Organic pollutants are chemical compounds that contain carbon and have an adverse effect on the environment. The organic pollutants such as dyes, pesticides, surfactants, phenols etc. are resistant to the environmental degradation. The natural chemical, biological, and photolytic processes fail to degrade them. These recalcitrant organic pollutants can accumulate in the environment and do harm to animals and humans [1]. The anaerobic and aerobic biological processes are mostly employed for the treatment of such organic pollutants. However, these processes are slow and their treatment efficiencies are not always acceptable for the recalcitrant organic pollutants [2]. Conventional techniques such as adsorption, precipitation and flocculation, reverse osmosis, simply concentrates the organic pollutants from the solution phase to solid phase, which generates secondary wastes.

India with more than one billion population is a growing economy. It is essential that along with the industrial growth, environment should also be protected to the extent that it can support life without adverse effects. Water, an elixir of life, is one of the first victims of the environmental pollution. Use of water purification system in average Indian home and present quality of many other water resources are indicators of the poor quality of water for human consumption. To meet the consumption demands of water of a developing country like India, use of technologies that could treat and recycle waste water efficiently and economically need to be explored. Therefore, there is a pressing need to look for technological solutions which could efficiently and economically mitigate environmental issues related to waste water at larger scale.
Not meeting discharge limits, effluents from textile, pharmaceutical and other industries pollute water. These effluents contain not only dyes, pesticides and drugs but also several other organic contaminants. Nitroaromatic compounds are important building blocks for the large scale synthesis of pesticides, pharmaceuticals, plastics, azo dyes and explosives and pollute directly or indirectly the river and ground water. In the present study, we have chosen representative water polluting molecules namely (1) textile dye (Reactive Dye), (2) pharmaceutical drug, Ibuprofen (IBP) and (3) nitro compound, 4-nitrophenol (4-NP).

Radiation technology is gaining world over recognition as effective method to degrade varieties of organic pollutants in waste water [3]. Gamma radiation from isotopic source like Cobalt-60 and electron beam accelerators are generally used. In this process, energy from these sources is directly and indirectly deposited into the pollutants to degrade them. The extent of the degradation is affected by irradiation conditions and dose rate of the radiation source.

The advanced oxidation processes (AOPs), involving generation of hydroxyl radicals (\(^\cdot\)OH), are emerging out to be efficient and effective oxidation processes leading to complete degradation of organic pollutants with minimized productions of sludge, secondary waste and toxic intermediates. The fenton and photo-fenton processes [4], photo-catalytic treatment [5], electrochemical oxidation [6], ultrasonic treatment [7], combination of ozone and hydrogen peroxide [8] are some of the popular AOPs. Radiation technology using high energy ionizing radiation is also one of the promising AOPs, which can effectively degrade organic pollutants in aqueous solution with least secondary waste. Further, radiation technology can also be applied for the treatment of coloured and turbid solutions at room temperature.
In the present study, radiation effects on the aqueous solutions of the above mentioned organic compounds viz. reactive red 120 (RR-120), IBP and 4-NP have been investigated by using gamma and electron beam radiation with a primary objective of understanding their degradation and degradation mechanisms so that the process can be optimized for its effective utilization on industrial scale. Some AOPs along with irradiation were evaluated to improve overall efficiency and economics of the process. The thesis has been divided into four chapters.

Chapter 1: Introduction

This chapter has been divided into three sections.

Section 1: Environmental impact of organic pollutants

This section gives the literature review on the nature and environmental impact of the organic pollutants and other auxiliary chemicals present in waste water.

Section 2: Advanced Oxidation Processes (AOPs)

This section gives an overview of the AOPs used for the wastewater treatment. A general introduction of use of radiation technology for the treatment of the waste water is also briefly discussed in this section. The major advantages and limitations of use of radiation technology are included in this section.

Section 3: Radiation Chemistry of water

Water plays an important role in degradation of organic pollutants using radiation technology. Different types of radiation sources and fundamental reactions of radiolysis of water are discussed in this section.
Chapter 2: Experimental

The instruments and various techniques used in the present study are discussed in this chapter. It includes the brief principle and descriptions of instruments such as UV-Vis spectrophotometer, Chemical Oxygen Demand (COD) / Biological Oxygen Demand (BOD) / Total Organic Carbon (TOC) analyzer, pH meter, Fourier Transform Infra-Red (FTIR) Spectrophotometer, High Performance Liquid Chromatography (HPLC), Electron-Spray-Ionization (ESI-) and Gas-Chromatography (GC-) mass spectrometer. Methods and procedures used for gamma radiolysis, pulse radiolysis and electron beam irradiation are also described in this chapter.

Chapter 3: Decolouration and degradation of Reactive Red-120

The three sections of this chapter describe various results and discussions on irradiation of RR-120 using gamma radiation, electron beam and other AOPs such as ozonolysis and photocatalysis.

Section 1: Radiolysis of aqueous solution of Reactive Red - 120 (RR-120)

This section describes results of radiation induced decolouration and mineralization of the textile dye RR-120 on gamma radiolysis and electron beam irradiation under varying oxidizing and reducing radiolysis conditions. The mechanism of observed changes with various oxidizing and reducing radicals are explained by gamma radiolysis and pulse radiolysis experiments. Various reaction rates of the dye with these different radicals determined using pulse radiolysis are given. The bimolecular reaction rate constants were observed to be of the order of $10^9-10^{10}$ M$^{-1}$ s$^{-1}$. The results of TOC determined at different doses under aerated and oxygen saturated solutions of the dye have been given. Similar studies were also carried out using electron beam irradiation. In addition, the study gives results of biodegradability which
was investigated by monitoring BOD$_S$/COD ratio. The biodegradability index of waste water, BOD$_S$/COD ratio was observed to be ≥ 0.3-0.5 indicating enhanced biodegradability of the irradiated dye solution.

**Section 2: Effect of low dose pre-treatment irradiation on the microbial decolouration and degradation of Reactive Red-120 (RR-120) dye**

The section deals with the results and discussions on low dose irradiation of aqueous solution of RR-120 dye combined with microbiological treatment using *Pseudomonas* sp. SUK1 under static incubation. The results indicated that there is an enhancement of biodegradation of aqueous RR-120, 150 ppm, dye solution irradiated at 0.5 and 1.0 kGy doses. The enhancement of biodegradation is attributed due to the enhanced enzymatic activity of microorganisms feeding on the fragmented dye molecules produced on irradiation. The degradation products were studied using HPLC, FTIR, ESI-MS and GC-MS. The treated dye solution tested on plants revealed that the combined radiation-microbial treatment of RR-120 did not produce any toxic effects. The results of this study indicated that combined use of radiation technology and microbial degradation is more effective and economic.

**Section 3: Advanced oxidation process for treatment of simulated textile dye waste water**

The real textile dye effluents not only contain dyes but also several other chemicals including surfactants, sequestering agent, pH-adjusting acids, inorganic salts etc. These auxiliary chemicals contribute to about 83% of the organic load and cause a negative impact to the aquatic lives by decreasing dissolved oxygen concentration in the water streams. A simulated textile dye waste water (STDWW) was prepared by mimicking the compositions of the dye bath used in dye industries and exposed to...
different AOPs including radiation technology. This section discusses the results which indicated that it is better to use H2SO4 instead of acetic acid as a pH-adjusting agent for meeting stipulated discharge limits of treated waste water. Use of K2S2O8 reduced the radiation dose requirement and brought the degraded STDWW below discharge limits of 250 ppm. The comparative results of gamma and electron beam radiolysis in the presence of K2S2O8 with other AOPs viz. photocatalysis and ozonolysis in terms of oxygen-equivalent chemical-oxidation capacities (OCC) for 28% mineralization of STDWW were calculated as 0.08, 0.04, 6.29, 9.29 kg equiv. O2 m-3 respectively.

The pulse radiolysis studies revealed that the favourable reaction of SO4•-(produced by the radiolysis of K2S2O8) with SDBS (the most robust organic component of STDWW) producing benzyl and hydroxycyclohexadienyl type of radicals enhanced the extent of mineralization of STDWW during radiolysis in the presence of K2S2O8.

**Chapter 4: Degradation of Ibuprofen (IBP) and 4-nitrophenol (4-NP)**

The two sections of this chapter describe various results and discussions on irradiation of IBP and 4-NP by using gamma radiation.

**Section 1: The oxidative radiolysis of IBP in presence of K2S2O8**

This section describes results of gamma radiolysis of the aqueous solution of IBP, a model pharmaceutical compound, in the presence and absence of K2S2O8. The extent of mineralization was investigated by measuring absorbance in the UV-visible spectra, decrease in the COD and the TOC content of aqueous IBP solution at different doses. The results indicated that gamma radiolysis, in presence of K2S2O8, required much lesser radiation dose compared to IBP solutions without K2S2O8 for the same extent of mineralization. Though the presence of K2S2O8 increased the yield of the oxidizing radicals by a factor of 2.2, degradation was increased by ~5 times. The pulse radiolysis
study of IBP solutions was carried out under different radiolytic conditions to understand the mechanism of mineralization of IBP during gamma radiolysis in the presence of K₂S₂O₈. It was found that unlike 'OH radical, the SO₄⁻ radical preferentially produced benzyl type of radicals via formation of benzene radical cation. The results concluded that the gamma radiolysis in the presence of K₂S₂O₈ can be one of the efficient AOPs for degradation of IBP present in aqueous solutions.

Section 2: Radiolysis of aqueous solution of 4-NP

This section describes the results of gamma radiolysis of aqueous solution of 4-NP under different radiolytic conditions. The extent of decolouration of N₂ purged 4-NP solutions containing tert-butanol at 2 kGy dose was found to be maximum. Solutions purged with N₂ alone gave minimum decolouration. The mechanisms of reactions of 4-NP with different oxidizing (viz. 'OH, N₃⁻) and reducing radicals (viz. (CH₃)₂C‘OH, e⁻aq) were also investigated by pulse radiolysis at pH 5.2 and 9.2. The results indicated that reaction between 4-NP and 'OH led to the formation of π-complexes, which subsequently decayed by first order process producing semiquinone radical at pH 5.2. On the other hand, the phenolate anion and the π complex were produced by the reaction between 'OH and 4-NP at pH 9.2. The formation of one electron oxidized species is also confirmed by the reaction between N₃⁻ radical with 4-NP at pH 5.2 and 9.2. The transient spectra of the reaction between 4-NP and (CH₃)₂C‘OH were similar to the transient spectra of the reaction between 4-NP and e⁻aq. The reducing nature of the electron adduct of 4-NP was studied by the electron transfer reaction with methyl viologen (MV²⁺). The overall studies showed that gamma irradiation could be an efficient and promising method for the degradation of 4-NP in aqueous solutions.
Summary

The work carried out in this thesis indicates that radiation technology can be successfully used for degradation of organic pollutants such as RR-120 dye, ibuprofen and 4-nitrophenol present in waste water. It was observed that process efficiency and economics can be significantly improved when irradiation is done in combination with microbial degradation. Use of K$_2$S$_2$O$_8$ and H$_2$SO$_4$ was highly beneficial for reducing radiation dose requirement and achieving the discharge limits of the effluents. The increased mineralization efficiency of organic pollutants on irradiation was due to involvement of various transient species formed on irradiation of K$_2$S$_2$O$_8$ and particularly SO$_4^{\cdot-}$ and benzyl type of radicals. Considering all the factors, use of radiation technology for degradation of organic pollutants can be considered even better than other AOPs like ozonolysis and photocatalysis.

References


