Chapter I
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Introduction

1.1 Introduction

Water is one of the most important commodities which man has exploited than any other resource for the sustenance of life. The quantity of this utilizable water is very much limited on earth. Though, water is continuously purified by evaporation and precipitation, pollution of water has emerged as one of the most significant environmental problems in recent times [1]. The pollution of water has caused by both organic and inorganic substances depending on the source of generation. One of the main current concerns in environmental sciences is the increasing occurrence of organic wastewater contaminants in the natural water environment. The problem was first identified in the late seventies, and throughout the last twenty-five years, there have been an increased number of reports on the presence of these chemical compounds in natural water systems. The concentrations measured range from the order of a few nanograms per liter in surface waters to a few micrograms per liter in wastewater effluents. For most substances, such concentrations do not pose an immediate threat to the environment and human health but are alarming because the effects and fate of these anthropogenic chemicals in the environment are not clearly understood. The most important sources of organic matter in water are the disposal of municipal sewage, industrial waste water, urban and rural run off and the detritus formed by indigenous primary and secondary production. The principal type of industry which contribute to water pollution in India are chemical and pharmaceuticals, coal washeries, soap and detergents, pulp and paper, sugar, distilleries, dyeing, tanneries, steel mills, fertilizers etc., [2]. The industries like food processing, dairy, paper and pulp, sugar, distilleries, breweries, tanneries, textile and others have considerable quantities of organic matter of varying nature beside other pollutants. Also there are certain chemical industries like dyes pigment manufacturing, polymer and pesticides whose waste water containing organic compounds which are either slowly biodegradable or resistance to biological treatment [3].

The release of these effluents into the water bodies which are rich in organic load bring about adverse effect on the aquatic organisms and degrade the quality
of water to render it unfit for a variety of uses. It also brings about characteristic changes in the bodies of water which can range from simple aesthetic to complex chemical and biochemical effects [4]. The removal of such hazardous pollutants from its sources of generation is necessary to protect public health and environment. To overcome this conventional microbiological degradation needs the assistance of new technologies to degrade hazardous persistent materials by chemical oxidation, like advanced oxidation processes.

1.2 Advanced Oxidation Processes (AOP)

It refers to a set of chemical treatment procedures designed to remove organic and inorganic materials in waste water by oxidation. It involves in-situ generation of highly potent oxidants such as the hydroxyl radical (OH’), which have recently emerged as an important class of technologies for accelerating the oxidation and hence destruction of a wide range of organic contaminants in polluted water and air [4].

1.2.1 Hydrogen Peroxide/Ozone (H₂O₂/O₃)

When O₃ is added to water, it participates in a complex chain of reactions that result in the formation of radicals such as the hydroxyl radical (OH’) and the superoxide radical (O₂‘) [5]. When H₂O₂ is added with this reaction, H₂O₂ combines with ozone to enhance the transformation of O₃ to OH’ in solution. H₂O₂ is a weak acid, which partially dissociates into the hydroperoxide ion (HO₂¯) in water. H₂O₂ reacts slowly with O₃, whereas the HO₂¯ ion can rapidly react with O₃ to form OH’ [6].

\[
\begin{align*}
H₂O₂ + H₂O & \rightarrow HO₂¯ + H₃O⁺ \\
O₃ + HO₂¯ & \rightarrow OH’ + O₂¯ + O₂
\end{align*}
\]

(1.1)  
(1.2)

1.2.2 Ozone/UV (O₃/UV)

Due to the relatively high molar extinction coefficient of ozone, LP-UV or MP-UV (LP- low power, MP- medium power) radiation can be applied to ozonated water to form highly reactive hydroxyl radicals [7]. The use of UV irradiation whether MP-UV, LP-UV, or P-UV to produce hydroxyl radicals with ozone occurs by the following reaction.
O₃ + H₂O $\xrightarrow{\text{hv}}$ O₂ + H₂O₂ ($\lambda < 300$ nm) \hfill (1.3)

2O₃ + H₂O₂ $\rightarrow$ 2 OH⁺ + 3O₂ \hfill (1.4)

As the above reactions illustrate, photolysis of ozone generates hydrogen peroxide and thus, O₃/UV involves all of the organic destruction mechanisms present in H₂O₂/ O₃ and H₂O₂/ UV AOPs. These mechanisms include direct reaction with ozone, direct photolysis by UV irradiation, or reaction with hydroxyl radicals [8]. Previously O₃/UV, LP-UV lamps were used extensively [8, 9]. However, MP-UV and P-UV are receiving increased attention due to their disinfection capabilities and direct photolysis benefits.

1.2.3 Hydrogen Peroxide/UV (H₂O₂/UV)

As in the O₃/UV process, the effectiveness of the H₂O₂/UV process relies on several synergistic oxidation mechanisms for the destruction of organics. The oxidation of organics can occur by either direct photolysis or reactions with hydroxyl radicals. Hydroxyl radicals are produced from the photolytic dissociation of H₂O₂ in water by UV irradiation [7, 9]. As in the O₃/UV and H₂O₂/O₃ systems, the degradation of organics is primarily due to the oxidation reactions initiated by the highly reactive hydroxyl radicals.

H₂O₂ $\rightarrow$ 2 OH⁻ ($\lambda < 300$ nm) \hfill (1.5)

OH⁻ + Organics $\rightarrow$ Oxidation by-products \hfill (1.6)

1.2.4 E-beam Treatment

E-beam treatment refers to the use of ionizing radiation from an electron beam source to initiate chemical changes in aqueous contaminants. In contrast to other forms of radiation, such as infrared and UV, ionizing radiation from an E-beam is absorbed almost completely by the electron orbitals of the targeted compounds, thus increasing the energy level of its orbital electrons. The energy level of radiation is sufficiently high to produce changes in the molecular structure of compounds, but is too low to induce radioactivity [10, 11]. Electron beam processes use the portion of the electromagnetic spectrum between 0.01 eV and 10 eV. Within 10⁻¹⁶ to 10⁻¹² seconds, E-beam irradiation (^^^) of water results in the formation of electronically excited species, including ions and free radicals along the path of the electrons. The products of direct reactions of water molecules with
the electron beam are formed in isolated volumes referred to as “spurs.” As these spurs expand through diffusion, a fraction of the initial products escape into the bulk solution and transfer their energy to other aqueous chemical species, causing more reactions to occur [12]. After approximately $10^{-7}$ s, oxidizing species, such as hydroxyl radicals, and reducing species, such as aqueous electrons and hydrogen atoms, are formed from the E-beam irradiation of water [12, 13]. The net reaction is shown below.

$$\text{H}_2\text{O} + ^{^\text{2.7}}\text{OH}^- + 0.6 \text{O}^-\text{e}_{\text{aq}}^- + 0.45 \text{H}_2 + 2.6 \text{H}_3\text{O}^+ \quad (1.7)$$

The combination of products that result from this reaction creates a unique environment where oxidizing and reducing reactions occur simultaneously [13]. The oxidizing species, OH⁻, and the reducing species, e⁻aq, are expected to be present in similar steady state concentrations. These two species, along with another reducing species, the hydrogen atom (H⁻), are the most reactive products of this reaction and control the rate of the electron beam process for organic destruction.

1.2.5 Cavitation

As in other AOPs, the primary mechanism for organic removal by cavitation is through reaction with hydroxyl radicals. Cavitation occurs in liquid when bubbles form and implode in pump systems or around propellers. The rapid implosion of cavitation micro-bubbles results in high temperature at the bubble/water interface, which can trigger thermal decomposition of the organics in solution or thermal dissociation of water molecules to form extremely reactive radicals. The extreme conditions generated during cavitation decompose water to create both oxidizing (OH⁻) and reducing (H⁻) radical species [14, 15]. There are three methods of producing hydroxyl radicals using cavitation - namely, ultrasonic irradiation or sonication, pulse plasma cavitation, and hydrodynamic cavitation. Sonication causes the formation of micro-bubbles through successive ultrasonic frequency cycles until the bubbles reach a critical resonance frequency size that results in their violent collapse [15, 16]. Pulse plasma cavitation utilizes a high voltage discharge through water to create micro-bubbles. In hydrodynamic cavitation, micro-bubbles are generated using high velocity or pressure gradients [17-21]. The production of OH⁻ through cavitation processes can be enhanced with the use
of ozone. Gas-phase ozone thermally decomposes in the micro-bubbles, yielding oxygen atoms and molecular oxygen. This results in a number of reactions that subsequently yield hydroxyl radicals [15].

\[
\begin{align*}
O_3 + H_2O & \rightarrow O_2 + 2 OH^- \quad (1.8) \\
O_3 + OH^- & \rightarrow HO_2^- + O_2 \quad (1.9) \\
O_3 + HO_2^- & \rightarrow OH^- + O_2^- + O_2 \quad (1.10)
\end{align*}
\]

1.2.6 Fenton’s Reaction

Hydrogen peroxide reacts with iron (II) to form Fenton’s reagent (an unstable iron-oxide complex) that subsequently reacts to form hydroxyl radicals (Fenton, 1894) [22].

\[
\begin{align*}
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH^- + OH^- \quad (1.11)
\end{align*}
\]

This reaction can occur either in homogeneous system with dissolved ferrous iron or in heterogeneous systems in the presence of complexed iron such as goethite (FeOOH). The by-product ferric iron in turn reacts with peroxide or superoxide (O$_2^-$) radical to reproduce ferrous iron.

\[
\begin{align*}
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + O_2^- + 2H^+ \quad (1.12) \\
O_2^- + Fe^{3+} & \rightarrow Fe^{2+} + O_2 \quad (1.13)
\end{align*}
\]

In the above three reaction cycles H$_2$O$_2$ is fully consumed producing OH$^-$ in the process.

1.2.7 Photocatalytic Oxidation

Heterogeneous photocatalysis in the presence of semiconductor materials [23 – 26] is an advanced oxidation process developed in these last years. This new method has shown to be effective for the oxidation of a lot of organic and inorganic compounds under mild temperature and pressure conditions with a measurable rate upto negligible concentration levels. Among its relevant applications [27 – 29] the main one is related to the degradation of environmental pollutants present in water and air. During the photocatalytic oxidation hydroxyl and hydroperoxyl radicals are produced by the semiconductor surface when irradiated to light in contact with water [33-34]. The electrons in the
semiconductor surface gets excited when exposed to the UV photons which will make the electrons to move from the valence band to the conduction band. During this process free electrons (e\textsuperscript{−}) will be available in the conduction band and electron-deficient holes (h\textsuperscript{+}) are created in the valance band. Equations 1.14-1.19 are the main reactions that take place on the semiconductor surface when exposed to UV light. Water is absorbed on to the surface of the semiconductor resulting in the formation of H\textsuperscript{+} and OH\textsuperscript{−} ions as given in Eq.1.14 and 1.15. Hydroxyl radicals are produced by the oxidation of water (Eq.1.16) or oxidation of hydroxyl ions (Eq.1.17), where hydroperoxyl radicals are obtained from the superoxide anion (O\textsubscript{2}−) as given in Eq. 1.18 and 1.19.

\[
\begin{align*}
2\text{H}_{2}\text{O} + 4\text{h}^+ & \rightarrow 4\text{H}^+ + \text{O}_2 & (1.14) \\
2\text{H}_{2}\text{O} + 2\text{e}^- & \rightarrow 2\text{OH}^- + \text{H}_2 & (1.15) \\
\text{H}_2\text{O} + \text{h}^+ & \rightarrow \text{OH}^+ + \text{H}^+ & (1.16) \\
\text{OH}^- + \text{h}^+ & \rightarrow \text{OH}^* & (1.17) \\
\text{O}_2 + \text{e}^- & \rightarrow \text{O}_2^- & (1.18) \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2^- & (1.19)
\end{align*}
\]

Various semiconductor materials (for example, TiO\textsubscript{2}, ZnO, Fe\textsubscript{2}O\textsubscript{3}, CdS, ZnS, and so on) have been tested as photocatalysts. However, as a result of different problems mainly related to the photocatalyst stability under irradiation in water, it is generally accepted that TiO\textsubscript{2} in anatase form is the most reliable material for wastewater treatment [29-32]. TiO\textsubscript{2} shows low-cost and high-photostability. Aqueous suspensions of this semiconductor can be activated by radiation with wavelength lower than 380 nm and in this situation a lot of redox reactions can occur at the catalyst surface.

During 1839, Becquerel reported that when a silver chloride electrode immersed in an electrolyte solution which was connected to a counter electrode, was illuminated to sunlight, the voltage and an electric current were produced [35]. Later in 1955, Brattain and Garret worked on germanium semiconductor electrodes, which gave rise to the photovoltaic phenomenon called the “Becquerel effect”, from which the new era of photoelectrochemistry came into existence [36]. In 1972 photocatalytic splitting of water on the TiO\textsubscript{2} electrode surface was
discovered by Fujishima and Honda which was called as “Fujishima and Honda effect” from where the new era of heterogeneous photocatalysis started [35]. In recent years lots of work on the heterogeneous photocatalysis has been carried out and their application in different fields has been studied.

The industrial effluents can be treated efficiently by biological processes because, it contains nutrients for microorganisms in sufficient quantities. Biological treatments like Activated Sludge Process (ASP) and Trickling Filter (TF) require high cost techniques, while Oxidation Ditch, Aerated Lagoon, Stabilization Ponds are the low cost methods. These conventional treatment methods do not degrade the effluent up to the limit it can be recycled and also require detention time of several days. However, photocatalytic detoxification is a process where a semiconductor upon adsorption of a photon acts as a catalyst in producing reactive radicals, mainly hydroxyl radicals, which in turn can oxidize organic compounds and totally neutralize them. It completely destroys the organic and inorganic compounds in the water instead of simply removing or displacing them. Since the Photocatalytic Detoxification (DF) Process is driven by light, outdoor facilities can be constructed that make use of a free source of energy received from the sun. The combination of light and catalysts has proven very effective for water purification. Photocatalytic oxidation, using solar energy as a photon source, was demonstrated in the mid-1980s by Ahmed and Ollis [37]. The use of solar radiation for the photocatalytic oxidation of organic contaminants in waste water is fast developing application [38-41]. In some cases, such as removal of color and reduction of chemical oxygen demand (COD) in industrial wastewater, photocatalytic oxidation may be the only environmentally benign effective treatment available [42].

1.3 Scope of the Thesis

The scope of this research work is the hydrothermal preparation and the characterization of photocatalytic compounds. To investigate the application of these photocatalytic compounds in the photodegradation of a few hazardous organic molecules like dye stuffs and some selected industrial effluents. Although research on photocatalytic methods of organic destruction is a topic of vast interest for the past few decades, it seems to be an interesting area of study till date. The impregnation of photocatalytic materials onto solid supports and
introducing the foreign materials or the metal oxide into the semiconductor to alter the band energy of the semiconductor is an advanced and thirsty area of study in the present day research, which is the focus of the present thesis. The study is based on the degradation of various textile dyes like, indigo carmine, cibacron yellow dye, fast green dye, amaranth dye and industrial effluents like textile, silk, distilleries, and pharmaceutical industries.

Important parts of the study are:

- Hydrothermal preparation of some selected fine photocatalytic composites like (1:1) TiO$_2$: CNT, ZnO: CNT, TiO$_2$: MoO$_3$, ZnO: MoO$_3$ composites; metal oxide doped ZnO compounds; W$^{+6}$:TiO$_2$ and Ti$^{+4}$: AlPO$_4$. Also attempts to produce cost effective designer photocatalytic materials with higher efficiency. The study of the effect of pressure and temperature conditions, pH of the starting media, type of the solvent, metal oxide source, experimental duration, etc., on products obtained.

- Characterization of the prepared photocatalytic materials by XRD, SEM, FTIR, DLS, Photoluminescence spectroscopy and UV- VIS spectroscopy.

- To investigate the photocatalytic efficiency of the prepared catalysts by studying the degradation of various model dye compounds and also to study the degradation efficiency in the treatment of real time industrial effluents.

- To study the effect of these prepared photocatalytic compounds under various rate determining parameters like initial dye concentration, amount and type of the catalyst, pH of the aqueous medium, intensity and type of the illuminating light and the solution temperature on the degradation.

- To propose the complete degradation mechanism for the model compounds considered in the degradation studies.

- To conclude the study by highlighting the efficiency of the technology in the destruction of organics.

Chapter 1 starts with a general introduction of “water” and the causes of water pollution. It also describes the need for an Advanced oxidation processes (AOP) in the destruction of pollutants and also describes various AOP in brief.
Chapter 2 gives detailed information of photocatalyst, its history, fundamentals and principles of photocatalysis, photocatalytic materials, supports in photocatalysis, doping of a photocatalytic material, applications of photocatalysis, comparison of AOP’s, materials employed for the preparation of photocatalytic materials and various techniques used in the preparation of photocatalytic material.

Chapter 3 describes the various reagents employed in the present work, hydrothermal apparatus used in the preparation of potocatalytic compounds and a brief description of the instruments used in the characterization of the prepared samples.

Chapter 4 explains the application of hydrothermal technique in the present work and the experimental methodology employed in the preparation of highly efficient photocatalytic compounds. The characterization of the photocatalytic compounds prepared and discussion are given in detail.

Chapter 5 covers the experimental results of the photocatalytic degradation of dyes like Indigo Carmine, Fast Green and Cibacron Yellow and industrial effluents using the photocatalytic compounds prepared. A focus is given to understand the photodegradation reaction with respect to time, light source, catalyst loading and pH. A detailed step-by-step probable reaction mechanism for the degradation of the dyes has been described.

Chapter 6 gives conclusions based on the present work. Highly efficient designer photocatalytic materials like TiO$_2$, ZnO and hybrid photocatalytic materials like (1:1) TiO$_2$: CNT, ZnO: CNT, TiO$_2$: MoO$_3$, ZnO: MoO$_3$ composites and metal oxide doped ZnO compounds, W$^{5+}$:TiO$_2$, Ti$^{4+}$: AlPO$_4$ etc., can be prepared under mild hydrothermal conditions. The photocatalytic degradation of various dyes like Indigo Carmine, Fast Green and Cibacron Yellow and various industrial effluents has been studied in detail using the as-prepared photocatalytic materials.
Reference

5. J. Hoigne, H. Bader, Water Research, 10 (1976) 377-386