potential, and the reduction potential of electron acceptor more positive than the conduction band potential. In water photocatalysis, the dissolved oxygen is normally present and act as electron acceptor. Several metal oxide and sulfide semiconductors have band edge positions outside the reduction potential of O$_2$/O$_2^-$ and ·OH/H$_2$O. They include TiO$_2$ (Ebg = 3.0~3.2 eV), SrTiO$_3$ (Ebg = 3.2 eV), ZnO (Ebg = 3.2 eV), and Cds (Ebg = 2.5 eV).
However, experiments in water-free, organic solvents have displayed only partial oxidation of organics. The complete mineralization to CO$_2$, common in aqueous solutions, was not observed [58]. The presence of water or hydroxyl groups appears to be essential for complete oxidative destruction of organic pollutants.

The photocatalytic process can thus be represented by following reactions [58-60]:

Excitation \[ \text{ZnO} + h\nu \rightarrow e^-_{\text{cb}} + h^+_{\text{vb}} \] (1.24)

Recombination \[ h^+_{\text{vb}} + e^-_{\text{cb}} \rightarrow \text{ZnO} \] (1.25)

Charge Trapping \[ h^+ \rightarrow h^+_{\text{tr}}, \quad e^- \rightarrow e^-_{\text{tr}} \] (1.26)

Electron charge transfer \[ e^-_{\text{tr}} + \text{O}_2 \rightarrow \text{O}_2^- \] (1.27)

Hole charge transfer \[ h^+_{\text{tr}} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \] (1.28)

According to the equations above, the prime reactive species present in aqueous photocatalysis are therefore trapped positive holes, OH radicals and superoxide. A probe selected to evaluate photocatalytic processes should have response to these species.

1.6 Thesis organization

The objective of the present research work is a model study of the real treatment of textile wastewater that is contaminated by methylene blue. The degradation process was carried out using undoped ZnO nanorods and ZnO nanorods doped with aluminium, strontium and lithium as catalysts. This thesis is organized into six chapters.
The first chapter of the thesis is of introductory nature and dedicated to explain the importance of photocatalysis and its current status. It also briefs about the various water treatment methods for water purification, advanced oxidation technology, techniques of AOT, UV driven AOT and fundamentals of semiconductor photocatalysis.

The second chapter deals with the principles of photocatalysis. Photocatalytic reactions, recombination process of electron-hole pairs, role of photo generated electrons and holes in the photocatalytic process and the photocatalytic oxidation have been discussed in detail.

The third chapter comprises of three sections. Introduction to zinc oxide, applications of zinc oxide, zinc oxide characteristics and properties of zinc oxide are discussed in the first section. In the second section, preparations of seed layer using dip coating method and growth of ZnO nanorods by hydrothermal method are reported. In last section, preparation of aluminium, strontium and lithium doped zinc oxide nanorods are explained.

The fourth chapter presents the structural and optical studies of the undoped ZnO nanorods and the ZnO nanorods doped with aluminium, strontium and lithium. The results are investigated through X-ray diffraction (XRD), Energy dispersive analysis X-ray (EDAX), Scanning electron microscope (SEM), UV-visible spectroscopy (UV) and Photoluminescence Spectroscopy (PL).

In the fifth chapter, the photocatalytic degradation of the methylene blue dye using undoped ZnO nanorods and ZnO nanorods doped with aluminium, strontium and lithium by varying irradiation time and catalyst area are discussed and its corresponding degradation efficiencies are reported. This chapter also deals with experimental setup of photocatalytic reactor.

The sixth chapter is carried out with the important conclusions drawn from the results of various properties of undoped and doped ZnO nanorods and photo catalytic degradation of methylene blue. The list of publications, presentations along with conference participation details are given in the appendix.
References


