I

Introduction
CHAPTER I

INTRODUCTION

It is true that water existed on this planet long before life first evolved and that all the complex chemical processes involved in the development and maintenance of living organisms are therefore sensitively attuned to physical properties of liquid water. Indeed, water is described as the matrix of life.

Since a long time, natural processes have not been able anymore, to rectify the environmental load caused by the ever-increasing world population and industrialization. Water reserves are the main issue of interest, because pollution from both the atmosphere and soil will eventually enter the aqueous phase by deposition and percolation respectively.

Sources of pollution are both natural and manmade. Pollution by mankind is caused by e.g. nutrition, transportation, accommodation, synthesis and energy exploitation. Although probably not always acknowledged, chemical activity is indispensable to sustain life; also it needed to comply with a high standard of living. Examples are medicaments, cleaning and disinfecting products, cosmetics, stabilizers, artificial fertilizers, pesticides, fuel, batteries, polymers (thermoplastics, thermosetting resins, elastomers, fibers, etc), paints and dyes.

Both synthesis and application of these products cause environmental pollution. In addition to biological wastes like carbohydrates, proteins, urea, fats, food and vegetation residues and carbon dioxide, we also encounter priority compounds like hazardous organics. These materials exhibit carcinogenic, mutagenic and/or teratogenic properties, which implies that a no-effect-level in fact does not apply for these compounds. In addition, priority compounds can be highly persistent.

The immediate and nuisance-free removal of such hazardous pollutants from its sources of generation, followed by treatment, reuse, or dispersal into the environment is necessary to protect public health and environment. Conventional microbiological degradation desperately needs the assistance of new technologies, like for instance
advanced oxidation processes, to degrade hazardous persistent materials by chemical oxidation.

1.1 Advanced oxidation processes

Advanced Oxidation Processes (AOP) aim at the in-situ production of strong oxidizers. The strongest oxidizers known are xenonfluoride (XeF) and possibly H₄RnO₆, but these oxidizers are not commercially attractive for water treatment because, of both extreme reactivity and remaining toxicity in reduced form. Also, halogen-based oxidizers are not acceptable as oxidizer, because they halogenate organic materials to e.g. trihalomethanes [2], which are very harmful compounds; in addition their reaction leads to salt formation. It is obvious, that metal-based oxidizers like permanganate (MnO₄⁻) and dichromate (Cr₂O₇²⁻) also are not desirable. Of interest are thus oxygen based halogen/metal-free oxidizers like the hydroxyl (OH), atomic oxygen (O), ozone (O₃) and hydrogen peroxide (H₂O₂).

Next, a concise description is presented for major AOP with regard to the generation of oxygen-based halogen-free oxidizers, particularly hydroxyl radicals.

1.1.1 Ozone-UV oxidation

In the ozone-UV technology [3, 4], hydroxyl radicals are produced from ozone, water and UV photons; high-pressure mercury or xenon lamps deliver the photons, see Equation 1.1.

\[ \text{O}_3 + \text{H}_2\text{O} + \text{hv} \rightarrow 2\cdot\text{OH} + \text{O}_2 \quad \nu \leq 310 \text{ nm} \quad (1.1) \]

Ozone is produced on location by an ozonizer, which converts atmospheric or pure oxygen into ozone by corona discharges [4, 5]. These electrical discharges are produced in a barrier discharge electrode setup, where the electrodes are separated by a dielectric material e.g. glass or ceramic at a thickness of about 0.5-3 mm. Commercial ozone generators are based on different electrode configurations, e.g. fluid-cooled shell and tube type generators for generation of large ozone amounts and air-cooled plate type generators for small amounts. Cooling is very important, to prevent decomposition of ozone.
1.1.2 Hydrogen peroxide-UV and Fenton oxidation

Hydrogen peroxide is decomposed by UV photons into hydroxyl radicals [6], see Eq. 1.2a. Also, the reaction of hydrogen peroxide with iron (II) ions produces hydroxyl radicals; this reaction is known as the Fenton reaction (Eq. 1.2b) [7]. In addition, Fe(III) ions contribute to hydroxyl radical formation by Eq. 1.3c/d (Fenton like reaction) and indirectly by regeneration of Fe(II).

\[
\begin{align*}
H_2O_2 + \text{hv} & \rightarrow 2'OH & 250 \text{ nm} < \text{v} > 300 \text{ nm} \\
Fe^{2+} + H_2O_2 & \rightarrow 'OH + OH^- + Fe^{3+} \\
Fe^{3+} + OH^- & \rightarrow Fe(OH)^2+ \\
Fe(OH)^2+ + \text{hv} & \rightarrow 'OH + Fe^{2+} & \text{v} = 350 \text{ nm}
\end{align*}
\]

(1.2a) (1.2b) (1.2c) (1.2d)

1.1.3 Wet oxidation

In wet oxidation, water with dissolved oxygen is used to oxidize the target compound [8, 9]. The process can be performed at subcritical (4 Mpa < P < 20 Mpa, 513 K < T < 593 K) or supercritical conditions (P > 22.1 Mpa, T > 647 K). These conditions enable optimal solubility of oxygen and organic compounds in water. Equations 1.3a-h are the main reactions. Hydroxyl radicals are produced from the dissociation and oxidation of water (Eq. 1.3a,b). Hydroperoxyl radicals are formed from the oxidation of water (Eq. 1.3b) and the target compound RH (Eq. 1.3f). Hydroxyl radicals are also produced from hydrogen peroxide (Eq. 1.3d) and from the reaction of atomic oxygen with the target compound (Eq. 1.3h). Hydrogen peroxide is produced by recombination of hydroperoxyl radicals (Eq. 1.3c) or by reaction of hydroperoxyl radicals with target compound (Eq. 1.3g). Atomic oxygen is produced from the dissociation of oxygen (Eq. 1.3e). Although the hydroperoxyl radical is less reactive than the hydroxyl radical, it plays an important role because of its relative abundance.

\[
\begin{align*}
H_2O & \rightarrow 'OH + H \\
H_2O + O_2 & \rightarrow 'OH + HO_2 \\
2HO_2 & \rightarrow H_2O_2 + O_2 \\
H_2O_2 & \rightarrow 2'OH
\end{align*}
\]

(1.3a) (1.3b) (1.3c) (1.3d)
1.1.4 Radiolysis

Irradiation of water by high-energy photons or electrons dissociates water molecules into hydroxyl radicals and hydrogen atoms or ionizes water molecules, see Eq. 1.4a,b [10, 11]. Ionized water molecules react with water to produce hydroxyl radicals, see Eq. 1.4c. By saturation of water with nitrous oxide (N₂O), solvated electrons (Eq. 1.4d) are converted into hydroxyl radicals (Eq. 1.4e). Also the target compound is dissociated or ionized. Halogenated target compounds RXn react rapidly with solvated electrons, see Eq. 1.4f. High-energy photons are obtained from a radioactive source (60Co-γ) and electrons are produced by an electron beam accelerator or a Van de Graaff generator.

\[ \text{O}_2 \rightarrow 2\text{O} \]  
\[ \text{RH} + \text{O}_2 \rightarrow \text{R} + \text{HO}_2 \]  
\[ \text{RH} + \text{HO}_2 \rightarrow \text{R} + \text{H}_2\text{O}_2 \]  
\[ \text{RH} + \text{O} \rightarrow \text{R} + \cdot\text{OH} \]  
\[ \text{RH} + \text{O}_2 \rightarrow \text{R} + \cdot\text{OH} \]  
\[ \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H} \]  
\[ \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + e^- \]  
\[ \text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \cdot\text{OH} \]  
\[ e^- + \text{H}_2\text{O} \rightarrow e_{aq}^- \]  
\[ \text{N}_2\text{O} + e_{aq}^- + \text{H}_2\text{O} \rightarrow \text{N}_2 + \cdot\text{OH} + \text{OH}^- \]  
\[ \text{RXn} + e_{aq}^- \rightarrow \text{RXn}^- + \text{X}^- \]

1.1.5 Ultrasonic irradiation

The introduction of ultrasonic energy into a liquid causes electrohydraulic cavitation [12, 13]. The applied frequency range is from 15 KHz up to 1 MHz. The generation of ultrasound energy can be performed by electromechanical (piezoelectric or magnetostrictive) or liquid-driven (liquid whistle = low intensity) transducers. The cavitation process involves the oscillation of the radii of pre-existing gas cavities by the periodically changing pressure field of the ultrasonic waves. The rapid implosion of the eventually instable gas bubbles causes adiabatic heating of bubble vapour phase. In this way, localized and transient high temperatures and pressures are reached, e.g. P>300 bar.
and T>3300 K in aqueous solution. These vigorous conditions invoke dissociation and pyrolysis of the liquid phase molecules and present target compounds. Water will be dissociated into hydroxyl radicals and hydrogen atoms, see Eq. 1.5a. Organic compounds are dissociated into radicals (Eq. 1.5b,c) and functional groups like carboxyl and nitro groups are removed see Eq. 1.5d,e.

\[
\begin{align*}
H_2O & \rightarrow \cdot OH + H \\
AB & \rightarrow A + B \\
RXn & \rightarrow RXn-1 + X \\
RCOOH & \rightarrow RH + CO_2 \\
RNO_2 & \rightarrow RO + NO
\end{align*}
\]

1.1.6 Electrical discharges

The discharge of electric energy into a dielectric medium may cause dissociation, ionization and excitation of the dielectric molecules or atoms [14]. Depending on the energy input, the produced plasma is non-thermal or thermal. In the thermal plasmas the ionization level is very high, about 10^{-2}. Examples of thermal electrical discharges are lighting and arc discharges. Corona and glow discharges are non-thermal plasmas. Their ionization level is very low, about 10^{-6}. Corona discharges in water produce hydroxyl radicals and hydrogen atoms from the dissociation and ionization of water molecules see Eq. 1.6a-c. Other than the cited reactions below, many other possible reactions exist [15].

\[
\begin{align*}
H_2O + e^- & \rightarrow \cdot OH + H + e^- \\
H_2O + e^- & \rightarrow H_2O^+ + 2e^- \\
H_2O^+ + H_2O & \rightarrow H_3O^+ + \cdot OH
\end{align*}
\]

1.1.7 Photocatalytic oxidation

Photocatalytic oxidation produces hydroxyl and hydroperoxyl radicals at an irradiated semiconductor surface in contact with water [16, 17]. Excitation of electrons in the semiconductor surface layer by UV photons will promote electrons from the valence band to the conduction band. In this way electron-deficient holes (h^+) are created in the
valance band and free electrons (e⁻) will be available in the conduction band. Equations 1.7a-f are the main reactions that take place at the irradiated semiconductor surface. Water is absorbed on to the surface, resulting in the formation of H⁺ and OH⁻ ions, see Eq 1.7a, b. Hydroxyl radicals are produced by the oxidation of water (Eq 1.7c) or oxidation of hydroxyl ions (Eq 1.7d), while hydroperoxyl radicals are obtained from the superoxide anion (O₂⁻), see Eq 1.7e, f:

\[
\begin{align*}
2H₂O + 4h⁺ &\rightarrow 4H⁺ + O₂ \quad (1.7a) \\
2H₂O + 2e &\rightarrow 2OH⁻ + H₂ \quad (1.7b) \\
H₂O + h⁺ &\rightarrow OH⁻ + H⁺ \quad (1.7c) \\
OH⁻ + h &\rightarrow OH⁻ \quad (1.7d) \\
O₂ + e⁻ &\rightarrow O₂⁻ \quad (1.7e) \\
O₂ + H⁺ &\rightarrow HO₂ \quad (1.7f)
\end{align*}
\]

Some practical semiconductors are titanium oxide (TiO₂), zinc oxide (ZnO) and cadmium sulfide (CdS). The most well known is the anatase TiO₂.

Looking into the past glory of the semiconductor photochemistry, in 1839, Becquerel [18] reported that a voltage and an electric current were produced when a silver chloride electrode, immersed in an electrolyte solution and connected to a counter electrode, was illuminated with sunlight. It was not until 1955, with the pioneering work of Brattain and Garret [19] on germanium semiconductor electrodes by which the origin of this photovoltaic phenomenon, called the "Becquerel effect," was understood and the modern era of photoelectrochemistry was born. Later way back in 1972 Fujishima and Honda discovered the photocatalytic splitting water on TiO₂ electrodes. This event marked the beginning of a new era in heterogeneous photocatalysis [18]. After this, an intensive work is being carried out in this area.

1.2. Thesis scope

The scope of this research work is the investigation of the applicability and technical feasibility of the photocatalytic degradation of a few hazardous organic molecules and some selected industrial effluents using the prepared hybrid photocatalytic materials.
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 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, rhodamine B, acid violet and pesticide like DDT and finally some selected real-time industrial effluents.

Key parts of the study are: (i) hydrothermal synthesis of some selected photocatalytic designer particulates like TiO$_2$ and ZnO, and also to understand various hydrothermal experimental parameters, which play an important role in the efficiency of the final product; (ii) to impregnate photocatalysts like TiO$_2$ and ZnO onto the surface of activated carbon by employing various hydrothermal conditions to obtain highly efficient hybrid materials; (iii) characterization of the prepared photocatalytic designer particulate materials by XRD, SEM, FTIR and Positron annihilation spectroscopy; (iv) to envisage the photocatalytic efficiency of the prepared catalysts by studying the degradation of various model dye compounds and also to extent its applicability in the treatment of real time textile effluents; (v) to study the effect of various rate determining kinetic 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; (vi) to propose the complete degradation mechanism for the model compounds considered in the degradation studies; (vii) to conclude the study by highlighting the efficiency of the technology in the destruction of organic.

Chapter 1 starts with a general introduction describing the potential of "water" and also describes the need for an advanced oxidation processes (AOP) in the destruction of pollutants. It also describes various advanced oxidation processes in brief.

Chapter 2 comprises three sections. In the first section a detailed description is presented with regard to the fundamentals and principals of photocatalysis, photocatalytic materials, supports in photocatalysis and applications of photocatalysis. The second describes a brief comparison of various AOP and the advantages of photocatalysis have been highlighted. In the third section the basics of activated carbon, its structure,
porosity, the phenomenon of adsorption and application has been discussed. An emphasis has been given to the usage of activated carbon as catalyst and photocatalyst support.

Chapter 3 describes the employed reagents, hydrothermal apparatus used in the synthesis and impregnation, a brief description of the instrumentation engaged in the characterization of the samples.

Chapter 4 explains the experimental methodology employed in the synthesis of designer particulates and preparation of highly efficient hybrid photocatalytic materials. Results and discussions of the characterization studies employed.

Chapter 5 represents the experimental results of the photocatalytic degradation of dyes and effluents. Sections 5.2 to 5.4 describe the degradation of textile dye indigo carmine, acid violet and rhodamine b respectively. A focus is given to understand the photodegradation reaction kinetics and to derive the order of the reaction. A detailed step-by-step probable reaction mechanism for the degradation of all the dyes has been described. In section 5.6 the preliminary study on the degradation of the DDT has been described. Under section 5.7, the degradation of various industrial effluents has been described.

Chapter 6. The conclusions are summarized in this chapter. Highly efficient designer photocatalytic materials like TiO₂, ZnO and hybrid photocatalytic materials like TiO₂:AC and ZnO:AC could be synthesized by mild hydrothermal conditions. The photocatalytic degradation of various dyes like indigo carmine, acid violet, rhodamine B, pesticide like DDT and various textile effluents has been studied in detail using the as-prepared designer/composite materials.
References

5. R. E. Kirk, D. F. Othmer, Encyclopedia of Chemical Technology