SYNOPSIS

Environmental pollution has become unacceptable, as awareness of its effects on the environment has increased. Unfortunately, it is not possible to replace all the industrial processes generating polluting wastes with clean alternatives. Therefore, treatment both at source and after release must be considered as alternatives in many cases. Current legislation and recent waste management strategies have been emphasizing on waste minimization, recycling and remediation rather than disposal. Persistence of recalcitrants in the environment is a matter of significant concern owing to their potential toxicity, mutagenicity, carcinogenicity and ability to bioconcentrate in the trophic ladder. These perspectives constantly drive the need for the development and application of environmentally benign remediation techniques.

Research into newer and efficient wastewater treatment technologies to degrade the complex refractory molecules like phenols into simpler moieties is vital to abate the deteriorating water quality. In India, multisubstituted phenolics (nitro, chloro & methyl) are produced in larger amounts by the chemical industry and are important building blocks of the large-scale synthesis of pesticides, pharmaceuticals, wood preservation agents and phenolic resins. Biological processes are ineffective in treating such recalcitrant at lower concentrations and, at higher concentrations inhibit the growth of microorganisms. Other conventional treatment methodologies like adsorption, incineration etc., are either ineffective or environmentally incompatible. Chemical oxidation process is an alternative technology that can be successfully applied to a broad spectrum of organic compounds. Among these, advanced oxidation processes (AOP’s) are innovative environmental remediation technologies that are gaining importance for
degradation of most of the organic pollutants. The suitability of Advanced Oxidation Processes (AOPs) for aqueous pollutant degradation was recognized in the early 1970's and much research and development work has been undertaken to commercialize some of these processes.

Advanced Oxidation Process (AOP), an emerging technology generates hydroxyl radicals in sufficient quantities to oxidize majority of the complex chemicals. Hydroxyl radicals are more powerful oxidants than the chemical agents used in traditional chemical processes. Hydroxyl radicals are also characterized by a little selectivity of attack, attractive feature for an oxidant to be used in wastewater treatment. Several organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals. Advanced oxidation processes are gaining importance in the area of wastewater treatment, since these processes result in complete mineralization with operation even at mild conditions of temperature and pressure.

**BRIEF DESCRIPTION OF THE THESIS**

Industrial use of phenol and its derivatives over the past decades has led to severe environmental pollution. The total waste generation comprising these hazardous substances in the southern state of Andhra Pradesh, India is estimated as 6884 TPM (tons per month). Out of this around 190.3 TPM constitute phenolic wastes disposed mainly by petrochemicals, pharmaceuticals and polymer industries. Hence, in this PhD programme, the author has systematically investigated the application of advanced oxidation processes in the degradation and mineralization of recalcitrant compounds. In view of this, the author has taken up studies pertaining to the degradation of nitro, chloro and methyl substituted phenols like
4C-2NP, 2C-4NP, 2C-5MP, 4C-3MP & 2,4,6 T using various advanced oxidation processes.

AOP Technologies used in the present study

- Ultraviolet Irradiation (UV)
- Hydrogen Peroxide/ Ultraviolet Irradiation (H₂O₂/UV)
- TiO₂-catalyzed UV Oxidation
- Fenton’s reaction
- Photo-Fenton reaction

**ORGANIZATION OF THE THESIS**

The thesis is organized into seven chapters.

In Chapter 1, a general introduction on water contamination, constituents found in wastewater, global scenarios, various treatment methods, constituents concern in wastewater and various terminologies involving this methodology are described. The chapter also presents an overview of the chosen model compounds along with the scope and objectives of the study.

**Objectives:**

- Photodegradation with UV light
- Peroxide mediated photodegradation of the selected compounds with H₂O₂
- Fenton and Photo Fenton assisted mineralization of the listed recalcitrant compounds
- Photocatalytic degradation of the selected compounds using TiO₂ as catalyst.
The above selected methodologies will be screened for various compounds listed with various operating parameters like pH, compound concentration, peroxide concentration, iron concentration and catalyst dosage.

Evaluation of the degradation of the compound in terms of COD reduction and compound reduction.

Proposal of a general empirical kinetic equation on successful degradation of the selected compounds.

The elucidation of various degradation pathways thus depends on various factors mentioned and the present work aims at elucidating the degradation mechanism.

Finally, a comparative assessment of AOPs will be done in the present study in terms of cost to evaluate the efficacy of the treatment system.

Chapter 2 provides an extensive review on the various advanced oxidation processes like peroxide mediated oxidation (UV/H₂O₂), Fenton’s oxidation, Photo-Fenton’s oxidation and Photocatalysis with TiO₂, followed by their application in the treatment of the chosen model compounds.

Chapter 3 describes in detail the theoretical aspects of the treatment methodologies used in this study. The fundamental mechanisms, advantages and drawbacks, as well as the state of art of these AOPs are depicted in this chapter. The chapter also emphasizes on the importance of various operating parameters in the degradation of organic pollutants. The operating parameters studied in the present thesis include – effect of pH, effect of concentration of H₂O₂, effect of iron concentration and effect of catalyst dosage.

Chapter 4 discusses the materials and methods used in carrying various advanced oxidation processes. A detailed experimental protocol for the degradation
of the listed compounds is presented in this chapter. Photoreactor with 16W UV lamp is described in detail along with experimental set-up. The chapter also presents a detailed methodology of the various processes whose performance signifies the success of AOPs listed in the present study. Detailed analytical procedures along with standard protocols are also presented in this chapter.

**Chapter 5** discusses the results of the study carried out using advanced oxidation processes in the treatment of various substituted phenols. The performance of each treatment (UV, UV/H$_2$O$_2$, Fenton, UV/Fenton & UV/TiO$_2$) is evaluated in terms of compound and COD reduction. In context of the above methods, various operating parameters such as effect of pH, effect of concentration of compound, effect of peroxide concentration, effect of iron concentration and effect of catalyst dosage are all studied and optimized. The best operating conditions are finally selected for comparing the performance of different AOPs in treating the substituted phenols (SPs). Among all the AOPs studied, photofenton process is found to be more efficient in degrading the substituted phenols while peroxide mediated oxidation is found to be the least effective. Mineralization achieved by UV process is very little because the compound undergoes photochemical reaction as a consequence of light absorption and rarely these transformations contribute to compound removal. Removal of SPs by UV/ H$_2$O$_2$ is also very slow and incomplete. Fenton and UV/TiO$_2$ process is able to destroy SPs effectively but rather have difficulty in mineralizing the compounds completely. Among the substituted phenols, 4C-3MP is found to be the most readily oxidized compound while 2C-4NP is found to be the least oxidizable. This may be attributed to the ring deactivating character of the nitro group, which makes it least viable
for hydroxyl radical. The degradation trends for the substituted phenols followed the order:

\[
\text{4-chloro3-methylphenol} > \text{2-chloro5-methylphenol} > \text{2,4,6 Trichlorophenol} > \text{4-chloro 2-nitro phenol} > \text{2-chloro 4-nitro phenol}.
\]

The differences in the degradation rates might be due to the differences in the SPs attached to the phenolic ring.

Total mineralization of the compound should be considered since the intermediate products of some compounds can sometimes be more toxic than the original compound itself. Therefore, reduction of COD is also monitored along with SPs concentration. UV alone could not totally remove COD. But UV in combination with H\textsubscript{2}O\textsubscript{2} showed considerable reduction in COD. However in the presence of TiO\textsubscript{2} as catalyst, UV enhanced the reduction of COD compared to H\textsubscript{2}O\textsubscript{2} as catalyst. The COD reduction with photo Fenton process is found to be more efficient compared to Fenton. This can be explained by the complete oxidation of all Fe\textsuperscript{+2} to Fe\textsuperscript{+3} enhanced by UV.

From the experimental results, kinetic constants are derived by fitting the experimental data using Pseudo first order kinetics. Since reaction mechanisms are complex for the photo catalytic degradation of organic compounds, a rigorous kinetic study cannot be performed. However, when the experimental data is plotted it looked like a first order reaction with respect to SPs degradation. Therefore, an approach to this kinetic study is performed by assuming that the photodecomposition reaction followed first order kinetics.

**Chapter 6 & 7** presents final conclusions drawn from the entire Ph.D work along with future scope of the work. The objective of this work was the examination of
SPs degradation in aqueous solutions using UV, UV/H₂O₂, Fenton, UV/Fenton & UV/TiO₂ with considerable effect of substitutions on the degradation of SPs.

- The results of this study showed the degradation of SPs to be strongly accelerated by the photochemical oxidation processes.
- Neither UV nor H₂O₂ alone could degrade SPs. The combination of UV to the system i.e., UV/ H₂O₂ process enhanced SPs degradation rate but still required relatively long reaction periods with poor minimization efficiency.
- The degradation rate can be accelerated using high-pressure mercury vapour lamps instead of medium pressure lamps.
- The advantages of the photo-Fenton process as an oxidative pre-treatment step over other photochemical treatment processes are easy handling of the method, because no specific technical equipment is necessary, low investment, less energy demand, and harmless process products.
- This study has proven that UV/Fenton can be a successful pretreatment before biological remediation.
- Among the SPs studied, 4C-3MP, 2C-5MP & 2,4,6-TCP degraded much faster than 4C-2NP & 2C-4NP indicating faster degradation of chloro methyl phenols than chloro nitro phenols.

Thus, the rate of degradation is primarily determined by the nature of substitution and is less dependent on the position of the substituent group.

Finally, bibliography for the entire thesis is included in the last section of the thesis.