Chapter 1

Introduction
1.1. General

The increased applications of fertilizers, pesticides and herbicides in modern agriculture and related fields and the ever-expanding chemical industry resulted large amounts of chemical waste materials disposed in rivers, seas and ocean. The major consequence of such increased use of pollutant chemicals is that water resources become heavily charged with pollutants. New technologies are being developed in the past few years for the destruction of hazardous organic chemicals that pollute drinking water. Major contaminants which persist in water and cause many ecological problems include pesticides, herbicides, dyes, detergents and a wide variety of industrial effluents. The conventional methods used for the purification of drinking water such as flocculation, filtration, sterilization, reverse osmosis and adsorption on activated carbon have proved to be inadequate to degrade the stable aromatic ring of these pollutants. Direct photodegradation under sunlight and biodegradation have little effect on most of these pollutants and those with sufficient solubility in water are capable of penetrating deep into soil and even reach ground water.

The behavior of triazine derivatives in environment is gaining vital importance since many of these are widely used as herbicides. Techniques for the removal of triazine derivatives from ground and surface water constitute a major part of water purification research as these are extensively used as herbicides in many countries.\textsuperscript{1,2} Triazine derivatives are used for the prevention of growth of weeds in railway tracks in western countries and also in gardens, lawns \textit{etc.}\textsuperscript{3} S-triazine herbicides are commonly used to control broad leaf and grass weeds in corn and other crops.\textsuperscript{4,5} The main mode of action of triazine herbicides is the disruption of the light reactions of
Chapter 1

photosynthesis. The maximum permissible concentration of triazines for human consumption is set to be 0.1 ppb. However, their concentrations have been reported to exceed this value in drinking water and hence their degradation studies in aqueous medium are of vital importance. Almost all triazines absorb light of wavelength $\leq 250$ nm and hence cannot be directly photolysed by exposure to sunlight. Decontamination processes using microorganisms like bacteria are relatively very slow and are therefore almost inefficient in the case of triazines and thus they persist in soil resulting in the contamination of drinking water. Similar to other pollutants, the conventional methods used for the decontamination of wastewater are not effective in the case of triazines and hence more work is being concentrated for the development of new technologies for their complete degradation.

1.2. Advanced Oxidation Processes (AOPs)

The concept of advanced oxidation process was introduced first in 1987 by Glaze et. al. AOPs have been developed to detoxify non-biodegradable wastewater. In general, processes that generate the highly reactive radical, the hydroxyl radical ($^\cdot$OH) which is capable of oxidizing organic contaminants in water are named as AOPs. $^\cdot$OH is one of the most powerful oxidizing agents with $E^0$ 2.8V, which can attack organic molecules rather nonselectively, with rate constants ranging from $10^6$ to $10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$. Due to its high reactivity, $^\cdot$OH is very unstable and must be continuously generated in situ. The most widely studied homogeneous AOPs include H$_2$O$_2$/UV, ultrasound, O$_3$/UV, radiolysis of water and aqueous solutions under oxidizing conditions, Fenton reaction (Fe$^{II}$/H$_2$O$_2$) and photo-Fenton reaction (Fe$^{II}$/H$_2$O$_2$/UV). The most commonly used heterogeneous photocatalytic oxidation systems are TiO$_2$/UV and TiO$_2$/H$_2$O$_2$/UV.
The important measure of the success of an AOP is the extent of mineralization of target pollutants to CO$_2$ and inorganic ions as this denotes the overall destruction of possibly toxic organic intermediates in addition to the parent contaminant itself.\textsuperscript{14} One common problem with AOP is the high demand of electrical energy and UV-lamps, which increase the total cost of these processes. A very promising possibility of cost reduction is the application of sunlight for irradiation purposes.\textsuperscript{15}

Generally the presence of *OH scavengers in the reaction system will reduce the effectiveness of AOPs. If the organic contaminants themselves are subject to direct or sensitized photolysis which thus takes away a part of the incident intensity of light, the capability of AOPs will be diminished. Before selecting a particular AOP for a specific contaminant, the potential of different AOPs for that specific use has to be evaluated especially with regard to the cost-effectiveness among different AOPs as well as to conventional processes.\textsuperscript{13} AOPs can also be combined with other treatment methods to achieve optimum cost-effective results.

### 1.2.1. Hydrogen peroxide/ UV process

Although H$_2$O$_2$ is a strong oxidant (E$^0$ = 1.8 V at pH $\sim$ 0 and 0.87 V at pH = 14), oxidation by H$_2$O$_2$ alone is not effective for the purification of some polluted waters; for example, those containing chlorinated aromatic compounds.\textsuperscript{16} Utilization of UV light has proved to activate H$_2$O$_2$ and increase the efficiency of oxidation.

As early as in 1952, Hunt and Taube had proved that the primary process in the UV photolysis of H$_2$O$_2$ is the generation of two *OH.\textsuperscript{17} The molar extinction coefficient of H$_2$O$_2$ was determined as 19.6 dm$^3$mol$^{-1}$s$^{-1}$.\textsuperscript{18} Since 1960s, many studies have indicated that H$_2$O$_2$/UV process can oxidize a
wide variety of aqueous organic contaminants. The photolysis of H$_2$O$_2$ in pure water has been studied extensively since 1950.

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \quad (1.1) \]

\[ \text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (1.2) \quad k_{\text{H}_2\text{O}_2} = 2.7 \times 10^7 \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1} \]

\[ \text{HO}_2^- + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (1.3) \quad k = 6 \times 10^9 \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1} \]

\[ \text{HO}_2^- + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (1.4) \quad k = 8.3 \times 10^5 \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1} \]

It is clear from the above reaction that the highly oxidizing \( \cdot \text{OH} \) generated is responsible for the fast degradation of organic water pollutants. Because of the low extinction coefficient of H$_2$O$_2$, relatively higher molar ratios of H$_2$O$_2$ to substrates are recommended. However at very high H$_2$O$_2$ concentrations excess H$_2$O$_2$ will scavenge \( \cdot \text{OH} \) according to the following reaction,

\[ \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OOH} + \text{H}_2\text{O} \quad (1.6) \]

and thus decrease the \( \cdot \text{OH} \) concentration. Hence an optimum concentration of H$_2$O$_2$ relative to the concentration of substrates is to be used.

UV wavelengths of 200 – 280 nm can dissociate H$_2$O$_2$. Mercury lamps which emit at 254 nm are most commonly employed.

Advantages of H$_2$O$_2$/UV process are the cheap and easy-to-handle oxidant, its infinite solubility in water and simple reactor set-up. On the other side, the low value of absorption coefficient of H$_2$O$_2$ and low quantum efficiency of \( \cdot \text{OH} \) production at \( \lambda > 250 \) nm result in a low overall efficiency of the process.
1.2.2. Fenton reaction

In 1894, Henry John Horstman Fenton reported the oxidation of tartaric acid to dihydroxy maleic acid in the presence of low concentrations of ferrous salts and H$_2$O$_2$. Later he proved that this reagent could oxidize some other hydroxy acids also. Forty years later Haber and Weiss suggested that oxidation of ferrous ion by H$_2$O$_2$ generates *OH as the active intermediate.

According to Haber and Weiss,

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{FeOH}^{2+} + ^\cdot\text{OH} \] (1.7)

\[ ^\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^\cdot \] (1.8)

\[ \text{HO}_2^\cdot + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} + ^\cdot\text{OH} \] (1.9)

\[ \text{Fe}^{2+} + ^\cdot\text{OH} \rightarrow \text{FeOH}^{2+} \] (1.10)

Fenton’s reaction is given by the following reaction.

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + ^\cdot\text{OH} + \text{OH}^- \] (1.11) \[ k = 76 \text{ dm}^3 \text{ mol}^{-1}\text{s}^{-1} \]

In the absence of any added substrate *OH will oxidize a second molecule of ferrous ion as shown below.

\[ ^\cdot\text{OH} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- \] (1.12) \[ k = 3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1}\text{s}^{-1} \]

In the preceding years, various metal ions and their complexes in their lower oxidation states like Cu(I), Ti(III), Cr(II) and Co(II) were shown to have oxidative features similar to Fenton’s reagent. The mixtures of these metal compounds with H$_2$O$_2$ were named Fenton-like reagents. Later, organic peroxides were used in the place of H$_2$O$_2$ and the oxidation of the metal ion by ROOH yields alkoxyl radicals.

\[ \text{ROOH} + \text{M}^{n+} \rightarrow \text{M}^{(n+1)+} + \text{OH}^- + \text{RO}^\cdot \] (1.13)
Only in acidic conditions $^\cdot$OH can be the predominant active oxidant.\textsuperscript{41} The optimum pH range for the effective treatment by Fenton’s reagent is 3 to 3.5.\textsuperscript{42} At pH values below 3, the scavenging effect of H\textsuperscript{+} ion on $^\cdot$OH becomes severe. The drop in efficiency on the basic medium is due to the change of iron from a hydrated ferrous ion to a colloidal ferric species that decomposes H\textsubscript{2}O\textsubscript{2} to H\textsubscript{2}O and O\textsubscript{2} without forming $^\cdot$OH.\textsuperscript{41,42}

The $^\cdot$OH generated in the Fenton reaction can react with aqueous organic pollutants whereby intermediate radicals are produced which can be oxidized by Fe(III) or reduced by Fe(II) forming stable products. The reaction scheme can be represented as,\textsuperscript{41,43}

\begin{align}
RH + ^\cdot$OH & \rightarrow R^* + H\textsubscript{2}O \quad (1.14) \\
R^* + Fe\textsuperscript{3+} & \rightarrow \text{Product} + Fe\textsuperscript{2+} \quad (1.15) \\
R^* + Fe\textsuperscript{2+} & \rightarrow \text{Product} + Fe\textsuperscript{3+} \quad (1.16) \\
R^* + ^\cdot$OH & \rightarrow R$-$OH \quad (1.17)
\end{align}

The rate constants for the above reactions are substrate-specific.

The use of Fenton’s reagent to oxidize toxic organics began in late sixties. Now, there are several reports that show Fenton reaction can effectively be used for the destruction of several aqueous organic pollutants.\textsuperscript{24,44-56} The major advantages of Fenton’s reagent as a hazardous waste treatment technology are, (i) both iron and H\textsubscript{2}O\textsubscript{2} are cheap and non-toxic, (ii) there is no mass transfer limitation due to its homogeneous catalytic nature, (iii) there is no involvement of light so that the reactor design is much easier than UV-light systems.\textsuperscript{41} Free radical scavengers can inhibit the process. The reaction is also inhibited by phosphates, EDTA, formaldehyde, oxalic acid, citric acid, $etc.$, which can form iron chelates. Furthermore, in
cases where the oxidation products themselves react with Fe (II) and remove it from the reaction medium, rate of Fenton oxidation will be low.

An alternative interpretation of the Fenton reaction also exists from as early as 1932 that postulates the formation of a ferryl cation as shown below.\(^\text{57}\)

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{FeO}^{2+} + \text{H}_2\text{O} \quad (1.18)
\]

Some reports assume the initial Fe(II)-H\(_2\)O\(_2\) reaction to be a two-electron process to yield Fe\(^{IV}\)OH which in turn decomposes to Fe(III) and \(^*\text{OH}.\(^\text{57,58}\) In some cases the ferryl radical decomposes rapidly but in the presence of suitable ligands around iron \(e.g\). porphyrin rings, the Fe(IV) state might be stabilized sufficiently to become the primary oxidant which can oxidize organic compounds but in a way quite distinguishable from free \(^*\text{OH}.\(^\text{58}\)

From a detailed literature search in this area one can observe that the involvement of \(^*\text{OH} to a greater extent depends on the nature of the substrates and reaction conditions. Hence the favorable conditions where \(^*\text{OH is the major reactive species have to be clearly established for each reaction.\n
1.2.3. Photo-Fenton reaction

In Fenton reaction, Fe(III) ions get accumulated in the reaction medium and after all the Fe(II) ions are exhausted, the reaction practically stops. By irradiating the system with UV or UV-Visible light, the accumulated Fe(III) can be reduced to Fe(II)\(^\text{59-61}\) whereby the Fenton reaction can be made catalytic in iron.

\[
\text{Fe}^{3+} + \text{H}_2\text{O} \xrightarrow{hv} \text{^*OH} + \text{Fe}^{2+} + \text{H}^+ \quad (1.19)
\]
Thus the efficiency of dark-Fenton reaction can be increased in both ways, one by generating an additional \( ^\bullet \text{OH} \) in the above step and the other by recycling Fe(II).

Photo-Fenton process gives optimum results at pH around 3 where almost 50% of the Fe(III) exists as Fe(OH)\(^{2+} \) complex which is the major photoactive species that generates \( ^\bullet \text{OH} \) upon illumination.\(^{42} \) Below this pH the concentration of Fe(OH)\(^{2+} \) declines and at higher pH the Fe(III) precipitates as oxyhydrates.\(^{52} \) The major advantage of this process is its light sensitivity up to wavelengths of 600 nm, i.e., illuminations by visible light can be utilized which overcomes the common drawback of relatively high cost for UV-lamps and electrical energy compared to other AOPs. The major disadvantage is the necessity of iron removal after the reaction but this problem can be circumvented by the immobilization of iron, e.g., on membranes.\(^{62,63} \) The photo-Fenton reaction has been effectively utilized for the detoxification of water polluted with several pesticides and organics.\(^{45,61,63-71} \)

Recently some controversies on the actual nature and identity of the oxidizing species in photo-Fenton reaction can be seen in the literature. Some predict the involvement of a second oxidant in addition to \( ^\bullet \text{OH} \) in the oxidation of organic compounds, which is proposed to be a high-valent oxo-iron complex.\(^{73} \) The behavior of this additional oxidant is proposed to be ferryl-like (Fe\(^{IV}=O \) or Fe\(^{V}=O \))\(^{73} \). The absorbance of FeO\(^{3+} \) extends well into visible region and that of FeO\(^{2+} \) extends to at least 340 nm.\(^{72} \) Laser flash photolysis results are in accordance with the literature on high-valent oxo-iron species and that the complex [Fe\(^{III} \)-OOH]\(^{2+} \) formed between H\(_2\)O\(_2 \) and Fe(III) is the precursor for the ferryl species.

\[
[\text{Fe}^{\text{III}}\text{-OOH}]^{2+} \xrightarrow{\text{hv}} [\text{Fe}^{\text{III}}\text{-OOH}]^{2+} * \quad (1.20)
\]
Introduction

\[
[\text{Fe}^{III} - \text{OOH}]^{2+} \quad \rightarrow \quad \text{Fe}^{IV} = \text{O} \leftrightarrow \text{Fe}^{III} - \text{O}^* + \cdot \text{OH} \quad (1.21)
\]

\[
[\text{Fe}^{III} - \text{OOH}]^{2+} \quad \rightarrow \quad \text{Fe}^{IV} = \text{O} + \text{OH}^- \quad (1.22)
\]

Here iron is formally in the +4 oxidation state and the structure is a hybrid with unpaired electron density on oxygen.

Reaction of \( \cdot \text{OH} \) can proceed by addition to double bonds having sufficient electron density or by hydrogen abstraction from alkyl or hydroxyl groups or by electron transfer. In contrast, the reaction of \( \text{Fe}^{4+}_{aq} \) with an organic compound proceeds exclusively by an electron transfer mechanism as neither addition nor H-abstraction is possible by it. In such a case, different oxidation products will be formed by the action of the two oxidants, \( \cdot \text{OH} \) and ferryl species.\(^{73,74}\)

Latest reports suggest that this new oxidant may have a significant effect on product distribution. The reaction mechanism largely depends on the nature of the pollutant molecule and the concentration of iron species and \( \text{H}_2\text{O}_2 \) in the reaction mixture. Further research is required to establish clearly the contributions of the additional oxidant.

1.2.4. Photoproduction of \( \cdot \text{OH} \) from Fe(III)-hydroxy complex

Photolysis of Fe(III) in aqueous solutions was first studied as a way to recycle the Fe(III) generated during Fenton reaction to Fe(II) and it was found that photolysis of aqueous solutions of Fe(III) in acidic pH can act as an efficient way to generate \( \cdot \text{OH} \). In acidic media many Fe(III)-hydroxy complexes would be formed of which Fe(OH)\(^{2+}\) is the major species.\(^{75}\)

\[
\text{Fe}^{3+} + \text{H}_2\text{O} \quad \leftrightarrow \quad \text{Fe(OH)}^{2+} + \text{H}^+ \quad (1.23)
\]

\[
\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad \leftrightarrow \quad \text{Fe(OH)}_2^{+} + 2\text{H}^+ \quad (1.24)
\]
The hydrolytic speciation of Fe(III) species was calculated by Faust and Hoigne based on equilibrium constants and found that the dominant monomeric Fe(III)-hydroxy complex in the pH range 2.5 to 5 is Fe(OH)$_2^{2+}$.\textsuperscript{75}

As early as in 1951, ferric ion was found to undergo ligand-to-metal charge-transfer reactions in the excited state.\textsuperscript{76-78} The major complex Fe(OH)$_2^{2+}$ photolyses efficiently at low pH to generate *OH along with Fe(II).\textsuperscript{75-78}

\[
\text{Fe(OH)}^{2+} \xrightarrow{hv} \text{Fe(OH)}^{2+*} \quad (1.25)
\]

\[
\text{Fe(OH)}^{2+*} \rightarrow \text{Fe}^{2+} + \text{*OH} \quad (1.26)
\]

The molar extinction coefficient of Fe(OH)$_2^{2+}$ at 313 nm is 1760 dm$^3$ mol$^{-1}$ cm$^{-1}$.\textsuperscript{75}

Due to the fact that the charge-transfer band of Fe(OH)$_2^{2+}$ strongly overlaps with the solar UV-spectrum, the photolysis of this complex is possible using solar irradiation\textsuperscript{75} and this is one AOP that can be performed using sunlight.

*OH is considered to be the most potent oxyradical in the atmosphere and the major source of atmospheric *OH is the solar photolysis of Fe(III)-hydroxy complex.\textsuperscript{75,80-82} According to the reports of Faust and Hoigne, Fe(OH)$_2^{2+}$ is the dominant monomeric Fe(III)-hydroxy complex in clouds and fog with pH range 2.5 to 5, which is their characteristic pH range and the photolysis of this complex is responsible for the generation of *OH. Many atmospheric waters are expected to contain Fe(OH)$_2^{2+}$ in concentrations $> 0.1$ µmol as soluble iron species which are major constituents of polluted waters.\textsuperscript{75} Several reports have proved that this reaction can be effectively utilized for the efficient detoxification of several water pollutants.\textsuperscript{79,83-89}

However, there are reports that predict another mechanism whereby organic compounds are degraded in presence of aqueous ferric ion. Here, the
Fe(III) is proposed to form complexes with organic pollutant molecules which act as ligands and these complexes absorb solar energy which result in the electron transfer from organic ligand to Fe(III) and generates Fe(II) and an organic radical.\textsuperscript{74,83} In the presence of dissolved oxygen the organic radical could be further oxidized by O\textsubscript{2}.

\[
\text{Fe(III)} + \text{Org} \quad \longrightarrow \quad \text{Fe(III)-Org Complex} \quad (1.27)
\]

\[
\text{Fe(III)-Org Complex} \quad \xrightarrow{hv} \quad \text{Fe(II)} + \text{Org Radical} \quad (1.28)
\]

\[
\text{Fe(II)} + \text{Org Radical} + \text{O}_2 \quad \longrightarrow \quad \text{Fe(III)} + \text{Oxidized Org} \quad (1.29)
\]

Zuo and Hoigne proposed that the important chemical constituents in the troposphere, \textit{viz.}, oxalic, glyoxalic and pyruvic acids are removed from the atmosphere in the presence of Fe(III) by the above mechanism.\textsuperscript{84} However another report on a photochemical study on aqueous ferric ions using pulsed laser confirmed the role of \textit{\textcopyright}OH as the major active species in the degradation of xylidines in aqueous solution.\textsuperscript{90}

In the reaction of Fe(III) with humic substances Liu \textit{et. al.} have undoubtfully proved the the photoproduction of \textit{\textcopyright}OH from Fe(III) in an experiment with humic acid.\textsuperscript{88} They also propose Fe(OH)\textsuperscript{2+} as the dominant Fe(III)-hydroxy complex in the pH range 2.5 to 5 which on photolysis yields \textit{\textcopyright}OH. Furthermore, if organic ligands are present in the reaction medium, Fe(III)-org complex is proposed to be the main species of Fe(III)\textsuperscript{88} (reaction 1.27 to 1.29).
1.2.5. O₃/ UV process

Although ozone is widely used as an oxidant, its reaction with many pollutants is very slow. Hence oxidative power of ozone is ‘activated’ by a combination of ozone with UV-radiation which generates •OH. Upon irradiation O₃ is decomposed into O₂ and oxygen atom O(¹D) which is a very short-lived species.

\[
\begin{align*}
O_3 & \overset{hv}{\longrightarrow} O_2 + O^* \quad (1.30) \\
O^* + H_2O & \longrightarrow 2•OH \quad (1.31)
\end{align*}
\]

The O₃/UV can be effectively used for the degradations of organic pollutants.

1.2.6. O₃/ H₂O₂ process

Combination of O₃ with H₂O₂ is reported to generate •OH.

\[
2O_3 + H_2O_2 \longrightarrow 2•OH + 3 O_2 \quad (1.32)
\]

Hydrogen peroxide in aqueous medium decomposes to yield hydroperoxide ion (HO₂⁻) which upon reaction with ozone generates •OH. This AOP also is used for the degradation of several pollutants.

1.2.7. Photocatalysis

Semiconductors, in particular titanium dioxide, have gained much attention in the photocatalysis of water purification. TiO₂ particles, as an aqueous suspension or as a layer on a support, if irradiated with electromagnetic radiation of energy \( \geq \) band gap energy (i.e., energy gap between valence band (VB) and conduction band(CB)), electrons will get excited from VB to CB thereby creating holes in the VB.
Thus the role of oxygen is critical in suppressing full charge-recombination of hole-electron pair which would reduce the efficiency of the system.\textsuperscript{102}

In addition to \textsuperscript{*}OH, the holes in the VB are also powerful oxidants which can oxidize the pollutants.\textsuperscript{103} The $\lambda_{\text{max}}$ of TiO$_2$ is around 340 nm. This has the great advantage of using sunlight for photolysis of pollutants. Several reports can be available on the mineralization of water pollutants using this AOP.\textsuperscript{104-106}

\subsection*{1.2.8. Sonolysis}

Ultrasonic irradiation of aqueous solution induces acoustic cavitations. Sound travels through a liquid as a wave consisting of alternating compression and rarefaction cycles. If sound wave has sufficiently high pressure amplitude, it can overcome the intermolecular forces binding the fluid. Then the liquid breaks down and voids will be created, \textit{i.e.}, cavitation bubbles will be formed.\textsuperscript{107} Upon collapse of these bubbles high temperatures and pressures are generated inside the bubbles. Under such extreme conditions, water molecules are dissociated into \textsuperscript{*}OH\textsubscript{(g)} and \textsuperscript{*}H\textsubscript{(g)}. The chemical destruction of compounds dissolved in the liquid has been demonstrated to occur by pyrolytic reaction inside the cavitation bubbles or oxidation by \textsuperscript{*}OH in the bulk medium.\textsuperscript{108-110}

\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^\cdot & (1.36) \\
\text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{O}^\cdot & (1.37)
\end{align*}
Also,

\[ \text{H}_2\text{O} + \cdot\text{O} \rightarrow \cdot\text{OH} + \cdot\text{OH} \quad (1.38) \]

\[ \text{H}_2\text{O} + \cdot\text{H} \rightarrow \text{H}_2 + \cdot\text{OH} \quad (1.39) \]

In the past few years, sonochemistry has emerged as an AOP for the destruction of hazardous organic compounds in aqueous solution.

### 1.3. Radiation chemistry

The chemical effects produced on exposure of materials to high-energy ionizing radiation are the essence of radiation chemistry. Radiation-chemical changes are generated by a mixture of reactive intermediates that include both ions and excited molecules and at a later stage of the process, free radicals. Electromagnetic radiation in the UV and visible region of the spectrum can also initiate chemical reactions but the major difference between radiation chemistry and photochemistry lies in the higher energy of radiations employed in radiation chemistry which can cause the generation of ions and radicals whereas photochemistry causes only electronic excitation. The major ionizing radiations include X-ray, α-ray (helium nuclei), β-ray (beam of electrons), γ-ray etc. The sources of radiation used in radiation chemistry fall into two groups. The first category are those employing natural or artificial radioactive isotopes which include the classical radiation sources radium and radon and artificial radioisotopes like cobalt-60, cesium-137 (γ-ray) and strontium-90 (β-ray). The second group includes X-ray generators, electron accelerators of various types like linear accelerator (Linac), van de Graaff accelerator, cyclotron, febetron and pelletron.
1.3.1. Interaction of ionizing radiation with matter

When matter is exposed to ionizing radiations ionization and electronic excitation are the major effects. The specific energy loss of the incident photon during this process is given by linear energy transfer (LET). The three different modes of interaction by which energy is transferred to matter, which depend on the energy of incident photon, are the photoelectric effect, the Compton effect and pair production. In photoelectric effect, a photon with energy < 100 keV is absorbed completely with the ejection of an electron bound to an atom. The kinetic energy acquired by the ejected electron \( E \) is in accordance with the Einstein’s equation \( E = h \nu - I_B \) where \( h \nu \) is the energy of a photon in the beam and \( I_B \) the binding energy of the electron in the atom. The energy imparted to the residual atom is negligibly small in this case.\(^{115}\) The binding energies of various electrons in an atom vary depending on its energy levels. So the ejected electrons called photoelectrons will have different energies.\(^{114}\)

In Compton effect, only a part of the energy of the incident photon (with energy between 0.1 and 10 MeV) is absorbed which lead to the ejection of a loosely bound electron usually called the Compton electron together with a secondary photon with reduced energy propagating in a changed direction.\(^{114,115}\)

In contrast to photoelectric and Compton effects, pair production involves the interaction of photons with the nucleus of the atom which results in the complete disappearance of the incident photon with the generation of a positron and electron pair.\(^{115}\)

1.3.2. Radiation chemical techniques

Interaction of ionizing radiation with matter induces chemical processes where both short-lived intermediates and stable products are
generated. The kinetics of formation of transients, their decay and spectral characteristics can be studied using pulse radiolysis. Ideas about stable products are obtained both qualitatively and quantitatively using common analytical techniques like HPLC, HPLC-ES-MS, GC-MS etc. after subjecting to $\gamma$-irradiation.

1.3.2.1. Pulse radiolysis

It is a technique most suitable for the kinetic study of fast reactions. The delivery of ionizing radiation to a chemical system in the form of short pulses generates a nonequilibrium system where significant concentrations of transient species may be produced and monitored as a function of time by various methods before the disappearance of these active entities. As the rate constants for the reaction of these intermediates are very high ($10^{10} \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1}$) short pulse times are necessary. Thus, the half-lives of most of these reactions are in the microsecond range. The high-energy electron sources used are linear accelerator (linac), van de Graff accelerator and Febetron.

The linac is a traveling wave accelerator which utilizes an arrangement of microwave cavities in series to accelerate electrons along a path defined by the oscillating polarity of the field. Electrons are injected in pulses into the accelerator tube and get accelerated by the electric field of the electromagnetic wave. The accelerated electrons are delivered in pulses of a few nano- or microseconds duration with a repetition rate of the order of 500 pulses s$^{-1}$. The particular advantage of linac lies in the ease of generation of electrons with very high energy in the range 10 to 20 MeV that can provide deep penetration of electrons and uniform distributions of ionization events throughout the ionization chamber.
Depending on the nature of the reactions to be studied pulses of nanosecond or microsecond durations are applied to a cell containing the sample. The behavior of transients are monitored using various transient monitoring techniques like optical absorption, Raman spectroscopy, conductivity, polarography, electron spin resonance etc.\textsuperscript{114} The most widely used technique for the study of transient behavior is optical absorption spectroscopy which is applicable to most of the transients or combination of transients.\textsuperscript{115} The optical absorption spectra of the starting compound and the intermediate will be different. A pulse of high energy electrons are directed towards the sample cell and a transient recorder stores the detector signal as a function of time. If the transient species absorbs the light of the monitoring wavelength, a deflection in the detector signal will track transmittance changes $\Delta I$ in the cell. These changes will parallel the formation of transient species.\textsuperscript{115} The kinetic behavior of transients can be obtained from the changes in transmittance of monitoring light. Measurement of the incident intensity $I_0$ together with the above values can give the absorbance as a function of time at that monitoring wavelength. By measuring dose per pulse, these absorbance values can be normalized to the intensity of the electron beam. The absorbance of the transient as a function of wavelength at selected time scales after the pulse (time-resolved spectrum) can also be plotted. A particular wavelength is selected and the change in absorption at that wavelength as a function of time is monitored.\textsuperscript{114} The data are processed with the help of a computer.

1.3.2.2. Steady-state radiolysis

In the case of steady-state radiolysis, the substrate is subjected to irradiation by X-rays or $\gamma$-rays and the final stable products are analyzed using various analytical techniques like HPLC, HPLC-ES-MS, GC-MS etc. $\gamma$-Rays are electromagnetic radiation of nuclear origin with energies in the range
40keV to 4MeV. The $\gamma$-rays emitted by radioactive isotopes are either monoenergetic or have a small number of discrete energies. Cobalt-60 is the most widely used $\gamma$-source at the present time which gives out equal number of photons of energy 1.332 and 1.173 MeV. Cobalt-60, produced by irradiating cobalt in a nuclear reactor, provides higher energy and more penetrating $\gamma$-irradiation than cesium-137 which has an advantage of a longer half-life. Normally $\gamma$-photons lose the major part of their energy through a single interaction with substrate molecule.\textsuperscript{114} Pulse radiolysis data along with a clear idea about the stable end products after $\gamma$-radiolysis help to elucidate the complete mechanism of that particular reaction of the substrate molecule.

\textbf{1.3.3. Radiation chemistry of water and homogeneous aqueous solutions}

During the early years of radiation chemistry, studies were mainly conducted with gas-phase substrates. Increased interests in biological effects of ionizing radiation lead to more attentions in the chemical changes produced in water and aqueous solutions.\textsuperscript{117} Solutions, in contrast to gaseous reaction systems, showed a marked difference between radiation chemical and photochemical reactions. Unlike the latter case, ionizing radiation is absorbed by both solvent and solute and in dilute solutions the energy is almost entirely absorbed by solvent. Thus the radiolysis of water became a topic of interest to radiation chemists.\textsuperscript{114} The knowledge about the radiation chemistry of water is virtually complete now and water radiolysis provides a very convenient way of generating a variety of unstable species under well-defined conditions.\textsuperscript{115} Radiolysis of water is schematically represented in Scheme 1.1.\textsuperscript{114,115}
Scheme 1.1. Radiolysis of water

A radiation with sufficient energy such as a gamma photon from a $^{60}$Co source or a charged particle like an electron from an accelerator is used to ionize water molecules which can cause the liberation of an electron from a molecule of water. This electron usually has sufficient energy to ionize further water molecules and this will generate clusters of ions along the track of the ionizing photon. These clusters are called spurs. As mentioned above if the electron released has sufficient kinetic energy, it can cause further ionization. Finally, its energy falls below the ionization threshold of water and then it will get localized.
to a potential energy well long enough to become solvated. A subpicosecond laser study has showed that the electron gets solvated in less than $10^{-12}$ s. The physicochemical processes described in scheme 1.1 are complete by about $10^{-12}$ s after ionization event. Then the species $^\bullet$OH, e$^-_{aq}$, H$_3$O$^+$ and all radicals and molecular fragments resulting from the dissociation of excited-state molecules are in thermal equilibrium with bulk medium and these species cluster in spurs. These products subsequently start to diffuse and a fraction of them react with each other to form molecular or secondary radical products. They can escape into bulk solution and get homogeneously distributed throughout the medium. This is called spur-expansion and is complete in about $10^{-7}$ s. The products of radiolysis of water are shown in scheme 1.1.

1.3.3.1. Radiation chemical yields

In radiation chemistry, the yields of various species formed in the system as a result of absorption of energy from ionizing radiation are expressed in terms of G-values. This is defined as the number of molecules generated or destroyed per absorption of 100 eV of energy. In SI unit the G-value is expressed in mol J$^{-1}$ where one molecule per 100 eV is equal to 1.036 $\times$ $10^{-7}$ mol J$^{-1}$.

Primary yields are the yields of species remaining when all the spur reactions are complete, i.e., $10^{-7}$ s after ionization event. In principle, it is possible to measure the yields of radicals directly using pulse radiolysis but in practice only e$^-_{aq}$ can be measured in this way as H$^*$ and $^\bullet$OH have only weak absorption in the UV region that are usually masked by those of added solutes. H$^*$ and $^\bullet$OH can be measured by adding solutes that can give observable products under pulse radiolytic conditions.
The generally accepted values of primary yields in the pH range 3-11 are the following.

\[
\begin{align*}
G(\text{e}^-_{\text{aq}}) &\approx G(\text{^\bullet OH}) \approx G(\text{H}_3\text{O}^+) = 0.28 \, \mu \text{mol J}^{-1} \\
G(\text{H}^\bullet) &= 0.062 \, \mu \text{mol J}^{-1} \\
G(\text{H}_2) &= 0.047 \, \mu \text{mol J}^{-1} \\
G(\text{H}_2\text{O}_2) &= 0.072 \, \mu \text{mol J}^{-1}
\end{align*}
\]

1.3.3.2. Primary radicals and their properties

When dilute aqueous solutions are subjected to irradiation by fast electrons or a $^{60}$Co-$\gamma$-source, almost all energy is absorbed by water molecules and the observed chemical changes are brought about by the radical products of water radiolysis. The subsequent chemical changes reflect the nature of the solute.

**Figure 1.1.** Absorption spectra of e$^-_{\text{aq}}$, H$^\bullet$ and OH$^\bullet$.\textsuperscript{114}
1.3.3.2.1. The reducing radicals

The nature of the major reducing species was resolved by Hart and Boag who irradiated deaerated water with a high intensity electron pulse which showed a broad transient absorption band centered around 720 nm which was similar to the known absorption band of the solvated electron in liquid ammonia.\textsuperscript{119,120} The intensity of this transient absorption was reduced by low concentrations of electron scavengers like oxygen, CO\textsubscript{2} \textit{etc}. Finally it was concluded that the major reducing species in neutral and basic solutions is the hydrated electron and that in acidic solutions it is converted to hydrogen atom.

(a) \textbf{The hydrated electron}

It is one of the most powerful reducing agents with a standard reduction potential of \(-2.86\) V. It is regarded as an electron trapped by a small group of water molecules with orientations as a consequence of the electron’s presence. Properties of a hydrated electron are summarized in table 1.1.\textsuperscript{114}

\begin{table}[h]
\centering
\caption{Properties of hydrated electron}
\begin{tabular}{ll}
\hline
Radius of charge distribution & 0.25 to 0.3 nm \\
Diffusion Constant & \(4.9 \times 10^{-9}\) m\textsuperscript{2} s\textsuperscript{-1} \\
Absorption maximum wavelength & 715 nm \\
Energy equivalent & 1.73 eV (167 kJ mol\textsuperscript{-1}) \\
Extinction coefficient & \(1.85 \times 10^{4}\) dm\textsuperscript{3} mol\textsuperscript{-1} cm\textsuperscript{-1} \\
Standard reduction potential & \(-2.86\) V \\
Half-life & \\
\quad In neutral water (pH = 7.0) & \(2.1 \times 10^{-4}\) s \\
\quad In basic solution & \(6.6 \times 10^{-4}\) s \\
\hline
\end{tabular}
\end{table}
The reactions of hydrated electron are single electron transfer processes represented by,

$$e^{-}_{aq} + S^n \rightarrow S^{n-1}$$  \hspace{1cm} (1.40)

where \( n \) is the charge on the solute.\textsuperscript{114,115}

Reactions of \( e^{-}_{aq} \) with organic compounds are well studied and have shown to be those expected of a nucleophile. Thus its reactivity is greatly enhanced by electron withdrawing substituents adjacent to double bond or attached to aromatic rings. Negative ions formed by the reaction of \( e^{-}_{aq} \) with neutral species are Brownsted-Lowry bases and either dissociate to generate stable negative ions or react with water with the formation of OH\(^-\) and a radical.\textsuperscript{114} Examples are,

$$e^{-}_{aq} + H_2O_2 \rightarrow OH^- + ^{\bullet}OH$$  \hspace{1cm} (1.41)

$$e^{-}_{aq} + N_2O \xrightarrow{1.42} N_2O^\cdot \xrightarrow{H_2O} OH^- + ^{\bullet}OH + N_2$$  \hspace{1cm} (1.43)

These two reactions provide methods to convert \( e^{-}_{aq} \) to \( ^{\bullet}OH \) quantitatively and are useful in creating a completely oxidizing atmosphere in the radiolysis of water. Saturating with \( N_2O \) is preferred over \( H_2O_2 \) as \( H_2O_2 \) is reactive to \( ^{\bullet}OH \) as well as with many intermediates generated by \( ^{\bullet}OH. \textsuperscript{114} \)

The hydrated electron has an intense absorption maximum at 715 nm which is well separated from the spectra of most other chemical species and hence the reactions of \( e^{-}_{aq} \) can be easily followed using pulse radiolysis combined with kinetic spectroscopy.\textsuperscript{121}

(b) The hydrogen atom

It is the major reducing radical in acidic media only, not in alkaline or neutral solution. It is a less powerful reductant (\( E^0 = -2.3 \) V) than \( e^{-}_{aq}. \textsuperscript{114,115} \)
The major difficulty in documenting the properties and reactions of hydrogen atom is that it does not absorb in a readily accessible region of the spectrum.\textsuperscript{114}

In its reactions with many organic compounds, unlike $e^{-}_{aq}$, hydrogen atom generally abstracts a hydrogen to give molecular hydrogen. This difference between the two reducing radicals is utilized to measure $G(H^\bullet)$ at neutral pH by irradiating solutions containing both an electron scavenger and an organic compound that gives rise to $H_2$ with hydrogen atoms.\textsuperscript{114}

1.3.3.2.2. The oxidizing radicals

The hydroxyl radical $\cdot OH$ is the major oxidizing radical in the radiolysis of aqueous solutions. In strongly alkaline media $\cdot OH$ gets converted to $O^\bullet$. With high LET radiations reaction of $\cdot OH$ with $H_2O_2$ generates perhydroxyl radical $HO_2^\bullet$.\textsuperscript{114}

(a) The hydroxyl radical

It is one of the most powerful oxidants with a standard reduction potential of +2.7 V in acidic medium and 1.8 V in neutral solution.\textsuperscript{119} As $\cdot OH$ has a weak absorption in the UV range, its rate constants are usually measured by competition methods or by pulse radiolysis whereby a product with a sufficiently high extinction coefficient is generated.

The major reactions of $\cdot OH$ include,\textsuperscript{114,115,117}

(i) Hydrogen abstraction

With saturated organic compounds $H^\bullet$ abstraction is the usual way where an organic free radical is generated.

\[ \cdot OH + CH_3COCH_3 \rightarrow H_2O + \cdot CH_2COCH_3 \]  (1.44)
(ii) Addition

Aromatic substrates or those with carbon-carbon multiple bonds undergo addition reactions with *OH generating organic free radicals.

\[
\begin{align*}
*\text{OH} + \text{CH}_2=\text{CH}_2 & \rightarrow *\text{CH}_2-\text{CH}_2\text{OH} \quad (1.45) \\
*\text{OH} + \text{C}_6\text{H}_6 & \rightarrow *\text{C}_6\text{H}_6\text{OH} \quad (1.46)
\end{align*}
\]

Also, they give rise to stable products with radicals.

\[
\begin{align*}
*\text{OH} + \text{H}^* & \rightarrow \text{H}_2\text{O} \quad (1.47) \\
*\text{OH} + \text{HO}_2^* & \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (1.48)
\end{align*}
\]

(iii) Electron transfer

With inorganic solutes

\[
\begin{align*}
*\text{OH} + \text{S}^n & \rightarrow \text{OH}^- + \text{S}^{n+1} \quad (1.49) \\
*\text{OH} + [\text{Fe(CN)}_6]^{4+} & \rightarrow [\text{Fe(CN)}_6]^{3-} + \text{OH}^- \quad (1.50)
\end{align*}
\]

Table 1.2. Properties of hydroxyl radical\(^\text{114}\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion constant</td>
<td>(2.3 \times 10^{-9}) m(^2)s(^{-1})</td>
</tr>
<tr>
<td>Absorption maximum</td>
<td>230 nm, (\varepsilon_{230} = 53) m(^2)mol(^{-1})</td>
</tr>
<tr>
<td>(E^0) (acidic medium)</td>
<td>2.7 V</td>
</tr>
<tr>
<td>(E^0) (basic medium)</td>
<td>1.8 V</td>
</tr>
<tr>
<td>pKa</td>
<td>11.9 (\pm) 0.2</td>
</tr>
</tbody>
</table>

(b) The oxide radical anion (O\(^-\))

In strongly alkaline solutions, *OH gets rapidly converted to its anionic form O\(^-\). Because of the high pKa value of *OH, the reaction of O\(^-\) has to be studied in strongly basic medium. So fewer rate constants are available for O\(^-\). This shows that O\(^-\) is less active in hydrogen abstraction and slower in
addition to unsaturated and aromatic compounds than •OH. Thus, in contrast to •OH which behaves as an electrophile O•− acts as a nucleophile.\textsuperscript{114,115}

\[
•OH + OH^- \rightleftharpoons O^- + H_2O \quad (1.51)
\]

(c) The perhydroxyl radical

It is not a significant primary radical at low linear energy transfer. With high LET radiations where considerable interradical reactions occur in the track, reaction between •OH and H\textsubscript{2}O\textsubscript{2} generates HO\textsubscript{2}•.\textsuperscript{114,115} In oxygenated solutions,

\[
e^-_{aq} + O_2 \rightarrow O_2^{•−} \quad (1.52)
\]

\[
H^• + O_2 \rightarrow HO_2• \quad (1.53)
\]

1.3.3.3. Restricted radical source

Almost equal numbers of powerful oxidizing and reducing radicals are generated in the radiolysis of water. For chemical applications, it is more preferable to have totally oxidizing or reducing conditions. The usual method is the interconversion of primary radicals using appropriate solute molecules as scavengers.\textsuperscript{115}

(a) Oxidizing conditions

In order to obtain an almost totally oxidizing atmosphere in the radiolysis of water the following two reactions of e\textsuperscript{−}_{aq} are made use of.\textsuperscript{114,115}

\[
e^-_{aq} + H_2O_2 \rightarrow •OH + OH^- \quad (1.54)
\]

\[
e^-_{aq} + N_2O \rightarrow N_2O^- \xrightarrow{(1.55)} N_2O^- + H_2O \rightarrow •OH + OH^- + N_2 \quad (1.56)
\]

As H\textsubscript{2}O\textsubscript{2} is reactive towards •OH, N\textsubscript{2}O is preferred over H\textsubscript{2}O\textsubscript{2}. Moreover the product N\textsubscript{2} is inert towards attack of free radicals.\textsuperscript{114}
In N₂O saturated neutral solutions approximately 10% of the radicals available are H atoms and 90% are \( \cdot \text{OH} \) due to the slow reaction of N₂O and H\(^+\) \((k = 2.3 \times 10^6 \text{dm}^3\text{mol}^{-1}\text{s}^{-1})\).\(^{115}\)

(b) Reducing conditions

The most convenient method of generating totally reducing conditions is to scavenge \( \cdot \text{OH} \) using tert-butanol.\(^{114,115}\)

\[ \cdot \text{OH} + (\text{CH}_3)_3\text{COH} \rightarrow (\text{CH}_3)_2\cdot\text{CH}_2\text{COH} + \text{H}_2\text{O} \] \((1.57)\) \( k = 5 \times 10^8 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}\)

tert-butanol can scavenge H atoms also, but because of the low rate constant \((k = 8 \times 10^4 \text{dm}^3\text{mol}^{-1}\text{s}^{-1})\) the efficiency is low.\(^{114}\)

1.3.3.4. Secondary radicals

A large number of inorganic radicals can be generated by the reaction between primary radical products and appropriate inorganic solutes.\(^{114,115}\) For example,

\[ \text{e}^{-}\text{aq} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} \] \((1.58)\)

\[ \cdot \text{OH} + \text{Cl}^- \rightarrow (1.59) \text{ClOH}^{-} \rightarrow \text{Cl}_2^- + \text{H}_2\text{O} \] \((1.60)\)

If organic solutes are employed organic radicals can be produced.\(^{117}\)

\[ \cdot \text{OH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow (\text{CH}_3)_2\cdot\text{CHOH} + \text{H}_2\text{O} \] \((1.61)\)

\[ \text{e}^{-}\text{aq} + \text{CH}_3\text{COCH}_3 \rightarrow (1.62) (\text{CH}_3)_2\cdot\text{CO}^- \rightarrow (\text{CH}_3)_2\cdot\text{COH} + \text{OH}^- \] \((1.63)\)

\(\alpha\)-hydroxyalkyl radicals react with many organic and inorganic compounds mainly by reduction although abstraction and addition reactions are also possible and hence are most extensively studied organic free radicals in aqueous radiation chemistry.\(^{114}\)
Recently, the influence of ionizing radiation on many water pollutants have been investigated extensively and both pulse and steady state radiolysis methods have been reported to be useful for elucidating the radical reaction mechanisms and degradation pathways.122-130

1.4. General objectives

Many symmetrical 1,3,5 triazines are used extensively as herbicides in different parts of the world. These compounds are toxic and are relatively stable for long periods in the environment. Their persistence in natural water and even in ground water is detected even months after the applications. So reliable technologies are to be developed for the successful destruction or detoxification of these pollutants. Advanced Oxidation Processes (AOPs) are becoming increasingly popular for the effective degradation of organic pollutants to nontoxic compounds. AOPs generate hydroxyl radical (•OH) which can react nonselectively with almost all organic compounds at diffusion controlled rates.

Although there are many widely used homogeneous and heterogeneous AOP systems, the selection of a particular AOP for a specific pollutant will be completely fruitful only by understanding the chemistry behind the reactions. We have attempted to investigate the kinetic and mechanistic aspects of various AOPs when applied to some triazine derivatives. The selected triazine derivatives are atrazine (AT), 1,3,5-triazine (T), 2,4,6-trimethoxy-1,3,5-triazine (TMT), 2,4-dioxohexahydro-1,3,5-triazine (DHT) and 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid (CA)). We have made use of four major AOPs – photolysis of Fe(III)-hydroxy complex, photolysis of H2O2, dark Fenton reaction and radiation chemical technique. In all cases GC-MS and/or LC-MS/MS analyses were conducted and attempts have been made to elucidate the reaction mechanism in each case. The specific objectives are given in chapters 3-5.
References


