Chapter - 1

Introduction
1. **General Introduction**

Water is a precious natural resource that exists on planet earth, without which there would be no life. It is the basic requirement in all industrial processes. The wastewater has been generated by many industries *viz.*, textile, leather, pulp and paper, printing, photographs, cosmetics, pharmaceutical *etc*. Since, the textile industry used water as a primary medium for removing impurities, applying dyes and finishing agents, the main concern is therefore about the water discharged and the chemical load it carries. A number of chemicals that may be used in textile processes are worth mentioning for their potential negative effects on the environment and human health. These industries generate wastewater containing colour. Various types of dyes are used during manufacturing process, which contributes towards water pollution and leads to imbalance in bio-system (Bell and Buckley, 2003; McMullan *et al*., 2001).

These days, a large number of organic substances are introduced into the water system from various sources *viz.*, industrial effluents, agricultural runoff, chemical spills and so forth. Their toxicity, stability to natural decomposition and persistence in the environment are the cause of much concern to societies and regulatory authorities across the world.

Over the years, the discharge of waste into the environment was the way to eliminate it. The permitted discharge levels have been vastly exceeded, causing such environmental contamination that our natural resources cannot be used for certain purposes and their characteristics have been altered. Without being treated, dyes, phenols, pesticides, fertilizers, detergents and other chemical products are disposed directly into
the water sources. Currently, colour removal from the textile wastewater has become an issue because of the toxicity of the dyes and more over the coloured wastewater from the textile industries decreases the visibility of the receiving waters. Thus, there is an urgent requirement on the industries to minimize the release of coloured effluents, even a very small but visible release might be considered as toxicologically rather innocuous.

1.1 Dyes and their intermediates

In textile industry, dyes and their intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants (Arslan et al., 2000; Sauer et al., 2002) and nearly 10-15% of the dye is lost in the dyeing process and released into the effluent which is an important source of environmental contamination. Huge amount of water is used for dyeing and finishing of fabrics in the textile industries (Sreedhar et al., 2006; Saggioro et al., 2011).

The wastewater from textile mills has caused a serious impact on natural water bodies and land in the surrounding areas (Kanu and Achi, 2011). High values of COD, presence of particulate matter and sediments, chemicals which are dark in colour leading to turbidity in the effluents cause depletion of dissolved oxygen, which has an adverse effect on the aquatic ecological system. Dyes are designed to be chemically and photocatalytically stable and are highly persistent in natural environments. The improper handling of hazardous chemicals in textile effluent also has some serious impact on the worker’s health and safety putting them into the high risk bracket for contracting skin diseases like chemical burns, irritation, ulcers and respiratory problems (Uzoekwe and Oghosanine, 2011; Neppolian et al., 2002 and Mathur et al., 2012).
1.2 Dye classification

The first organic dye namely Mauvine was synthesized by William Henry Perkin in 1856, while many natural dyes have been discovered. But, it was in the last century the synthetic organic dyes became more popular owing to their variety, better imparting property to the fabric materials. Over 700000 tons of approximately 10000 types of dyes and pigments are produced annually worldwide, among them 50-70% are azo dyes (Zollinger, 1987).

All aromatic compounds absorb electromagnetic energy but, only those that absorb light with wavelengths in the visible range (~350-700nm) are coloured. Dyes contain chromophores, delocalized electron systems with conjugated double bonds, and auxochromes, electron-withdrawing or electron-donating substituent's that cause or intensify the colour of the chromophore by altering the overall energy of the electron system. Usual chromophores are -C=C-, -C=\(\text{N}\)-, -C=O-, -N=N-, NO\(_2\) and quinoid rings, while the auxochromes are NH\(_3\), COOH, SO\(_3\)H and OH groups. Based on chemical structure or chromophore, 20-30 different groups of dyes can be discerned. Each different dye is given a C.I. (Colour Index) generic name determined by its application characteristics and its colour (Abrahart, 1977). The Colour Index discerns different application classes which are as follows.

1.2.1 Acid dyes

Acid dyes are water soluble anionic dyes, its imparting nature is attributed to salt formation between anionic groups of the dyes and cations of the fiber. They are called acid dyes because, they are normally applied to the nitrogenous fibers of fabrics in
organic or inorganic acid solutions. Chemical reactions between the dye and fiber form an insoluble colour molecule on the fiber. These dyes are mostly used for applying the fibers such as silk, wool and nylon. These are direct dyes and no modernity is needed to apply them.

Fig. 1: Structure of Acid Orange 27

1.2.2 Basic dyes

Basic dyes are water soluble cationic dyes which react with the acidic groups on fibers that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is used for the application of the dye to the fibers. Colour fastness on acrylic is generally excellent, fastness on natural fibers is generally poor.

Fig. 2: Structure of Basic Orange 5

1.2.3 Direct or substantive dyes

A dye class based on the application method, which is essential by immersion of fiber in a solution of dye without the need for other chemicals to bond with the dye to the fiber. These dyes are normally carried out in a neutral or slightly alkaline dye bath
containing ionic salts and electrolytes, at or near boiling point, with the addition of either sodium chloride or sodium sulfate. Direct dyes are used on cotton, paper, leather, nylon and silk. They bond with fibers by an electrostatic force.

![Structure of Direct Black 38](image)

**Fig. 3: Structure of Direct Black 38**

### 1.2.4 Mordant dyes

These require a mordant, which improves the fastness of the dye against water, light and perspiration. The most important mordant dyes are the synthetic mordant dyes or chrome dyes used for wool. Selection of mordant is very important as it has a say in the final coloration of the dyeing process. Natural dyes have come under this category. Synthetic mordant dyes or chrome dyes are important mordant dyes used for wool, especially for black and navy shades.

![Structure of Mordant Blue 18](image)

**Fig. 4: Structure of Mordant Blue 18**
1.2.5 Vat dyes

The vat dyes are insoluble fast dyes incapable of dyeing directly, but are made to soluble when they are applied along with alkaline liquor which reduces it into water soluble alkali metal salt of the dye. The excess alkali remaining is removed by scouring process after keeping cloth for oxidation. The denim colour is due to Indigo Carmine, a vat dye.

![Structure of Indigo Carmine](image)

**Fig. 5:** Structure of Indigo Carmine

1.2.6 Reactive dyes

A dye which attaches to the fiber by forming a covalent bond, also called fiber reactive dye. These dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of the dyes. Reactive dyes are the best choice for dyeing cotton and other cellulose fibers at home or in the art studio. Reactive dyes are known for their bright colours and very good to excellent light fastness and wash fastness, though poor resistance to chlorine bleach.

![Structure of Reactive Red 189](image)

**Fig. 6:** Structure of Reactive Red 189
1.2.7 Dispersed dyes

These are colloidal and have very low water solubility. Most of these dyes are used for polyester, nylon, acetate and triacetate fibers. They are usually applied in a dye bath as dispersions by direct colloidal absorption. Disperse dyes exist in the dye bath as a suspension or dispersion of microscopic particles, with only a tiny amount in true solution at any time. They are the only dyes that are effective for normal polyester. Some types are used for nylon and acetate. Disperse dyes are also used for sublimation printing of synthetic fibers, and are the colourant used in crayons and inks sold for making iron-on transfers.

![Fig. 7: Structure of Coralene Dark Red F3BS](image)

1.2.8 Sulphur dyes

A class of dyes made by reacting sulfur with organic compounds, most are of unknown chemical structure. Sulfur dyes are insoluble in water, and must be converted to a soluble form for application. The process is a quite similar to that used for vat dyes. Sulfur dyes are typically inexpensive, but dull in colour. They generally have good wash fastness, but are sensitive to bleach. These dyes are employed for dark colours. These are sulfur compound applied with sodium sulfide followed by oxidation with chromate. Effluents from this dyeing consists considerable amounts of sulfide.
1.2.9 Azo dyes

Azo dyes are largest and most versatile dyes and represent the largest class of organic colourants listed in the Colour Index (60-70% of the total) and their relative share among reactive, acid and direct dyes is even higher, it can be expected that they make up the vast majority of the dyes discharged by textile processing industries. Anthraquinone dyes are the second largest class (~15%), followed by triarylmethanes (~3%) and phthalocyanines (~2%) of the entries in the Colour Index (Puvaneswari et al., 2006).

Azo dyes are synthetic colours that contain an azo group (-N=N-), as part of the structure. Most azo dyes contain only one azo group, but some contain two, three or more. Azo dyes can supply a complete rainbow of colours, mainly aromatic. Side groups around the azo bond mainly benzene and naphthalene rings help to stabilize the -N=N-group by making it part of an extended delocalized system and are responsible for imparting the colour of the dye with many shades and shining. These nucleophiles and aromatic groups together constitute the chromophores of the dye. The absorption and reflection of the UV and visible light by these chromagene ultimately causes the observed colour of the dye (Barbusinski and Majewski, 2003; Tripathi and Srivastava, 2011). Azo group does not occur naturally. Azo dyes are the largest group of dyes used for dyeing cotton fabrics in the industry.
1.3 Properties of azo dyes

The four types of azo dye properties are listed below:

- Azo dyes give bright, high intensity colours.
- They have fair to good fastness properties.
- The main advantage of these dyes is cost-effectiveness, due to the processes involved in manufacture.
- The general formula for the synthesis of an azo dye requires two organic compounds a coupling agent and a diazo component.
The major portion of azo dyes produced is consumed by the textile industries. Every year, more than 80,000 tones of azo dyes are produced and the majority of them are consumed by the textile industries for dyeing and printing processes (Ramesh et al., 2007).

1.4 Pollution aspects of the azo dyes

A vast number of azo dyes are produced of which, the fiber reactive azo dyes are of more significant due to its variety, characters, huge production, use and hence the pollution problems. These dyes are quick to fasten in wet process but, the reactive groups which are hydrolyzed prior to the process remain in the spent bath and end up into the effluent (Idaka et al., 1985; Bansal et al., 2011). The presence of azo dyes in textile effluents is of main environmental concern because of their widespread use, their producing potential toxic aromatic amines and low removal rate during various wastewater treatment processes (Chacko and Subramaniam, 2011). Further, about 15% of azo dyes applied remains unadsorbed and remain in spent bath during dyeing processes due to a low fixation degree of azo dyes to fabrics, resulting in the contamination of dyes in wastewater and released into the environment (Pekakis et al., 2006; Chen et al., 2006; Farah et al., 2007).

1.5 Toxicity of azo dyes

Azo dyes and nitrated polycyclic aromatic hydrocarbons are two groups of chemicals that are abundant in the environment. They cause severe contamination in rivers and ground water in the vicinity of dyeing industries (Riu et al., 1998). The impact of azo dyes in the food industry and their degraded products on human health has caused
concern over a number of years, in spite of legislation controlling their use in several countries. Over 3000 tons of azo dyes were certified in the year 1991 by the U.S. Food and Drug Administration (FDA) for use in foods, drugs and cosmetics; they constituted the largest group of certified colourants. Some azo dyes have been linked to human bladder cancer, splenic sarcomas, hepatocarcinomas and nuclear anomalies in experimental animals and chromosomal aberrations in mammalian cells. Some azo dyes induce liver nodules in experimental animals and there is a higher incidence of bladder cancer in dye worker exposed to large quantities of azo dyes. In mammals, both hepatic and bacterial azoreductases reduce the azo compounds to their corresponding amines (Bragger et al., 1997). Bacterial azoreductases are more active than hepatic azoreductases in reducing azo dyes and are capable of converting some azo dyes to mutagenic and carcinogenic amines.

Benzidine based azo dyes are widely used in the dye manufacturing, textile dyeing, colour paper printing and leather industries. In 1980, the National Institute for Occupational Safety and Health published a data after survey on carcinogenicity of Benzidine based dyes on the experimental animals and epidemiological studies on workers exposed to the dyes. Benzidine has been recognized as a human urinary bladder carcinogen and tumorigenic in a variety of laboratory animals (Haley, 1975). Experimental studies with rats, dogs and hamsters have shown that animals administered Benzidine and Benzidine-congener based dyes excrete potentially carcinogenic aromatic amines and their N-acetylated derivatives in their urine (Nony and Bowman, 1980). 1-amino-naphthalene forms as the intermediate in the manufacture of azo dyes, herbicides and rubber antioxidant (Boeniger, 1980). Occupational Health and Safety administration classifies 1-amino-naphthalene as a carcinogen (Powell et al., 1979).
Apart from the colouration, high COD, hindrance to the light penetration, hydrophobicity of azo dyes increase their toxicity. The presence of azo and sulfonate bonds are responsible for the recalcitrant nature of these dyes resulting in the potential xenobiotics in the environment. In general, physicochemical methods (coagulation and flocculation) produce large amounts of sludge which pose handling and disposal problems (Zom et al., 2000).

1.6 Dye effluent

Dye effluents are mainly released from the textile and other colour dyeing industries such as paper, painting, etc., and are most often released into the nearby water bodies making it to pollute. Among these textile industry accounts about 80% of the consumption of dyestuff (Mathur et al., 2005) and considered as one of the most chemically intensive industry where it is estimated that about 12% of total dyestuff used is going to be a waste every year (Roy et al., 2010).

In India a very large amount of synthetic organic dyes such as direct dyes, reactive dyes, processing dyes etc. are used and most of them are unfamiliar with the natural environment and persist for a long period of time. A dye used in the industry is more synthetic complex organic chemicals and shows high hydrostatic stability under neutral condition. Also, they found in dissolved state or in suspension in wastewater and hence remain in aquatic ecosystem for a long period posing a threat to the environment.

1.7 Treatment of dye effluent

The dyes have the complex organic structure and they remain fast to the fabric material for the lifetime and does not break down on exposure to the sunlight, water or soaps etc., these characters made them to use extensively and the same characters would
lead to the problem in treatment making the treatment process more difficult (Bhatkhande et al., 2001). The textile industry which is one of the highest amount of water consuming and extensive chemical industry produces the largest volume of wastewater and the studies of late have indicated that about 15% of dyes using in the industry flows into the wastewater making the treatment more problematic (Amin et al., 2008).

1.8 Methods for removal of dyes from wastewater

Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades to remove colour from dye contaminated wastewaters in order to cost effectively meet environmental regulatory requirements. Chemical and biological treatments have been conventionally followed till now. But these treatment methods have their own disadvantages. The aerobic treatment process is associated with the production and disposal of large amounts of biological sludge, while wastewater treated by anaerobic treatment method does not bring down the pollution parameters to the satisfactory level and activated charcoal adsorption and air stripping methods simply transfer the pollutants from one medium to another. They either transfer it to the atmosphere, which causes air pollution, or to a solid which is often disposed off in landfills or must be treated in an energy-intensive regeneration process. Merely transferring toxic materials from one medium to another is not a long term solution to the problem of hazardous waste load on the environment. The recent developments in water decontamination processes are concerned with the oxidation of these bio-recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species that degrade number of recalcitrant molecules into biodegradable compounds and the method is called Advanced Oxidation Processes (AOP’s).
Fig. 11: Main methods used for the removal of organic dyes from wastewaters
1.9 Advanced Oxidation Processes

Advanced oxidation processes (AOP's), uniting together ozone and high output ultraviolet technologies, in conjunction with hydrogen peroxide and catalyst are successfully used to decompose many toxic and bio-resistant organic pollutants in aqueous solution to acceptable levels, without producing additional hazardous by-products or sludge which requires further handling. Advanced oxidation processes involve the generation of hydroxyl (OH') radicals which oxidize the pollutants. After fluorine, the hydroxyl radical is the second strongest known oxidant having an oxidation potential of 2.8 eV. It is able to oxidize and mineralize almost every organic molecule, yielding CO₂ and inorganic ions (Eqs. 1 and 2).

\[
\text{OH'} + \text{RH} + \text{R'} + \text{H}_2\text{O} \\
\text{R'} + \text{O}_2 \rightarrow \text{RO}_2' \rightarrow \text{products and CO}_2
\]

(Eq. 1)  (Eq. 2)

Different combinations of homogenous and heterogeneous methods which involve the generation of free radicals are, (i) photochemical irradiation with ultraviolet light (coupled with powerful oxidizing agents like ozone, hydrogen peroxide and/or a semiconductor), (ii) Fenton and Photo-Fenton catalytic processes (iii) Electron Beam Irradiation technique and (iv) Sonolysis.

All these processes use UV range for degradation. The UV spectrum is arbitrarily divided into three bands: UV-A (315 to 400nm), UV-B (280 to 315nm) and UV-C (100 to 280nm). Of these bands UV-A and UV-C are generally used in environmental applications. UV-A radiations are referred to as long wavelength radiations or black light and UV-C is referred to as short wave radiations.

Advanced oxidation processes can be broadly classified into the following groups: Homogeneous photocatalysis, Heterogeneous photocatalysis.
1.9.1 Homogeneous photocatalysis

The applications of homogeneous photodegradation (single phase system) to treat contaminated water, involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. The major oxidants used are:

- Hydrogen peroxide (UV/H$_2$O$_2$)
- Ozone (UV/O$_3$)
- Hydrogen peroxide and Ozone (UV/O$_3$/H$_2$O$_2$)
- Photo-Fenton system (Fe$^{+3}$/H$_2$O$_2$)

<table>
<thead>
<tr>
<th>Method</th>
<th>Key Reaction</th>
<th>Drawbacks</th>
</tr>
</thead>
</table>
| UV/H$_2$O$_2$           | $\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \text{HO}^\cdot$ | 1. Low molar extinction co-efficient.  
2. Absorbs $\lambda < 300\text{nm}$, a lesser component in solar radiation. |
| UV/O$_3$               | $\text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O}^\cdot$ | Absorbs $\lambda < 300\text{nm}$, a lesser component in solar radiation. |
|                         | $\text{O}^\cdot$($\text{D}$)+$\text{H}_2\text{O}$ $\rightarrow$ $\text{HO}^\cdot + \text{HO}^\cdot$ |                                                                   |
| UV/H$_2$O$_2$/O$_3$    | $\text{O}_3 + \text{H}_2\text{O} + \text{hv} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$ | Absorbs $\lambda < 300\text{nm}$, a lesser component in solar radiation. |
| UV/H$_2$O$_2$/Fe       | $\text{H}_2\text{O}_2 + \text{Fe}^{+3} \rightarrow \text{Fe}^{+2} + \text{OH} + \text{OH}^\cdot$ | 1. Process is expensive.  
2. Sludge disposal problem formed during the process.  
3. Continuous supply of feed chemicals are required. |
| (Photo-Fenton)          | $\text{Fe}^{+2} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{Fe}^{+3} + \text{OH} + \text{H}^\cdot$ |                                                                   |

Table 1: Hydroxyl radical (OH$^\cdot$) generation in different AOP's (Homogeneous).
Many of the AOP's listed in Table 1 utilize the chemical, hydrogen peroxide. The oxidizing strength of hydrogen peroxide alone is relatively weak, but the addition of UV light enhances the rate and strength of oxidation through production of increased amounts of hydroxyl radicals. Hydrogen peroxide may also be used to enhance other AOP's if added in low concentrations, as the molecule easily splits into two hydroxyl radicals.

1.9.2 Heterogeneous photocatalysis

The heterogeneous photocatalytic process consists of utilizing the UV/visible radiation to photo-excite a semiconductor catalyst in the presence of oxygen. Under these circumstances oxidizing species, either bound hydroxyl radicals or free holes, are generated (Fig. 12). Using photocatalysis, organic pollutants can be completely mineralized reacting with the oxidizers to form CO$_2$, water of simple mineral acids. The process is heterogeneous because there are two active phases, solid and liquid. This process can also be carried out utilizing the near part of the solar spectrum ($\lambda < 380\text{nm}$) what transforms it into a good option to be used (Malato et al., 2002).

![Diagram](image)

**Fig. 12:** Photo induced charge transfer processes in semiconductor nanoparticles
The semiconductor may be in the form of a powder suspended in the water or fixed on a support. The most active photocatalyst for this application is the anatase form of TiO$_2$ because of its high stability, good performance (Andreozzi et al., 1999). The primary photocatalytic mechanism is believed to proceed as follows:

$$\text{TiO}_2 + \text{hv} \rightarrow e^-_{\text{CB}} + h^+_{\text{VB}} \quad \text{(Eq. 3)}$$

$$h^+_{\text{VB}} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \quad \text{(Eq. 4)}$$

$$e^-_{\text{CB}} + \text{O}_2 \rightarrow \text{O}_2^- \quad \text{(Eq. 5)}$$

$$2\text{O}_2^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- + \text{O}_2 \quad \text{(Eq. 6)}$$

$$\text{H}_2\text{O} + e^-_{\text{CB}} \rightarrow \text{OH}^- + \cdot\text{OH} \quad \text{(Eq. 7)}$$

In solids, the electrons occupy energy bands as a consequence of the extended bonding network. In a semiconductor, the highest occupied and lowest unoccupied energy bands are separated by a band gap, a region devoid of energy levels. Activation of semiconductor photocatalyst is achieved through the absorption of a photon of ultraviolet band gap energy which results in promotion of an electron (e$^-$) from the valence band (VB) into the conduction band (CB) with the generation of hole in the valence band (Fig. 12). The resulting hole is an oxidizing agent and the electron is a reducing agent. In the generally accepted mechanism for the photocatalytic process, the hole can react with water to generate the hydroxyl radical and the electron can reduce molecular oxygen, hydrogen peroxide or some other oxidizing agent in the solution. This creates the reactive radicals responsible for the removal of hazardous components from the water.
1.10 **Photocatalyst**

Research over the last three decades has not only confirmed the capability of sunlight for detoxification and disinfection but also accelerated the natural process by the use of catalysts. For oxidation reactions to occur the valence band (VB) must have a higher oxidation potential than the material under consideration. The redox potential of the valence band and the conductance band for different semiconductors varies between +4.0 and -1.5 volts. Therefore, by careful selection of the semiconductor photocatalyst, a wide range of species can be treated via these AOP processes. Metal oxides and sulphides represent a large class of semiconductor materials suitable for photocatalytic purposes.

Among the metal oxide photocatalysts, TiO$_2$ is most studied nanoparticles and frequently reported as an efficient photocatalyst in degrading many textile dyes. Many investigations have been carried out under UV radiation, since TiO$_2$ photocatalysts show relatively high activity and chemical stability under UV light (Yeber *et al.*, 2000) and absorbs only small portion of solar spectrum in UV region. Further, UV light accounts for the only small fraction (5%) of solar energy compared to visible light (45%), the technical use of TiO$_2$ is largely impaired. On the other hand, ZnO has approximately same band gap energy (3.2 eV) as TiO$_2$ and its photocatalytic capacity has been anticipated to be similar to that of TiO$_2$. Further, some studies have confirmed that ZnO exhibits more efficiency than TiO$_2$. The biggest advantage of ZnO is that, it absorbs over a larger fraction of the solar spectrum than TiO$_2$ (Behnajady *et al.*, 2006; Khodja *et al.*, 2001; Lizama *et al.*, 2002; Gouvea *et al.*, 2000).

With this background, the present work has been undertaken by synthesizing various new metal oxide semiconductor nanoparticles listed in Table 2, which have been
used for photocatalytic reactions. The VB and CB potentials, the band gap energy and wavelength required to activate the catalyst has been calculated by the Planck’s equation (Eq. 8).

\[ e = \frac{hC}{\lambda} \]

\( h \) = Planck’s constant, \( C \) = Velocity of light (speed of light), \( \lambda \) = wavelength of light

\[ h = 4.135 \times 10^{-15} \text{ eV}, \ C = 3 \times 10^8 \text{ m/s}, \ \lambda = \ldots \times 10^{-9} \text{nm} \]

Band gap energy (eV) = \( 4.135 \times 10^{-15} \times 3 \times 10^8 \times 10^9 \)

Band gap energy (eV) = \( \frac{1240}{\text{wavelength (nm)}} \) (Eq. 8)

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Band gap Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.2</td>
</tr>
<tr>
<td>CaAl₂O₄-I</td>
<td>2.8</td>
</tr>
<tr>
<td>CaAl₂O₄-II</td>
<td>2.7</td>
</tr>
<tr>
<td>CaZnO₂-I</td>
<td>2.5</td>
</tr>
<tr>
<td>CaZnO₂-II</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 2: Semiconductor photocatalysts
The present research work is focused on the development of solar active semiconductor photocatalysts with high azo dye degradation efficiency under visible light range of the solar spectrum. In the view of forgone observations, the present research work was aimed at the following objectives:

- Synthesis and characterization of nanoparticles such as ZnO, CaAl$_2$O$_4$-I, CaAl$_2$O$_4$-II, CaZnO$_2$-I and CaZnO$_2$-II.
- Application of these nanoparticles in the degradation of industrial dyes such as Violet GL2B and Coralene Dark Red 2B.
- Application of the synthesized nanoparticles in the degradation of textile coloured effluent.
- Analyzing the efficiency of these nanoparticles against the procured TiO$_2$ in the degradation of industrial dyes Violet GL2B, Coralene Dark Red 2B and textile effluent collected from Himatsingka Linens, Hassan.
- Investigation of influencing parameters i.e., catalyst dosage, effect of pH and dye concentration on the degradation efficiency using a standardized protocol.

Thus, the present thesis comprises of eight chapters. Each chapter has been further divided into sub chapters, sections and sub-sections as per the requirement.

Chapter-I deals with the general introduction and problems associated with industrial dyes, dyes and their intermediates, their classification, environmental concern. Azo dyes and their properties. Also, the pollution aspect of the azo dyes and their toxicity are discussed. Further, it also highlights on physico-chemical characterization of the dye effluents, treatment of dye effluents and methods to remove the dyes from wastewater using new advanced oxidation process.
Chapter-II reports the review of literature pertaining to photocatalytic degradation of industrial dyes and coloured effluents.

Chapter-III explains the materials and methods adopted for the studies.

Chapter-IV is devoted to the synthesis and characterization of \( \text{ZnO, CaAl}_2\text{O}_4\text{-I, CaAl}_2\text{O}_4\text{-II, CaZnO}_2\text{-I and CaZnO}_2\text{-II nanoparticles by using urea and acetamide as fuels.} \)

Chapter-V describes the photocatalytic activity of all the synthesized \( \text{ZnO, CaAl}_2\text{O}_4\text{-I, CaAl}_2\text{O}_4\text{-II, CaZnO}_2\text{-I and CaZnO}_2\text{-II nanoparticles and comparing their efficiency with the procured TiO}_2\text{ against the Violet GL2B an industrial dye in the presence of solar radiation.} \)

Chapter-VI reports photocatalytic activity of all the synthesized \( \text{ZnO, CaAl}_2\text{O}_4\text{-I, CaAl}_2\text{O}_4\text{-II, CaZnO}_2\text{-I and CaZnO}_2\text{-II nanoparticles and comparing their efficiency with the procured TiO}_2\text{ against the industrial dye Coralene Dark Red 2B in the presence of solar radiation.} \)

Chapter-VII describes the efficiency of photocatalytic activity of all the synthesized \( \text{ZnO, CaAl}_2\text{O}_4\text{-I, CaAl}_2\text{O}_4\text{-II, CaZnO}_2\text{-I and CaZnO}_2\text{-II nanoparticles and comparing their efficiency with the procured TiO}_2\text{ against the selected coloured effluent in the presence of solar radiation.} \)

Chapter-VIII deals with the overall conclusion of the work and recommendations for the further line of work.