SONOPHOTOCATALYSIS OF 4-CHLORO-2-NITROPHENOL USING TIO_2 PRESENT IN PHARMACEUTICAL INDUSTRIAL WASTEWATER

Thesis submitted in partial fulfillment of the requirements for the award of degree of

Master of Technology
In
Environmental Science and Technology

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Date
27. June. 2011

DECLARATION

I hereby declare that work embodied in dissertation entitled **"Sonophotocatalysis of 4-chloro-2-nitrophenol using TiO_2 present in pharmaceutical industrial wastewater"** is original piece of work and was conducted in the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala. The matter presented in this thesis has not been has not been submitted in part or full, to this or any other university/ institute for any degree or diploma.

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Certificate

This is to certify that this dissertation entitles **"Sonophotocatalysis of 4-chloro-2-nitrophenol using tio_2 present in pharmaceutical industrial wastewater"** is an authentic work carried out by Ms. Harmanpreet Kaur , student of Master of technology in **Environmental Science and Technology** of Thapar university, (Patiala), during the year 2010-2011, in partial fulfillments for award of the degree, associate ship, fellowship or any other similar title to any other university or institute.

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Abstract

The use of conventional water and wastewater treatment processes becomes increasingly challenged with the identification of more and more contaminants due to rapid growth of population and industrial activities, and which leads to diminishing availability of water resources. So, advanced treatment technologies have emerged in last decade to remove various potentially harmful compounds that could not be effectively removed by conventional treatment processes.

Pharmaceutical residues are detected in several compartments of the environment, especially the aquatic one. Most of them enter the environment by treated and untreated wastewater. New purification techniques are under investigation to find ways for eliminating these substances effectively. These days considerable interest has been shown by researchers all over the world in the field of advance oxidation processes.

Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical (˙OH) generation as the primary oxidant. These radicals are produced by means of oxidizing agent such as H_2O_2 and O_3, ultraviolet irradiation, ultrasound, and homogeneous or heterogeneous catalysts. In this process a new application of ultrasound on the photocatalysis i.e. Sonophotocatalysis are considering these days. It is for improving the performance of photocatalytic degradation of organic and inorganic contaminants in aqueous streams. Basically Sonophotocatalysis is the combination of two AOP's i.e. Sonolysis (use of ultrasound) and photocatalysis (use of UV).

A lot of research has been done on this technology in the recent years for the degradation of compounds like phenols and substituted phenols, alkyl halides, aromatics halides, substituted halides, inorganic chemicals, dyes, herbicides and pesticides etc. and this treatment technology shows that it has potential for the degradation and mineralization of these non-biodegradable compounds. So, we can say that Sonophotocatalysis has large capability for the water treatment.

The purpose of this project is to see whether this sonophotocatalytic treatment is viable for treating pharmaceutical compound 4-cholro-2-nitrophenol or not. Titanium dioxide was used as Photocatalyst. Experiments were performed in UV light at optimized condition. The degradation of compound has been investigated in terms of various process parameters like catalyst dose, pH, and concentration of oxidant. In this case the catalyst concentration was optimized at .3g/200ml, pH at 7 neutral and oxidant concentration at 1ml/200ml of the sample.

The results obtained were quit appreciable as it reduced COD from 980 to 40mg/l. The results of Sonophotocatalytic degradation of pharmaceutical compound showed that it could be used as efficient and environmental friendly technique for the complete degradation of recalcitrant organic pollutants which will increase the chances for the reuse of wastewater. The investigations demonstrate the importance of selecting the optimal degradation parameters for practical applications of this operation.

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CHAPTER 1 (a)

INTRODUCTION

1.1 Overview

"Water, Water, everywhere, nor any drop to drink".

These famous wording are from The Rime of the Ancient Mariner by Samuel Taylor Coleridge when the Ancient Mariner is stuck in the middle of the sea. And because the ancient mariner is on the open ocean, the water is all salty and unfit for consumption. And this situation will soon happen with us as water will be around us but not fit for consumption due to presence of pollutants in it.

In our Solar System, Earth is known as the water planet, and water is an unconditional requirement of life.

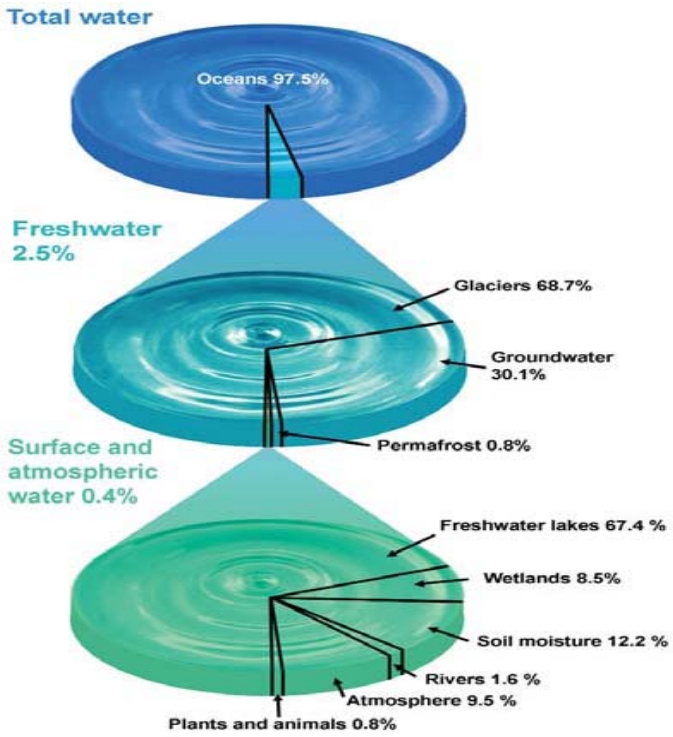

Figure-1.1 Global distribution of world's water

Over 97 percent of all water on Earth is found in the oceans. Rest of the 3 percent, most is locked up in glaciers and icecaps in Greenland and Antarctica, in saline inland seas or in the atmosphere, and is not readily available for consumptive use. Less than 1 percent of available water is usable by humans and other members of the Earth.

(**Understanding Global Water Distribution, 2003)**

1.2 Water pollution

Water is basic requirement in all industrial processes, domestic and commercial activities, so the waste water generated from different activities contains various contaminants which are harmful for both flora and fauna existing on this planet. Especially now in the developing world, pollution is increasing rapidly with urbanization and industrialization. And these industries generate a large number and variety of waste products. These wastes have very varied compositions depending on the type of industry and materials processed. The problem of adequately handling industrial waste water is more difficult due to its vary in nature from relatively clean rinse water to waste liquor than heavily laden with organic or mineral matter with corrosive, inflammable, poisonous or explosive substances. A large no. of organic pollutants coming from wide range of sources, which may enter in waste water, through various processes. Few of chemicals discharged by the various industries are provided in **Table 1.1**

Our environment is delicately balanced. It is a system of complex global chemical cycles working in synchronization using the limited natural resources. Hydrologic cycle which is one of the most important and yet highly unevenly distributed use of water with subsequent addition of contaminants has been disturbing the environmental balance. To prevent this, the techniques available for decontamination of wastewater are many, and the aim of these techniques is waste minimization and toxicity reduction. Thus, if these methods are implemented correctly, the development and growth can be sustained without destabilizing the hydrologic cycle. Preventing an effluent from entering into a large natural water source is the best option to control or limit its impact followed by minimization of the contaminants in it. **(Kularni A.A et al., 2002)**

Group	Material	Toxicity Ranking	Use
Aromatic Hydrocarbons	**Xylenes**	3 May contain benzene, a carcinogen	Aviation gasoline, protective coatings, solvent for alkyd resins, rubber cements, synthesis of organic chemicals
Phenols	**Phenol**	3 Questionable carcinogen	Making pharmaceuticals, chemicals, plastics, resins, rubber, refining oils, fertilizer, coke, paint removers, asbestos, perfumes, disinfectants, bactericide, fungicide
	Cresols	Toxic	Making disinfectants, perfumes, preserving agents or herbicide
Chlorinated Hydrocarbons	**Chlorophenols**	Questionable carcinogen, corrosive	Making dyes, making other chemicals
Nitroaromatic Hydrocarbons	**Nitrophenols**	3	Making fungicide, pesticide, dyes and other chemicals
	Nitrobenzene	3 Also called oil of mirbane, poison, reproductive effects	Making shoe polish, dyes, explosives, floor and metal polish, other chemicals and paints
	Aniline	3 Suspected carcinogen, mutagen, allergen	Dyes, coloured pencils, lithographic and other printing inks, perfumes, pharmaceuticals, nylon fibers, resins, industrial solvents, rubber processing
Sulphur Compounds	**Sulpholane**	Toxic	Natural gas processing, making electronics and plastics

where: 3 – severe toxicity, materials that can cause injury of sufficient severity to threaten life.
Data for total annual release in the USA in 2001, source: EPA.

Table 1.1 Use and hazard ranking information for chemicals (Sax & Lewis., 1992)

As a result of growth in industrialization amount of waste generated has increased and treatment or removal of thee contaminants from natural resources such as air or water in which they are released has progressed into special sciences, involving chemical, mechanical, and biological processes.

1.3 Waste water treatment processes

In order to achieve different levels of contaminant removal, individual waste-water treatment procedures are combined into a variety of systems, classified as primary, secondary, and tertiary waste-water treatment show in **Figure 1.2**.

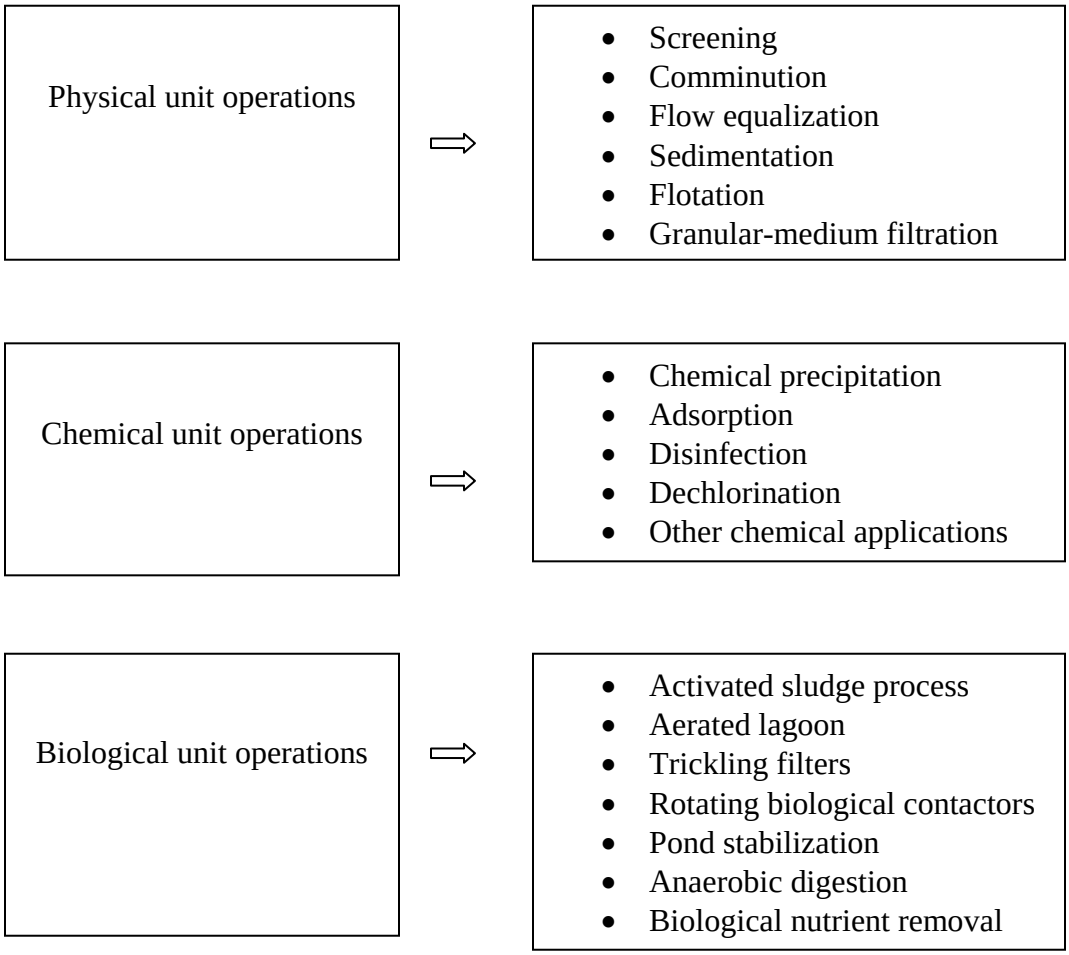

Figure 1.2: Waste-water treatment unit operations and processes

The use of conventional water and wastewater treatment processes become incrensingly challenged with the identification of more and more contaminats,rapid growth of population and industrial activites,and dimnishing availalability of water resources. **(Zhou.H and D.W. Smith, 2001)**

The major draw back of conventional methods is not able to treat toxic, non biodegradable organic pollutants so to meet the challenge of keeping progress in wastewater pollution abatement ahead of population growth, changes in industrial processes and technological developments, advance oxidation techniques have emerged in the past few years, in particularly for industrial waste water.

1.4 Emerging Technologies

All advanced oxidation processes (AOP) are characterized by a common chemical feature: the capability of exploiting the high reactivity of HO radicals in driving oxidation processes which are suitable for achieving the complete abatement and through mineralization of even less reactive pollutants. The different AOP are considered and critically presented according to their specific features with reference, whenever possible, to their real applications for water pollution abatement. (**Roberto Andreozzi et al.,1999)**

AOPs can be divided into established and emerging technologies based on the existing literature and the water treatment industry's experience with the technology. Emerging technologies are defined here as technologies that have very limited, if any, full-scale applications in drinking water treatment. **(Sunil Kommineni et al., literature review)**

Established Technologies	Emerging Technologies
• Hydrogen Peroxide/Ozone (H_2O_2/O_3)	• High Energy Electron Beam Irradiation (E-beam)
• Ozone/Ultraviolet Irradiation (O_3/UV)	• Cavitation (Sonication & Hydrodynamic)
• Hydrogen Peroxide/ Ultraviolet Irradiation (H_2O_2/UV)	• TiO_2-catalyzed UV Oxidation
	• Fenton's Reaction

Recently, considerably interest has been shown by all over the world in the application of ultrasound to improve the performance of photocatalytic degradation of organic and inorganic contaminants in aqueous streams. When ultrasound is combined with other AOPs, the combination would lead to faster degradation rates when compared to either method alone.

So, the process of Sonication (i.e. the act of applying sound usually ultrasound energy to agitate particles in a sample, for various purposes) can also be an attractive treatment option.

There is always scope for improvement, so we can use the application of ultrasound in conjugation with photocatalysis because many literatures have shown that the highest degradation and mineralization rate was attained with the combined use of photocatalysis and Sonolysis i.e. under Sonophotocatalytic conditions. If the two modes of irradiations (UV and ultrasound) are operated in combination, more number of free radicals will be available for the reaction thereby increasing the rates of reaction. **(Gogate P.R, 2008)**.

CHAPTER 1(b)

PHARMACEUTICAL WASTEWATER

1.5 Overview

Pharmaceuticals form a group of substances that are of considerable importance for society as healthcare tools. They are widely distributed, and there is a consistent global increase in the use of pharmaceuticals. Following this use is a corresponding increase in the generation of pharmaceutical waste. A variety of pharmaceuticals can be detected in surface, ground, and drinking water, so there are valid concerns about the potentially adverse environmental consequences of this contamination. The risk is directly proportional to the concentration of the chemical substances in various environmental compartments, and pharmaceutical waste adds to that risk if it is not managed properly.

The waste and disposal problem starts with the production of the pharmaceutical ingredient and finishes with the final disposal of a pharmaceutical product. During the manufacture and use of pharmaceuticals, lots of materials become contaminated with a pharmaceutical ingredient increasing the waste volume. Pharmaceutical waste is not only an environmental issue. Like other waste management, it is part of many peoples' working conditions in respect to how it is handled, contained and disposed of. Where there are issues with higher risk products, e.g., controlled drugs, increased security in handling pharmaceutical waste is also required.

Proper pharmaceutical waste management is complex thing in environmental management. Pharmaceutical waste may be present in any of the common physical forms like solids, liquids and gases and can be categorized in several ways, e.g., depending on source, physical state, hazard, security, handling and disposal.

1.5 a. Pharmaceutical waste be disposed of down the drain or via sewer systems

In many instances, at health care facilities and pharmacies, pharmaceuticals are sent to a regulated medical waste incinerator. Additionally, many pharmaceutical wastes are disposed of down the drain. USEPA generally considers sewer disposal inadvisable for pharmaceuticals and discourages this practice, unless specifically required by the label on

the particular pharmaceutical. In hospitals and other health care facilities, the practice of disposing of pharmaceuticals to sewers has taken place. This has occurred despite the potential adverse effects of introducing waste pharmaceuticals into the environment, and the inability of wastewater treatment plants to treat some pharmaceuticals effectively.

1.6 Occurrence and fate of pharmaceuticals in environment

Pharmaceuticals are excreted by humans, as a parent compound or metabolite, with urine (mainly) and faeces. Combined with other components of sewage they enter a sewage treatment plant (STP) where they do not get removed to a satisfactory degree so finally they end up in the environment. The medical compounds detected in the environment (water, soil) have recently deserved much attention. As having specific properties they may provoke effects to the aquatic and terrestrial ecosystems even at very low concentrations. They also possess several common features like e.g. polarity or persistence that implicate poor removal and bioaccumulation. **(K. Kujawa-Roeleveld et al., 2006)**

The occurrence of several pharmaceutical compounds have been reported in sewage treatment plant effluents as well as in surface waters in Germany, the Netherlands , Switzerland , Canada ,and the United States **(Kolpin, D.W et al., 2002)** . The detected compounds included antibiotics, anticonvulsants, painkillers, cytostatic drugs, hormones, lipid regulators, beta-blockers, antihistamines, and X-ray contrast media. The concentrations of these pharmaceuticals were in the range of µg/L to mg/L in sewage treatment plant effluents and surface water. In addition, a number of polar pharmaceutical compounds and metabolites, such as diclofenac, carbamazepine, sulfamethoxazole, and amidotrizoic acid, have been detected in groundwater samples at concentrations up to 1mg/L.There are several possible sources and routes for the occurrence of pharmaceutical compounds in the aquatic environment as shown in **Figure-2.1**

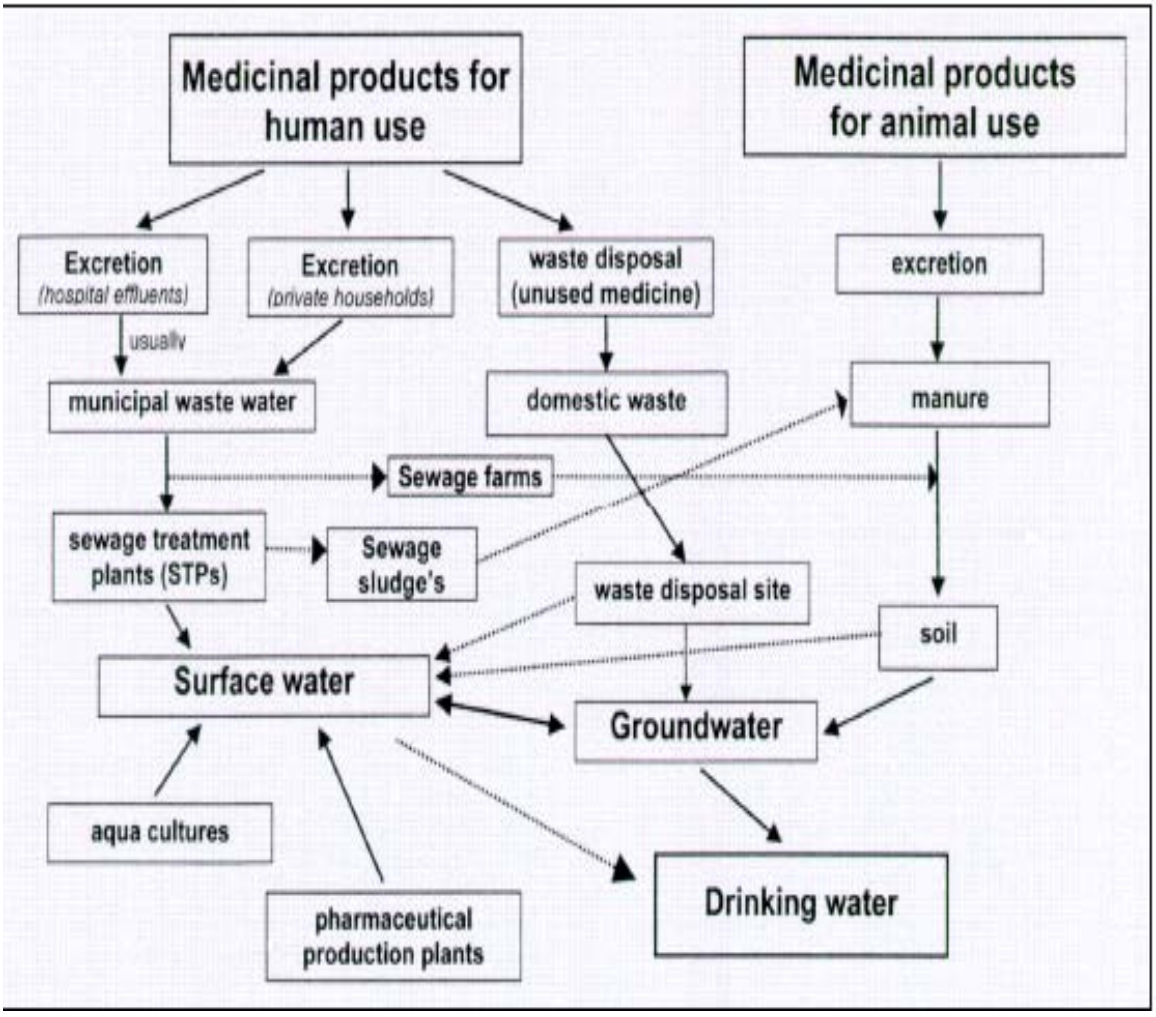

Figure 1.3 Overview about the pathways by which pharmaceutical waste enter the environment (Heberer, T. 2002)

1.7 Pharmaceutical active compound

Wastewater treatment plants usually exceed current discharge standards; the presence of unregulated pollutants in these effluents is of concern unregulated contaminants, or emerging pollutants of concern (EPOCs), are defined as substances that were previously undetected or had not been considered as a risk. The main sources of non-regulated contaminants in the environment are wastewater treatment plant effluents, which are not designed to eliminate these compounds. They are present in treated wastewaters at trace levels (µg/l to hg/l), and include personal care products, pharmaceuticals, surfactants, flame retardants, industrial chemicals, gasoline additives, and disinfection byproducts.

These contaminants do not need to be persistent in the environment to cause deleterious effects, since their high transformation and removal rates can be offset by their continuous introduction into the environment. Among the various substances that can be categorized as emerging pollutants, pharmaceutical active compounds (PhACs) are of special concern because of the volumes introduced to the environment, their endocrine disrupting activity, and a potential increase of bacterial resistance. It is estimated that hundreds of tons of PhACs are produced and consumed in developed countries each year Most of them end up being excreted completely unchanged or only slightly transformed conjugated to polar molecules.

Some PhACs are easily removed and degraded during sewage treatment, mainly by adsorption and bio-degradation; however, they can still be detected at the low μg/l level in treated effluents and receiving waters. This is the case for the analgesics acetylsalicylic acid (ASA), fenofibrate, and acetaminophen.

Some antibiotics also exhibit high removal rates when exposed to conventional activated sludge treatment. During this process, penicillins are hydrolyzed and tetracyclines precipitate with cations. Amoxicillin is also removed efficiently by biological treatment. These antibiotics are still found in receiving surface waters, however high rates of toxic degradation for Ibuprofen during bench scale experiments resembling wastewater treatment conditions and removals in the order of 96 to 99.9 percent during sewage treatment have been reported. In spite of these high removals, Ibuprofen is still detected in sewage effluents and surface waters at the μg/l level. Some drugs appear to degrade very little or none when treated with conventional activated sludge. That is the case for iodinated X-ray contrast media and the analgesic propyphenazone . **(Jose A. Polar, 2007)**

1.8 Environmental impacts of pharmaceuticals effluent

Health effects of the consumption of PhACs at low concentration levels are not fully understood, and it hasn't been determined yet if levels of PhACs found in drinking water pose a human health risk. PhACs' effects are tested on humans before being released to the public. These studies are characterized by high doses and short terms; however, little is known of the possible effects of long-term exposure at very low dosages (e.g. drinking water). Some research indicates that the low concentrations of PhACs and other contaminants present in drinking water are not harmful to humans from a toxicological point of view, but their presence is still not desirable as a precautionary principle. Others express their concern about the lifetime ingestion via drinking water of very low sub-therapeutic doses of several pharmaceuticals, which might pose a long-term risk for humans.

Also, pharmaceuticals that modulate endocrine and immune systems have a great potential of acting as endocrine disruptors. Antibiotics and antimicrobial agents (e.g. triclosan) are of concern because they could have direct effects over microbial populations, altering the community structure and increasing the resistance of human pathogens in the environment.

Endocrine disrupting compounds (EDCs) are chemicals that can either mimic natural hormones or increase or decrease hormone production. Compounds with estrogenic activity include a large number of natural and synthetic hormones, pharmaceuticals, pesticides, and industrial/household chemicals.

Acute effects are not the only concern affecting aquatic species. The continuous introduction of these chemicals into the environment could elicit imperceptible effects that might accumulate over time, causing profound ecological changes such as adaptation or ecological succession.

1.9 Conventional treatment methods

Untreated waste-water generally contains high levels of organic material, numerous pathogenic microorganisms, as well as nutrients and toxic compounds. It thus entails environmental and health hazards and, consequently, must immediately be conveyed away from its generation sources and treated appropriately before final disposal. The ultimate goal of waste-water management is the protection of the environment in a manner commensurate with public health and socio-economic concern obsessed earlier. As we discussed in first chapter about the conventional treatment technologies for treating waste water containing physical, chemical, biological processes. There are many limitations with the conventional system which have a propensity to use more chemical such as coagulant, polymer and chlorine during the extreme weather, which is actually not good for the consumer. And other drawback is its non ability to treat or degrade toxic and non biodegradable pollutants. So new technologies have made growing numbers of water treatment alternatives available and one of them is advance treatment method. It's a technology that reduces our dependent on chemical for treatment process and also helps us to treat various toxics present in wastewater. May be we can go for a chemical free treatment process in the future.

OBJECTIVES OF PRESENT STUDY

Main objective of my study is to treat those recalcitrant /non-biodegradable compounds present in pharmaceutical wastewater which are not treated by conventional treatment processes. In an attempt to increase the efficiency of decomposition of the impurities present in the wastewater and to improve the economics of the process, the work was carried out on the degradation of 4-chloro-2-nitrophenol using hetrogenous sonophotocatalytic (sonolysis + photocatalysis) treatment.

Combining of these two modes of irradiations i.e. US and UV eliminate the drawbacks of individual process and generate more number of hydroxyl radicals. This treatment does not transfer pollutants from one phase to another and leads to complete mineralization of organic non biodegradable compounds into simpler end products. The study was undertaken with the following objectives:

- To study the degradation of model compound using photocatalytic process used in pharmaceutical industry.
- To study the effect of various parameters such as concentration of catalyst, pH, H_2O_2 on degradation rate of these compounds and their kinetic studies
- To study the degradation of model compound using sonophotocatalytic process and calculate synergy.

CHAPTER 2

TREATMENT TECHNOLOGIES (Advance oxidation processes)

2.1 General Overview

In the past two decades, advanced oxidation processes (AOPs) have been proven to be powerful and efficient treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic contaminants. These technologies could be applied for contaminated groundwater, surface water, and wastewaters containing recalcitrant, inhibitory, and toxic compounds with low biodegradability as well as for the purification and disinfection of drinking water. Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical (**.**OH) generation as the primary oxidant (second highest powerful oxidant after the fluorine). These radicals are produced by means of oxidizing agent such as H_2O_2 and O_3, ultraviolet irradiation, ultrasound, and homogeneous or heterogeneous catalysts.

Investigators are trying to find better methods for **.**OH production. Hydroxyl radicals are non-selective in nature and they can react without any other additives with a wide range of contaminants whose rate constants are usually in the order of 106 to 109 $mol.L^{-1}.s^{-1}$. These hydroxyl radicals attack organic molecules by either abstracting a hydrogen atom or adding hydrogen atom to the double bonds. It makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization. A full understanding of the kinetics and mechanisms of all the chemical and photochemical reactions involved under the condition of use are necessary, by which, based on the well understood mechanisms, optimal conditions could be obtained. **(M. Mohajerani et al., 2009)**

Oxidizing species	Relative oxidation power
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, TiO_2^+	2.35

Table 2.1 Relative oxidation power of some oxidizing species (A.S. Stasinakis, 2008)

Advanced oxidation processes can be broadly classified into the following groups:

1. Homogeneous photocatalysis
2. Heterogeneous photocatalysis

2.2 Homogenous photocatalysis

In homogenous photocatalysis, a powerful UV lamp is used to illuminate the contaminated water in the presence of Fe^{3+}, O_3 or H_2O_2 which act as a catalyst and the reaction takes place in the bulk solution.

2.2.1 H_2O_2/UV Process

This process includes H_2O_2 injection and mixing followed by a reactor that is equipped with UV light (200 to 280 nm). During this process, ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical. The reactions describing UV/H_2O_2 process are presented below:

$H_2O_2 + h\nu \rightarrow 2\ HO\bullet$

$H_2O_2 + HO\bullet \rightarrow HO2\bullet + H_2O$

$H_2O_2 + HO2\bullet \rightarrow HO\bullet + H_2O + O_2$

$2HO\bullet \rightarrow H_2O_2$

$2\ HO_2\bullet \rightarrow H_2O_2 + O2$

$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2$

UV/H_2O_2 process is efficient in mineralizing organic pollutants. A disadvantage of this process is that it cannot utilize solar light as the source of UV light due to the fact that the required UV energy for the photolysis of the oxidizer is not available in the solar spectrum.

2.2.2 UV/ozone

Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of $^{\cdot}OH$ radicals:

$H_2O_2 \rightarrow HO_2^- + H^+$

$HO_2^- + O_3 \rightarrow HO_2 + O_3^-$

The reaction continues along the indirect pathway described above and $^{\cdot}OH$ radicals are produced. The combination of different reaction steps shows that two ozone molecules produce two $^{\cdot}OH$ radicals:

$2O_3 + H_2O_2 \rightarrow 2^{\cdot}OH + 3O_2$

2.2.3 $UV/O_3/H_2O_2$ process

In this process again HO radicals are considered to be the most important intermediates, initiating oxidative degradation of organic compounds. But here, compared to the rates of oxidative degradation observed in reactions in O_3/UV process with organic pollutants, the addition of hydrogen peroxide results in a enhancement due to dominant production of $HO^{\cdot}$ radicals. The addition of H_2O_2 to the UV/O_3 process accelerates decomposition of ozone resulting in increased rate of $HO^{\cdot}$ radicals generation. This is a very powerful method that allows a considerable reduction of the TOC. This process is the combination of the binary systems UV/O_3 and O_3/H_2O_2. **(Rodríguez.M, 2003)**

Mokrini et al., 1997 presented the degradation of phenol by means of this process at different pH, establishing the optimal H_2O_2 amount. A 40% of TOC reduction was achieved by this method. **Trapido et al., 2001** reported that the combination of ozone with UV radiation and hydrogen peroxide was found to be more effective for the degradation of nitrophenols than single ozonation or the binary combinations, increasing

the reaction rate and decreasing the ozone consumption when using low pH values. **Contreras et al., 2001** demonstrated that the addition of H_2O_2 to UV/O_3 system slightly improves the rate of TOC removal in solutions of nitrobenzene.

2.3 Heterogeneous photocatalysis

Heterogeneous photocatalysis can be defined as catalytic process during which one or more reaction steps occur by means of generation of electron-hole pair by suitable light on the surface of the solid semiconductor materials. The distribution and utilization of light energy due to the presence of solid catalyst material in liquid or gaseous mixtures makes this process more complex compared with homogeneous process.

In classical heterogeneous photocatalysis process, the reaction itself occurs in the adsorbed phase and the overall process can be decomposed into following steps:

1. Transfer of reactants from the bulk of fluid to the exterior surface of the catalyst.
2. Transfer of reactants from the external surface of the catalyst into its pore structure.
3. Adsorption of at least one of the reactants.
4. Reaction in the adsorbed phase.
5. Desorption of the products.
6. Transfer of products out of the pore structure to the exterior of the catalyst surface.
7. Transfer of products from the exterior surface of the catalyst to the bulk of the fluid.

(P.K dutta, 2004)

2.3.1 Photocatalysis or UV/TiO_2

The basis of photocatalysis is the photo-excitation of a semiconductor that is solid as a result of the absorption of electromagnetic radiation, often, but not exclusively, in the near UV spectrum. Under near UV irradiation a suitable semiconductor material may be excited by photons possessing energies of sufficient magnitude to produce conduction band electrons and valence band holes. These charge carriers are able to induce reduction or oxidation respectively.

Three components must be present in order for the heterogeneous photocatalytic reaction to take place: an emitted photon (in the appropriate wavelength), a

catalyst surface (usually a semi-conductor material) and a strong oxidizing agent (in most cases oxygen).

The heterogeneous photocatalytic process is initiated when a photon with energy equal to or greater than the band gap energy ($E_{hg)}$ of the photocatalyst reaches the photocatalyst surface, resulting in molecular excitation. (E_{ig}) is defined as the difference between the filled valence band and the empty conduction band of the photocatalyst, in the order of a few electron volts. This molecular excitation results in the generation of mobile electrons in the higher energy conduction band ($E_{d,}$) and positive holes in the lower energy valence band (E_{yh}) of the catalyst, according to equation 1 and the reaction illustrated in **Figure 2.1**.

photocatalyst —> $e^{-}+h^{+}$ (1)

The photocatalytic reaction proceeds via a series of chemical events, following the initiation step of pair electron-hole formation. This leads to the utilization of both the electron - hole h^{+} for oxidation processes and eventually to the capture of the e~ electron for reduction processes, as well as the potential formation of super oxides anions and hydrogen peroxide from oxygen.

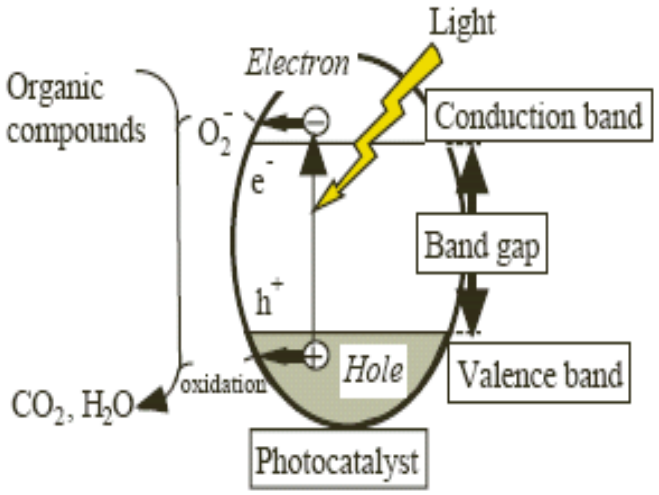

Figure 2.1: Basic mechanism of photolcatalytic reaction

The most effective photocatalyst for this purpose is titanium dioxide. This is a non-toxic, material that is a constituent of toothpastes and many cosmetics. Its reaction can be represented as a number of mechanistic steps. A photo-excited TiO_2 generates an electron and an electron-hole

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (2)$$

Electron transfer from the adsorbed substrate (RX_{ad}), adsorbed water or the OH_{ads} ion, to the electron-hole.

$$h^+ + RX_{ad} \rightarrow RX^+_{ad} \quad (3)$$

$$h^+ + H_2O_{ads} \rightarrow OH^{\cdot}_{ads} + H^+ \quad (4)$$

$$h^+ + OH^-_{ads} \rightarrow OH^{\cdot} \quad (5)$$

The third step is of great importance, mostly because of the high concentrations of OH^-, given water dissociation into ions.

$$H_2O \rightarrow OH^- + H^+ \quad (6)$$

Molecular oxygen acts as an acceptor species in the electron-transfer reaction.

$$e^- + O_2 \rightarrow O_2^- \quad (7)$$

Super-oxide anions, (equation7), can subsequently be involved in the following reactions.

$$O_2 + H^+ \rightarrow HO_2^{\cdot} \quad (8)$$

$$H^+ + O_2^- + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (9)$$

Photo conversion of hydrogen peroxide gives more OH' free radical groups.

$H_2O_2 + hv \rightarrow 2OH.$ (10)

Finally, $OH^{\cdot}$ radicals oxidize organic adsorbed pollutants (RXad) onto the surface of the titanium dioxide particles.

$OH^{\cdot}_{ad} + RX_{ad} \rightarrow$ Intermediate (11)

The OH radicals, as described by equation (11), are very reactive and attack the pollutant molecule to degrade it into mineral acids including carbon dioxide and water. **(Hugo de Lasa et al, 2005)**

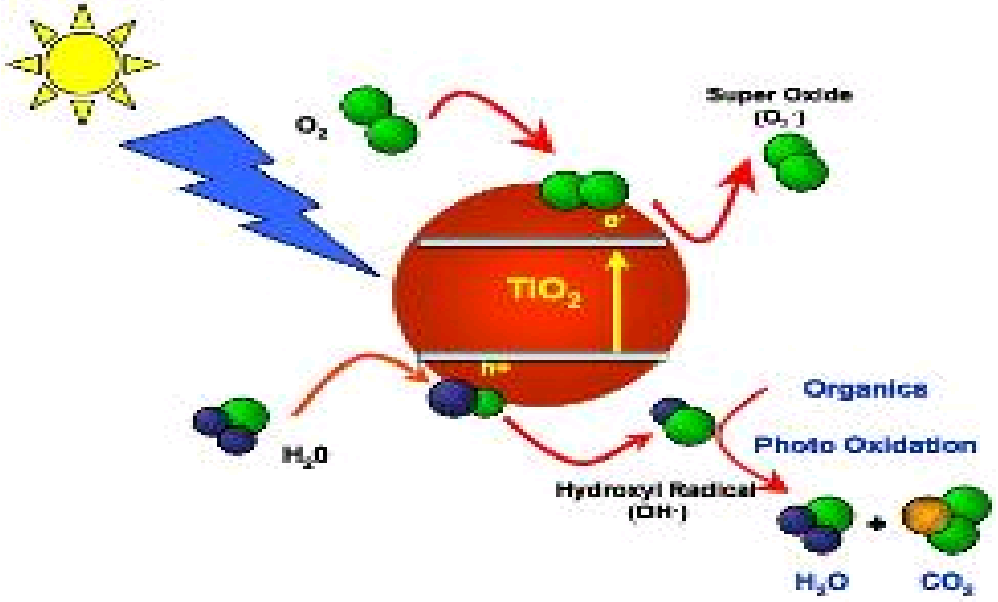

Figure 2.2: - Showing the working principle of TiO_2 catalyst

Comparision with other semiconductors

1) ZnO dissolved in acidic solutions.

2) CdS and GaP degraded during repeated catalytic cycles. **(Silva A.M.T et al., 2007*)***

Minero et al., 1994 studied the photocatalytic degradation of NB (Nitrobenzene) on TiO_2 and ZnO, reporting that complete mineralization with TiO_2 was achieved. **Mathew 1990**

also reported that more than 90% of NB mineralization was achieved with TiO_2 and sunlight. Phenolic compounds have been successfully degraded by photocatalytic process **(Giménez et al., 1996; Minero, C. et al., 1993**). Few studies have been found in the literature regarding the photocalytic oxidation of textile wastewaters.

S.No	Advantages
1	Inert (chemically and biologically).
2	Stable to corrosion.
3	Better from safety point of view.
4	Having low cost, limits the choice of convenient alternatives.
5	TiO_2 is of special interest as it can use natural UV.
6	An appropriate gap b/w valence and conduction band.
7	Band gap energy = 3.2 eV (VB energy = 3.1 eV & CB energy
8	Absorbs in near UV light (<387 nm) (i.e., natural (solar) energy)

Table 2.2: Showing the advantages of TiO_2

The modern boost in developing the technique of ultrasound treatment of aqueous systems is related to advances in sonochemistry and, in particular, accumulation of the results of ultrasound (ULS) action on organic and biological objects. Ultrasonic treatment has been successfully used in adsorption, chemosorption, and rectification processes and in ozone plants for wastewater treatment. The use of ULS simplifies the reactor design; its reliability and service life increase; energy consumption is reduced; mass transfer processes are speeded up; water purification is improved and accompanied by its simultaneous disinfection, deodorization, and decoloration.

2.4 Ultrasonic Cavitation / Sonication

Ultrasonic technology as an innovative technology may be used for water and wastewater treatment for pollution removal. This technology acts as an advanced oxidation process. Application of this technology leads to the decomposition of many complex organic compounds to much simpler compounds during cavitation process. It is one such recent technique which has been found to be substantially beneficial in wastewater treatment.

Ultrasound is the term used to describe sound energy at frequencies above the range that is normally audible to human beings (i.e.>16 kHz). At its upper limit ultrasound is not well defined but is generally considered as 5MHz in gases and 500MHz in liquids and solids which are subdivided to reflect applications. The range 20 to 100 kHz (though in certain cases up to 1 MHz) is designates as the power ultrasound reason, while the frequencies up to 1 MHz are known as high frequencies or diagnostics frequencies. Sound is composed from longitudinal waves comprising rarefactions (negative pressures) and Compressions (positive pressures). It is these alternating cycles of compression and rarefaction that, in high power ultrasonic applications, can produce a phenomenon known as “cavitation”.

Cavitation is described as the formation of microbubbles in solution that implode violently after reaching a critical resonance size. These microbubbles can be produced by a number of mechanisms:

1) Local increase in water velocity as in eddies or vortices, or over boundary contours;
2) Rapid vibration of the boundary through sonication;
3) Separation or parting of a liquid column owing to water hammer; or
4) An overall reduction in static pressure.

The rapid implosion of cavitation microbubbles results in high temperatures at the bubble/water interface, which can trigger Thermal dissociation of water molecules to form extremely reactive radicals. The extreme conditions generated during cavitation decomposes water to create both oxidizing (•OH) and reducing (•H) radical species.

There are three known methods of producing hydroxyl radicals using cavitation namely, ultrasonic irradiation or sonication, pulse plasma cavitation, and hydrodynamic cavitation. Sonication causes the formation of microbubbles through successive ultrasonic frequency cycles until the bubbles reach a critical resonance frequency size that results in their violent collapse. Pulse plasma cavitation utilizes a high voltage discharge through water to create microbubbles. In hydrodynamic cavitation, microbubbles are generated using high velocity or pressure gradients

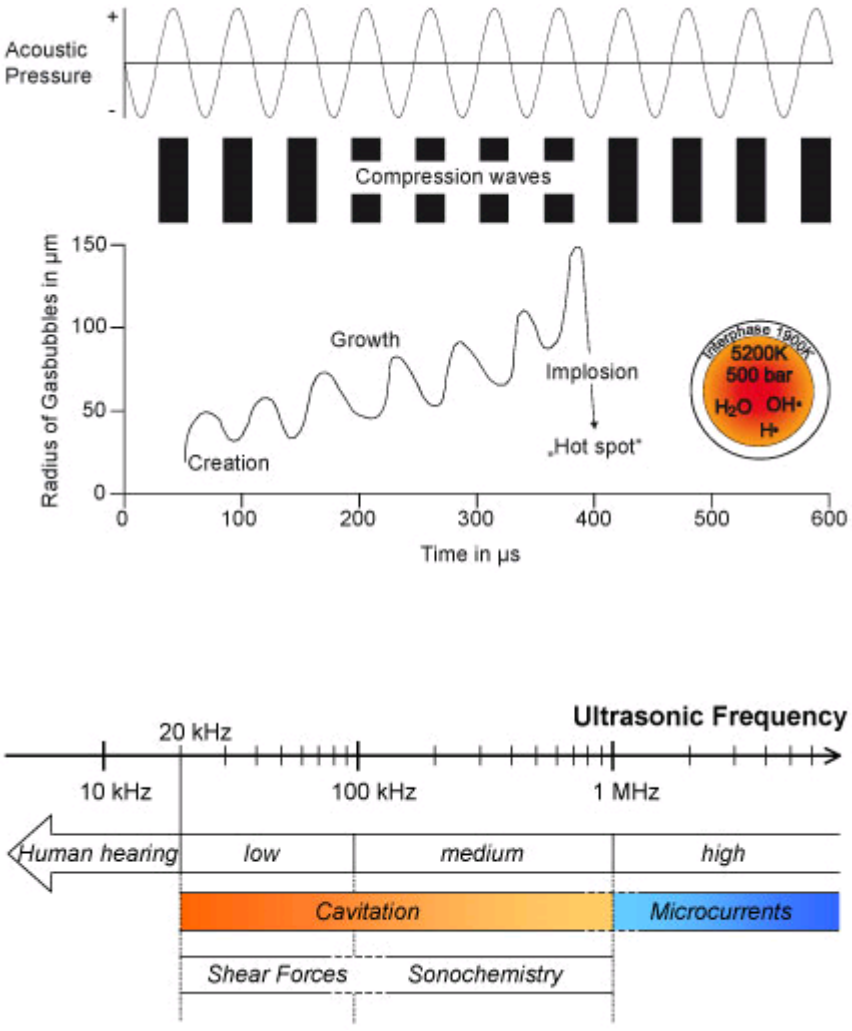

Fig 2.3: Principle of sonication and cavitation

The production of •OH through cavitation processes can be enhanced with the use of ozone. Gas-phase ozone thermally decomposes in the microbubbles, yielding oxygen atoms and molecular oxygen. This results in a number of reactions that subsequently yield hydroxyl radicals.

$O_3 + H_2O \rightarrow O_2 + 2\ \bullet OH$

$O_3 + \bullet OH \rightarrow HO^-_2 + O_2$

$O_3 + HO_2^- \rightarrow \bullet OH + \bullet O^-_2 + O_2$

The main factors that affect ultrasonic cavitation include:

1) The intensity of the ultrasound field (i.e., the frequency and amplitude of radiation);

2) The physical properties of the water (e.g., viscosity, surface tension, and vapor pressure);

3) The temperature; and

4) The presence of dissolved gas

S.no	Advantages
1.	Able to treat very toxic wastes at mild conditions.
2.	Environmentally friendly technology using only electricity as a reactant.
3.	The energy consumption depends on the chemical oxygen demand (COD).
4.	The sono- treatment can be simply stopped by switching the power off.
5.	Cost effective and safe.
6.	Fully-controlled by a computer.
7.	Even effluents with low conductivity can be treated.

Table 2.3: showing the advantages of sonication.

2.5 Sonophotocatalytic process

It is the combination of two advanced oxidation processes i.e. sonication and photocatalysis. The basic reaction mechanism for both ultrasound initiated degradation process as well as photocatalytic oxidation (either using UV light or solar energy) is the generation of free radicals and subsequent attack by these on the pollutant organic species. If the two modes of irradiations (UV and ultrasound) are operated in combination, more number of free radicals will be available for the reaction thereby increasing the rates of reaction.

The beneficial effect of coupling photocatalysis with sonolysis as well as adding hydrogen peroxide can be attributed to the increased production of hydroxyl radicals in the reaction system through the following steps, reactions (12)–(17)

(i) Water sonolysis (reactions (12) and (13)),

(ii) Reaction of H_2O_2 with the hydrogen atoms formed from water sonolysis (reaction (14)),

(iii)Hydrogen peroxide photolytic dissociation (reaction (15)),

(iv) Reaction of hydrogen peroxide with the super oxide radical anions formed during photocatalysis (reaction (16)),

(v) Reaction of hydrogen peroxide with conduction band electrons (reaction (17))

$$H_2O + \text{ultrasound} \rightarrow \dot{H} + HO^{\cdot} \quad (12)$$

$$H_2O + \text{ultrasound} \rightarrow \tfrac{1}{2} H_2 + \tfrac{1}{2} H_2O_2 \quad (13)$$

$$H_2O_2 + \dot{H} \rightarrow H_2O + HO^{\cdot} \quad (14)$$

$$H_2O_2 + h\nu \rightarrow 2HO^{\cdot} \quad (15)$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow HO\cdot + HO^- + O_2 \quad (16)$$

$$H_2O_2 + e_{cb}^- \rightarrow HO\cdot + HO^- \quad (17)$$

There have been several studies depicting the observed synergism and the enhanced rates of degradation for the combinatorial operation of sonochemical reactors and photocatalytic oxidation as compared with the sum of the individual processes.

(J. Madhavan et al., 2010) have given an extensive overview of different studies depicting the use of Sonophotocatalytic oxidation for treatment of ibuprofen. It has been observed that the rates of degradation. The sonolytic, photocatalytic and sonophotocatalytic degradations of IBP in the presence of homogeneous (Fe_{3+}) and heterogeneous photocatalysts (TiO_2) were studied. When compared with sonolysis and photocatalysis, a higher degradation rate was observed for sonophotocatalysis in the presence of TiO_2 or Fe_{3+} and also a slight synergistic enhancement was found with a synergy index of 1.3 and 1.6, respectively.

A lot of work has been done on it in recent years and many papers published for the degradation of dyes, phenolic compounds, alkyl halides, herbicides, surfactants etc. But as comparative to these a less work is done on pharmaceutical waste. Thus serious attention should be paid towards this issue as a variety of pharmaceuticals can be detected in surface, ground, and drinking water, so there are valid concerns about the potentially adverse environmental consequences of this contamination. The risk is directly proportional to the concentration of the chemical substances in various environmental compartments, and pharmaceutical waste adds to that risk if it is not managed properly. To cure such problems we have to apply advanced treatment options such as combine effect of ultrasound and photocatalytic process for degradation of compounds present in pharmaceutical wastewater.

CHAPTER 3

LITREAURE REVIEW

In many parts of the world, economic, social and political problems have arisen following rapid industrial development and urbanization, resulting in adverse effects on the quality of life. Urbanization in general initially places pressure on and overstrains public amenities. However, long-term and wider issues would eventually also be encountered as industrialization and urbanization exert pressure on the larger resource base that supports the community. This larger resource base includes forestry, freshwater and marine resources, as well as space suitable for further development. The difficulties associated with environmental degradation often originate from industrial development. They are amplified by rapid urbanization that is responsible for the growth of many major cities.

Rapid industrialization and its concentration in or near urban centers have placed very high pressures on the carrying capacity of the environment at specific locations. At these locations waterbodies such as rivers, lakes, and coastal waters have typically been severely affected. Freshwater is a vital natural resource that will continue to be renewable as long as it is well managed. Preventing pollution from domestic, industrial, and agro-industrial activities is important to ensure the sustainability of the locale's development. Undoubtedly the water pollution control efforts which have been underway in many countries have already achieved some success. Nevertheless the problems that are confronted grow in complexity and intensity. Recently, considerable intrest has been shown by researchrs all over the world in the application of ultrasound to improve the performance of photocatalytic degradation of organic and inorganic contaminants in aqueous streams.

Investigations dealing with the treatment of aqueous systems by physical methods show that ultrasound is an effective reagent less and highly ecological method of water purification of organic pollutants and microorganisms. This phenomenon involves creation, growth, and collapsing of bubbles or voids in the liquid under the impact of pressure fluctuations. Cavitation may cause the degassing of liquid; initiate free radical

reactions; speed up chemical reactions due to easier mixing of reagents; enhance the rate of emulsification; improve diffusion processes; create high concentration emulsions or homogeneous dispersions of particles; contribute to the extraction of substances; and remove or destroy specific particles from microorganisms.

Cavitation occurs whenever a new surface, or cavity, is created within a liquid. A cavity is any bounded volume, whether empty or containing gas or vapor, with at least part of the boundary being liquid. The collapse of the bubbles induces localized supercritical conditions: high temperature, high pressure, electrical discharges, and plasma effects. It has been reported that the gaseous contents of a collapsing cavity reach temperatures of $5500^{o}C$ and the liquid immediately surrounding the cavity reaches $2100^{o}C$. The pressure was estimated to be 500 atmospheres, resulting in the formation of transient supercritical water. Even though the local temperature and pressure conditions created by the cavity implosion are extreme, one can have good control over the sonochemical reactions. The intensity of cavity implosion, and hence the nature of the reaction, are controlled by such factors as acoustic frequency, acoustic intensity, bulk temperature, static pressure, and the choice of liquid or dissolved gas. The consequences of these extreme conditions are the cleavage of dissolved oxygen molecules and water molecules (into •H atoms and •OH radicals). From the reactions of these entities (•O, •H, •OH) with each other and with H_2O and O_2 during the quick cooling phase, HO_2• radicals and H_2O_2 are formed. In this molecular environment, compounds are decomposed. **(Chen Y.C, 2004)**

Many reports in the literatures have noted that a number of toxic or hazardous industrial chemicals could be destroyed by this novel technique. Following are some of the literatures:

Kritikos et al., 2007 concluded in his study that there is increase in photocatalytic activity with increase in TiO_2 loading, it means as we increase our catalyst it will result in more degrdation. He studied the degradation of reactive black 5 (a diazo dye) found in textile effluents, by means of ultra violet irradiation over TiO_2 suspension. The

simultaneous application of both ultra violet and ultra sound showed more beneficial results as compared to the both treatments occur separately. TiO_2 mediated UV photocatalysis is capable of completely decolurization RB5 solutions. It depends upon on the operating conditions such as type of concentration of catalyst, initial dye concentration, pH of the solution and the presence of dissolved gases in the reaction mixture

The study of sonolytic, photocatalytic and sonophotocatalytic degradations of ibrufen in the presence of homogeneous (Fe_3^+) and heterogeneous photo catalysts (TiO_2) was done by **Jagannathan Madhavan et al., 2010**.When compared with sonolysis and photocatalysis, a higher degradation rate was observed for sonophotocatalysis in the presence of TiO_2 or Fe_3+and gave the following observations

1. Sonolytic degradation followed first order dependence with respect to IBP.
2. Both TiO_2 and Fe_3+ sonophotocatalysis showed a slight synergy in the degradation of IBP when compared with the individual sonolysis and photocatalysis.
3. Mineralization using TiO_2 sonophotocatalysis was found to be an additive effect. However, a higher synergistic enhancement in the mineralization was obtained when Fe3+ was used as a photocatalyst and this may as a result of the complex formation of photoactive complexes between Fe_3+ and carboxylic acid intermediates. HPLC–MS was employed for the identification of the degradation intermediates. Sonication of IBP leads to the formation of its mono and di-hydroxylated intermediates.

A.S.Stasinakis, 2008 Investigated advance oxidation processes for the removal of recalcitrant organic constituents from municipal and industrial wastewater. The aim of this study was to review the use if titanium dioxide/uv light process in waste water. The major factors affecting these processes are the initial conc. of target compound, the amount of oxidation agents and catalysts, the light intensity, the irradiation time and the nature of wastewater's solution.

The rate of degradation and mineralization 1,4-dichlorobenzene (1,4-DCB) in the aqueous phase was investigated by **Elena Selli et al., 2008** under direct photolysisor

photocatalysis in the presence of commercial or sol–gel synthesized TiO_2, or under sonolysis at 20 kHz with different power inputs. The fastest degradation rate was attained under sonophotocatalytic conditions, with slightly higher energy consumption respect to sole photocatalysis. Ultrasound, though inducing 1, 4-DCB degradation at a lower rate, ensures parallel mineralization with lower energy consumption. Photocatalysis on TiO_2 particles leads to relatively fast 1,4- DCB degradation, though a relatively high amount of energy is consumed by the irradiation sources.

The study of Sonophotocatalytic/H_2O_2 degradation of phenolic compounds in agro-industrial effluents was done by **Adrian M.T.Silva et al., 2007**. Sonophotocatalytic treatment of a synthetic solution contain ing several phenolic compounds typically found in agro industrial effluents over Degussa Tio2 suspensions proved efficient in terms of specific pollutanats removal and solution mineralization. He concluded that the efficiency of photocatalytic degradation is a strong function of the applied UVA irradiation intensity.

A comparative study between the photocatalytic and sonophotocatalytic oxidation process of congo red was carried out by **N.J.B Perez, 2007** using titanium dioxide as a catalyst. the effect of parameters, such as the initial concentration of dye, the presence of oxygen and ultrasound, the TiO_2 crystalline structure and the amount of TiO_2, was studied using an inexpensive reactor. The oxidation and reduction processes of methyl orange was studied using the same reactor, but by changing the chemical environment in order to drive either the oxidation or the reduction reaction. The increase of congo red concentration produces quenching effect on the first order reaction rate. The latter fact was rationalized by the authors using electric theory which explain chemical and physical effects of ultrasonic cavitation. It showed that the densities for the oxidation process of the azodyes were higher when a conducting glass electrode covered with a thin film of TiO_2 was used as a working electrode instead of a platinum electrode. Finally it shows that ultrasound shows positive effect not only on oxidation reaction but also on reduction reaction as reduction process of methyl orange in the presence of ascorbic acid as hole scavenger.

The effect of ultrasound on the photocatalytic oxidation kinetics of elemental sulphur particles catalyzed by titanium dioxide was studied by **Mendez MA, 2007**, using a conductivity method to follow the reaction. The simultaneous use of TiO_2 photocatalyst and ultrasound has a positive effect on the oxidative reaction rate of sulphur particles. The zero-order oxidation rate constant of sulphur, reached after an activation period of approximately 150 min, was about 20 times higher when the reactor was sonicated, using an ultrasonic processor of 30 kHz, and this observation was explained by the formation of fused particles between sulphur and titanium dioxide induced by cavitation process. Finally, when the amount of sulphur is changed in the reactor, saturation kinetics seems to be the most appropriate model to describe the oxidation process in the presence of ultrasound and, in the other hand, when titanium dioxide was increased, a maximum rate was achieved when 0.56 g/L TiO_2 were used.

Y.suzuki et al., 1999 have worked on photo-catalytic oxidation of surfactant (polyoxyethylene-alkyl-ether,$C_{14}H_{29}O(CH_2CH_2)_7H$, here in after referred as SS-70) enhanced by high power ultrasound and showed that 1000 ml of 100ppm SS-70 is decomposed totally in about 20 minutes in the photo-catalytic process combined with the ultrasonic irradiation. Without ultrasonic irradiation, the decomposition needs more than 1 hour. It is also found that ultrasound has ability to decompose the surfactant by increasing the activity of the catalyst and mass transfer to the catalysts surface. The activity of catalyst increased by the destruction of surface of TiO_2 by ejecting flow from collapsing cavities .This results in mass transfer enhancement by decreasing the diffusion layer thickness around TiO_2 surface .It is found that the stirring speed largely influenced the degradation efficiency. In it aeration bubble is disintegrate d by stirring to produce micro sizes bubbles to enhance cavitation. The stirring was also caused the hydrodynamic cavitation to produce small bubbles from dissolved gases around the stirring turbine that become nuclei of cavitation as well as disintegrate aeration bubble.

Elena selli, 2002 investigated the synergistic effects of sonolysis combined with photocatalysis in the degradation of an azo dye in aqueous suspension. The degradation of the azo dye Acid Orange 8 in aqueous suspensions was systematically evaluated under sonolysis, photocatalysis and sonophotocatalysis as a function of dye concentration.

A comparative study between the sonolytic, photocatalytic and sonophotocatalytic oxidation processes of aqueous solutions of malachite green was carried out by **N. J. B.Perezin et al., 2007** in the presence of carbon tetrachloride, under a low power ultrasonic field (<15 W) and using titanium dioxide as a photocatalyst. The combination of ultrasound and CCl4 has a positive effect on the degradation rate of MG. it was not found synergy between sonolysis and photocatalysis when ultrasound was applied at low powers, both in the absence or in the presence of CCl4, during the oxidizing disintegration of MG. The advantage of the simultaneous use of photocatalysis and sonolysis lies on the faster elimination of some reaction intermediaries produced by ultrasound.

C. L. Bahena et al., 2008 have worked on the photocatalytic degradation of alazine and gesaprim commercial herbicides were carried out in aqueous TiO_2 suspensions under UV light. Degradation profiles were recorded by measuring the concentration of the active compounds present in the alazine (alachlor and atrazine) and gesaprim (atrazine) by HPLC as a function of irradiation time (sound and/or light). The photodegradation of these commercial herbicides was enhanced by the use of ultrasound in the presence of TiO_2 catalyst with very high decomposition yields of the active compounds reaching practically a complete mineralization in both commercial herbicides. Over 90% of the active component in the gesaprim was abated and those in alazine were completely degraded.

The sonolysis of diclofenac in water was investigated by J**. Hartmann et al., 2008** at ultrasound frequencies of 24 kHz, 216 kHz, 617 kHz, and 850 kHz and in the presence of various catalysts (TiO_2, SiO_2, SnO_2, and titanosilicate).out of them the irradiation at 617 kHz leads to the highest rate of degradationof diclofenac in water. The relative concentration of diclofenac in water decreased from 100% to 16% in the presence of titanium dioxide (P25) during 30 min irradiation**.**

A comparative assessment using various AOPs (UV, H_2O_2, UV/H_2O_2, Fenton, UV/Fenton and UV/TiO_2) was attempted by **P. Saritha et al., 2007** after initial

optimization studies, viz., varying pH, peroxide concentration, iron concentration, and TiO_2 loading. The degradation of the study compound was estimated using chemical oxygen demand (COD) reduction and compound reduction using spectrophotometric methods and further validated with high performance liquid chromatography (HPLC). The degradation trends followed the order: UV/Fenton > UV/TiO_2 > UV/H_2O_2 > Fenton >H_2O_2 >UV. The results of this study showed that the degradation of 4C-2- NP was strongly accelerated by the photochemical oxidation processes. Neither UV nor H_2O_2 alone could degrade 4C-2-NP. The combination of UV to the system i.e., UV/H_2O_2 process enhanced 4C-2-NP degradation rate but still required relatively long reaction periods with poor minimization efficiency. It can be inferred from the studies that UV/Fenton was the most effective in partial mineralization of 4C-2-NP. However, lower costs were obtained with H_2O_2.

The study of Degradation of 1,4-dioxane in water using TiO_2 based photocatalytic and H_2O_2/UV processes was done by **H.M. Coleman et al., 2007**. It involved the optimisation of the photocatalytic and H_2O_2/UVC processes for 1,4-dioxane removal. Different photocatalysts and loadings were investigated for the degradation of low concentrations of 1,4-dioxane in water including a commercial P25, TiO_2 photocatalysis completely mineralizes 1,4-dioxane to CO_2 in P25 suspension, MPC suspension and sol–gel reactors as does the H_2O_2/UVC process. Commercial P25 photocatalyst with UVA radiation shows the best performance in degrading 0.36 ppm 1,4-dioxane in water. The optimum H_2O_2 concentration giving the highest degradation rate in the H_2O_2/UVC process in the system studied was 30 ppm, giving a rate comparable to the photocatalytic sol–gel system. The addition of H_2O_2 to the photocatalytic system generally decreased the rate for the P25 reactor, but increased the rate for the MPC. The observations were attributed to a combination of photocatalyst activity, hydroxyl radical formation from hydrogen peroxide trapping electrons, formation of HO• radicals, radical–radical recombination and optimum H_2O_2/contaminant molar ratios .

The Sonophotocatalytic degradation of basic blue 9 industrial textile dye in the presence of ultrasound (20 kHz) over a TiO_2 slurry employing an UV lamp (15 W, 352 nm) was

studied by **González A.S and S.S Martínez, 2008** and showed that A negligible degradation of the BB9 dye can be observed under dark conditions with a color removal efficiency of 5% at 50 min of reaction time. The color removal efficiency increased up to 43% under sonolysis, 85% under photocatalysis and 97% under Sonophotocatalytic at 50 min of irradiation (sound and/or light) time. It was observed that the color removal efficiency was influenced by the pH of the solution, initial dye concentration and TiO2 amount and the highest degradation obtained at pH 7 and the optimal catalyst concentration reported in the literature for TiO_2 Degussa P25 ranges from 0.1 to 5.0 g l^{-1}**.**

Work on Sonophotocatalytic destruction of organic contaminants in aqueous systems on TiO_2 powders was done by **Lev Davydov et al., 2000.** They studied the effect of ultrasound on the photodegradation of salicylic acid on four commercial titania powders. The system exhibiting the highest enhancement was isolated. The use of ultrasound during photocatalysis had a pronounced effect on the rate and efficiency of salicylic acid destruction s as compared with UV-light photocatalysis alone. The possible reasons of the increased activity under ultrasonication were proposed: aggregate breakage and photocatalytic utilization of species produced by the ultrasound. The combination of the action of ultrasonic waves and UV-assisted photocatalysis yielded synergistic effects for the catalysts with smaller particle size (such as Hombikat), while no enhancement was observed for the largest particle size photocatalyst (Aldrich anatase). Degussa P25 exhibited the highest overall activity for the degradation of salicylic acid and moderate enhancement of activity by ultrasound. The presence of intermediates in the bulk solution was observed during the purely photocatalytic degradation of phenol. The presence of ultrasound, however, allows eliminating the toxic intermediates by the sonolysis in the bulk solution**.**

G.Ameta et al., 2009 have worked on Sonolytic, Photocatalytic and Sonophotocatalytic Degradation of Toluidine Blue. In their study they depict that the rate of the degradation is enhanced by the presence of visible light, ultrasound and photocatalyst. There is a supporting effect of these components towards each other in this reaction and thus, the dye can be degraded at a faster rate under these conditions.

Oocyte maturation in fish is triggered by maturation-inducing hormone (MIH), which acts on receptors on the oocyte surface. A synthetic estrogen, diethylstilbestrol (DES), possesses inducing activity of fish oocyte maturation, and a widely used biocide, pentachlorophenol (PCP), exhibits a potent inhibitory effect on fish oocyte maturation. the effects of the combined treatment by sonolysis with photolysis (sonophotocatalysis) to diminish the hormonal activity of DES and the maturation preventing activity of PCP was examined by **T. Tokumoto et al., 2008.** It was found that sonophotocatalysis, hormonal activity of DES was completely lost within 30 min and the inhibiting activity of PCP was lost within 120 min. These results demonstrated that sonophotocatalysis is effective for diminishing the endocrine-disrupting activity of chemical agents.

The accelerated sonophotocatalytic degradation of Reactive Red (RR) 120 dye under visible light using dye sensitized TiO_2 activated by ultrasound has been carried out by **S.K.Kavitha, and P.N.Palanisamy., 2011**. The effect ofsonolysis, photocatalysis and sonophotocatalysis under visible light has been examined to study the influence on the degradation rates by varying the initial substrate concentration, pH and catalyst loading to ascertain the synergistic effect on the degradation techniques. Ultrasonic activation contributes degradation through cavitation leading to the splitting of H_2O_2 produced by both photocatalysis and sonolysis. This increases the amount of reactive radical species inducing oxidation of the substrate and degradation of intermediates and is mainly responsible for the observed synergy

Chapter 4

Material and methods

This chapter deals with the materials and methods used during this research.

4.1 Materials:

4.1.1 Pharmaceutical compound

4-Chloro-2-nitrophenol (4C2NP) is known to cause severe pollution problems in aquatic environments. 4C2NP is widely used in pharmaceuticals industries, agriculture and related industries as an ingredient in pesticides and insecticides. However, it is highly toxic because it is refractory and hard to remove by conventional biological treatment processes.

4.1.2 Structure of compound

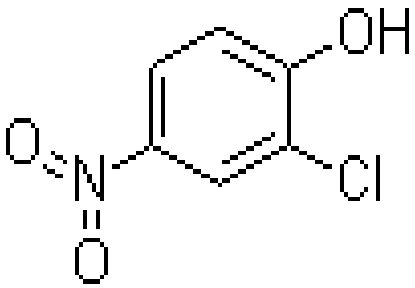

Figure 4.1: Structure of 4-chloro-2-nitrophenol

Full scan of compound was taken with the help of UV- Vis spectrophotometer and max. absorbance was observed at 234 nm .

4.2 Reagents and Chemicals used

The photo catalyst was TiO_2 P-25 (a mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30, procured from Degussa Company, India branch, Bombay). Hydrogen Peroxide (Ranbaxy laboratories) was used as an oxidant. COD of industrial effluent and treated sample was determined by using potassium dichromate solution

(Containing Mercuric sulphate and Concentration Sulphuric acid), COD reagent (containing Silver sulphate and Conc. Sulphuric acid), ferrous ammonium sulphate solution (0.05 N) and Ferroin indicator. In all experiments millipore water was used. Different normality of HCl and NaOH were used for adjustment of pH of stock solution.

4.3 Instruments used

4.3.1 pH meter

The pH of the solution was adjusted with the help of HCl and NaOH and measured with the help of pH meter. Instrument was calibrated with freshly prepared buffur solutions (of pH 4 and 9) from time to time throughout study. **(Figure-4.2)**

4.3.2 COD Digester

COD Digester was used for the digestion of samples in the process of COD determination. **(Figure-4.3)**

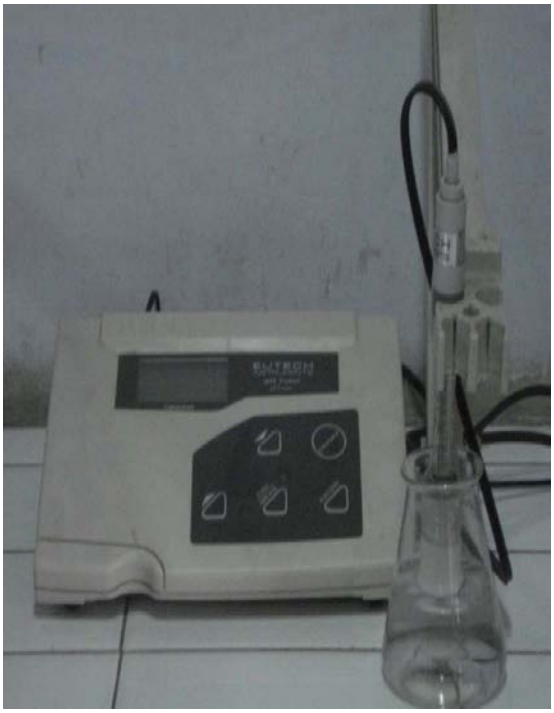

Figure 4.2: pH meter

Figure 4.3: COD digester

4.3.3 Spectrophotometer

The spectrum was taken with UV- vis. Spectrometer (Hitachi V- 500 UV/VIS (Japan) double- beam spectrometer. **(Figure-4.4)**

Figure 4.4: Spectrophotometer

4.3.4 Photocatalytic reactor

Comprising of a glass having three concentric cylinders, having outer ground glass jacket of borosil glass having socket and cone fitted with inlet and outlet tubes. And a cooling jacket of borosil glass with socket and inlet and outlet tubes is also provided; having capacity 200ml and a 125 watt UV bulb is used. Two reactors were used. **(Figure-4.5 and Figure-4.6)**

Figure 4.5: Two Photocatalytic reactors

Figure 4.6: UV bulb of 125 watts

4.3.5 Ultrasonic Bath

For Sonication ultrasonic bath is used having capacity 6.5 litre. Tank size is 12''x6"x6" (H) and U/S Power is 100 Watts U/S. Frequency is 33 ± 3 KHz and its model no. is EN 60 US. **(Figure-4.7)**

Figure 4.7: Ultrasonic bath

4.3.6 Sonophotocatalytic reactor

The immersion type photocatalytic reactor was placed in sonicator bath thus making sonophotocatalytic reactor. **Figure 4.8- Sonophotocatalytic reactor**.

4.3.7 Filtration

After photo catalytic treatment by photo reactor dye and effluent sample were filtered through syringe filters having Millipore filters of 0.45 um pore size.

Figure 4.8- Sonophotocatalytic reactor

4.4 Methods

4.4.1 Preparation of solution

a) Compound solutions:

The stock solutions were prepared by adding a known amount of compound into a small amount of deionized water in a 1-liter volumetric flask and filling it to the mark with millipore water. The flasks were covered with aluminum foil to avoid degradation by the laboratory fluorescent lights. Before the oxidation experiments could be performed, it was necessary to choose the appropriate concentration of compound solutions. For most of the experiments, stock solutions of 150 ppm concentration were prepared by dissolving 150 mg in millipore water and make the solution quantity to1 L. (If 1 g is

present in 1 L then solution is said to be1000 ppm and 0.15 g in 1000 ml then it becomes 150 ppm.)

b) Hydrogen Peroxide:

Hydrogen peroxide (30% w/v) was obtained from S.D. fine chem. limited having M.W. of 34.01. It implies that 100 ml of solution contains 30 g or 1 ml contains 300 mg. If this solution is diluted ten times then 1 ml contains 30 mg of H_2O_2. Hence for adding 300 mg/l of H_2O_2 in stock solution, add 10 ml in 1 L of stock solution or 1 ml of diluted peroxide solution in 100 ml of stock solution.

4.4.2 Estimation of COD

COD was estimated as per the standard method No. 5220C, page No.5-14 from Standard methods for the examination of water and wastewater, 1989(17thedition).

4.5 Degradation of compound

Photocatalysis: 4-chloro-2-nitrophenol solution of 150 ppm was prepared by Millipore water. 200 ml of sample taken in reaction vessel, 300mg of TiO_2 and 1ml of H_2O_2 was added, air is also supplied by the aerator during experimentation. Sample was taken in intervals of 15 minutes for first 1 hr and later after every half hr for 2 and half hrs. The concentration of these samples was detected by Spectrophotometer.

Sonophotocatalysis:

200 ml of 150ppm 4-chloro-2-nitrophenol solution was taken in reaction vessel, 300 mg of TiO_2 and 1ml of H_2O_2 was added, air is also supplied by the aerator. Then reaction vessel was placed in the Sonicator which is inside the photo reactor or UV chamber. Samples were taken in intervals of 15 minutes for first 1 hr and later after every half hr for 2 and half hrs. The concentration of these samples was detected by Spectrophotometer.

CHAPTER-5

RESULTS AND DISCUSSIONS

5.1 Compound Characteristics:

The compound sample of technical grade was taken and analyzed for its various parameters. The values of the various parameters are shown in **(Table 5.1)**

Parameters	Value
pH of compound	5.8(acidic)
COD of compound	980 mg/l (150 ppm concentration)
Max absorbance	234(nm)

Table 5.1: showing characteristics of 4-chloro-2-nitrophenol

5.2 Absorption spectra of 4-chloro-2-nitrophenol

The absorption spectrum of 4-chloro-2-nitrophenlol was recorded with a "UV- vis. Spectrometer (Hitachi V- 500 UV/VIS (Japan) double-beam spectrometer. The spectrophotometer measures the absorption spectrum using Scan software. The samples were placed in a quartz cell and the spectra were recorded in the wavelength range of 190–600 nm. Total 2 peaks were observed in absorption spetctra one is at 234nm and another is at 400nm. Compound shows absorbance at 400 nm (visible range) due to presence of color but max. absorption was shown at 234 (nm). Therefore Reduction 4C-2-NP concentration is measured at wavelength 234 nm.

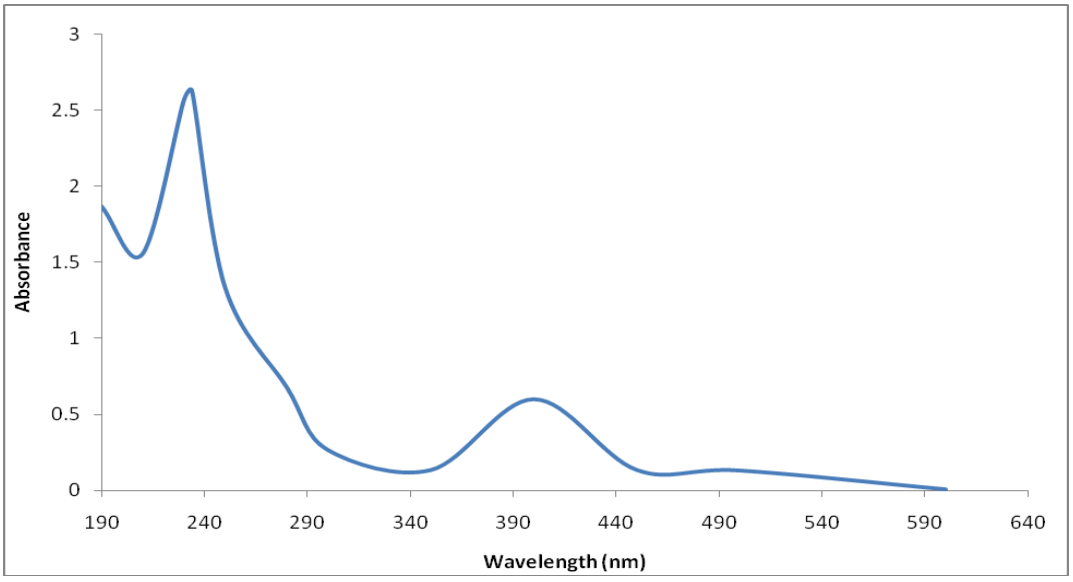

Figure 5.1: Showing absorption spectra of 4-chloro-2-nitrophenol before treatment

5.3 Standard curve of 4-chloro-2-nitrophenol

Figure 5.2 shows the standard curve for 4-chloro-2-nitrophenol which is prepared by plotting the absorbance of 4-C-2-NP solution of varying known concentration ranging from 10ppm to 100 ppm at 234 nm against concentration. From this graph we can calculate unknown concentration for 4-C-2-NP solution. Value of R^2 is .9951 and slope is .0363.

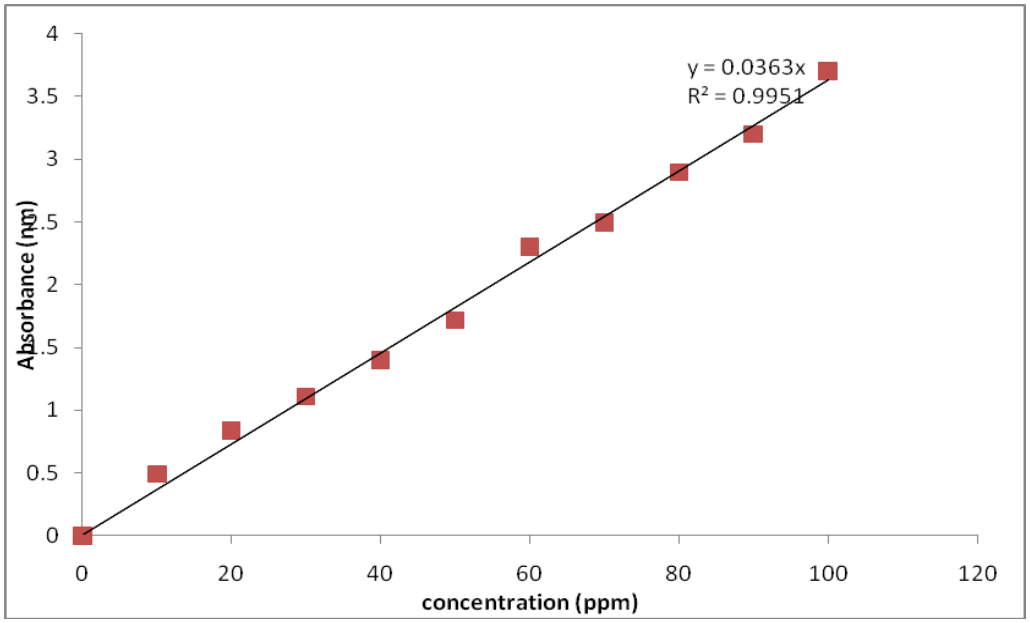

Figure 5.2: Showing standard curve of 4-chloro-2-nitrophenol

5.4 Preliminary studies

5.4.1 Dark adsorption studies: This study was carried out to know that how much adsorption was resulted from TiO_2. The addition of catalyst concentation in dark showed a very little decrease in concentration. The adsorption rate became constant after some time because of the monolayer formation on the catalyst surface. After monolayer formation, no free active sites were available for further adsorption so no further reduction in absorbance was observed. Thus results observed from adsorption experiment confirmed that decrease in concentration of compound was due to adsorption i.e. no degradation of the compound was confirmed.

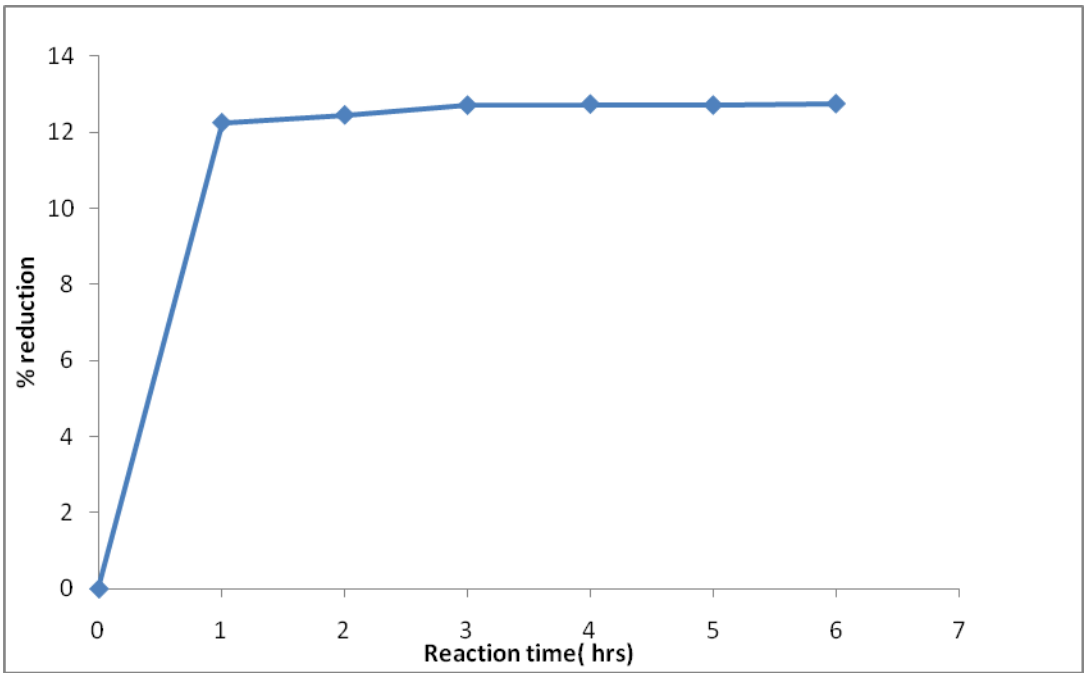

Figure 5.3: % Degradation due to adsorption phenomena

5.4.2 Photolysis (UV) of wastewater:

The parent compound is able to absorb part of the UV light, so its direct photolytic degradation in the absence of any photocatalyst was first investigated, to be compared with that of its photocatalytic degradation in the presence of TiO_2. So, the compound was irradiated under ultraviolet (UV) light alone in the absence of catalyst. It was observed

that after 5 hrs of UV treatment the degradation was not significant as compared to UV/TiO_2. **Figure-5.4** shows that there is only 9 % degradation due to photolysis.

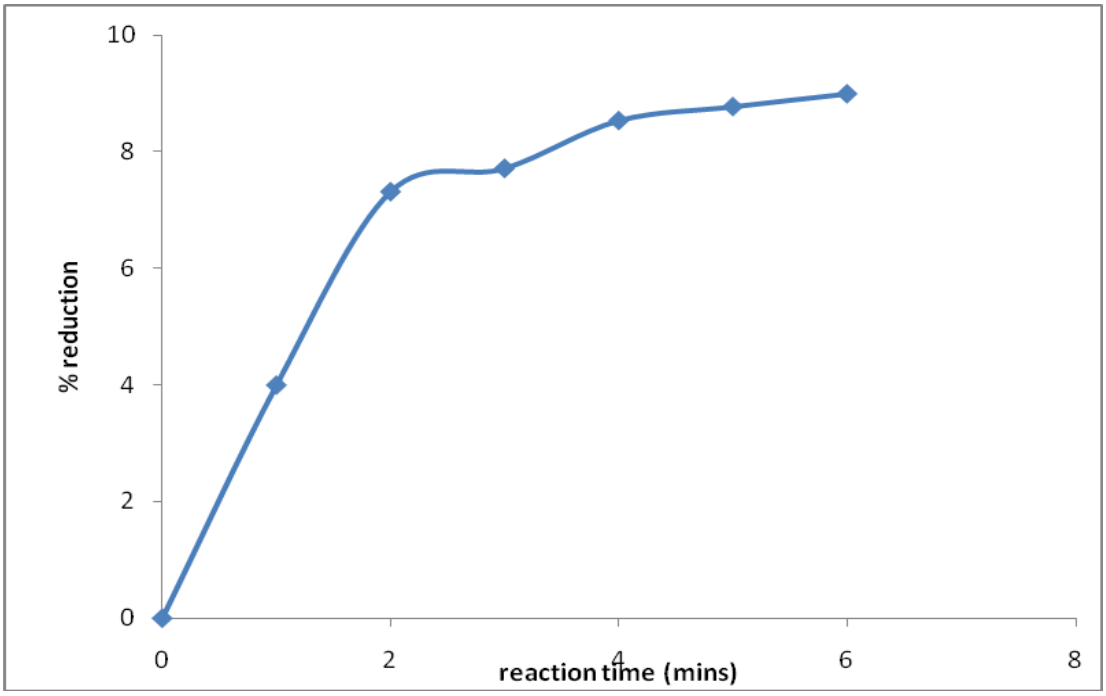

Figure-5.4 % Reduction due to photolysis

It was clear from the results of adsorption and photolysis **(Figure 5.3 and Figure 5.4)** processes that the rate of degradation in compound concentration was very less. Therefore some sort of advanced treatment was required to degrade the compound.

5.5 Photocatalytic treatment and process optimization

After the characterization of the raw compound, it was treated with the help of Photocatalytic treatment process. Photocatalytic treatment is affected by the following factors:

1) Concentration of the catalyst

2) Operating pH of the process

3) Concentration of the oxidant added

So the Photocatalytic treatment process was optimized for the following factors and these optimized conditions were used for the further actual treatment of the 4-C-2NP. Photocatalytic reactions can usually be described by a pseudo-first order kinectic expression.i.e.

$$-dC/dt = K_{UV} C_t. \text{ Or}$$

$$\text{i.e.} \quad \text{In } C_0/C_t = k_{UV}t$$

Where C_0 and C_t are the concentration of 4C-2-NP at times 0 and t, and k_{UV} is an apparent reaction rate constant.

Here plot of $\ln C_0/C_t$ Vs time was plotted and slope of graph will be apparent reaction rate constant (K).

5.5.1 Concentration of photocatalyst

To study the effect of catalyst dose on the degradation of compound, TiO_2 dose was varied from 0.1g/200ml to 0.8g/200ml during the photocatalytic treatment process. It was observed that the rate of photocatalytic process increases with increase in concentration of the catalyst up to certain limit and then becomes constant and starts to decrease after certain limit. The reason for this decrease in degradation rate is clustering of catalyst particles at higher concentrations and thus causing a decrease in the number of active sites on its free surface.

As the concentration of TiO_2 is increased, the number of photons absorbed from UV light and the number of compound molecules absorbed on the surface of catalyst are increased owing to an increase in rate of photocatalytic reaction. Above a certain level, the compound molecules available are not sufficient for the adsorption by the increased number of TiO_2 particles. Hence the increased catalyst amount is not involved in the catalytic activity and the rate does not increase with increase in the amount of catalyst beyond a certain limit. However after certain limit the no. of active sites on the surface of catalyst also decreases due to clustering of TiO_2 particles at higher concentrations.

Figure 5.5 and Figure 5.6 depicts that the maximum degradation was achieved with 0.3g/200ml concentration of photocatalyst. So an amount of 0.3g/200ml of TiO_2 has been taken for the subsequent experiments for the optimization of the operating pH and concentration of oxidant to be added.

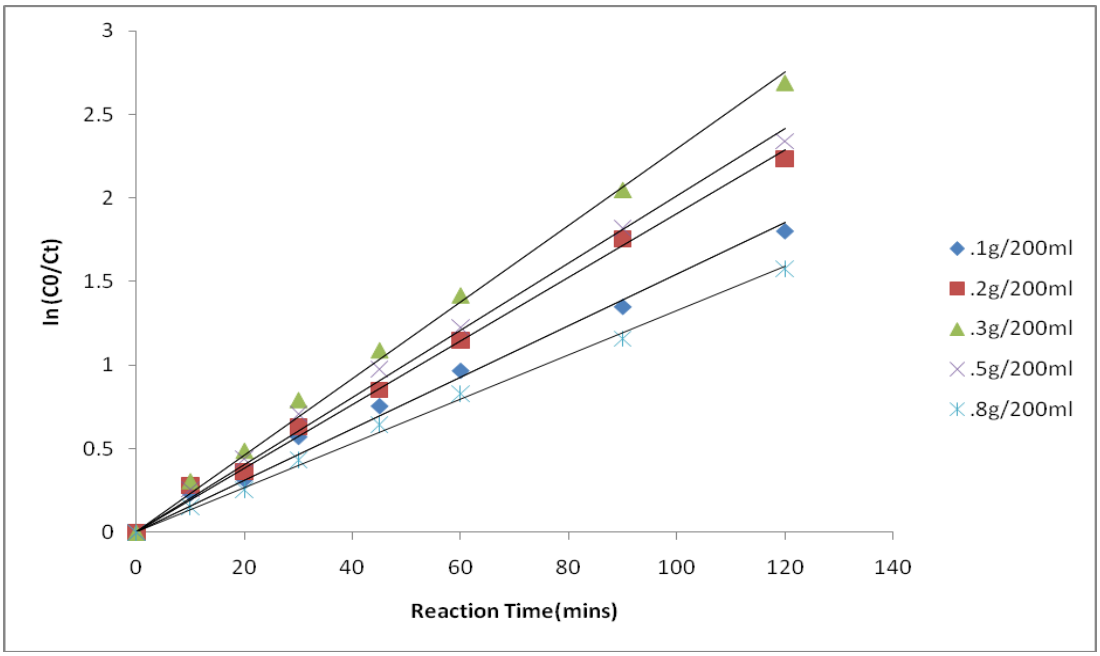

Figure 5.5: First order kinectic plot showing varying concentration of TiO_2 (C_0=150 ppm, pH= 5.8)

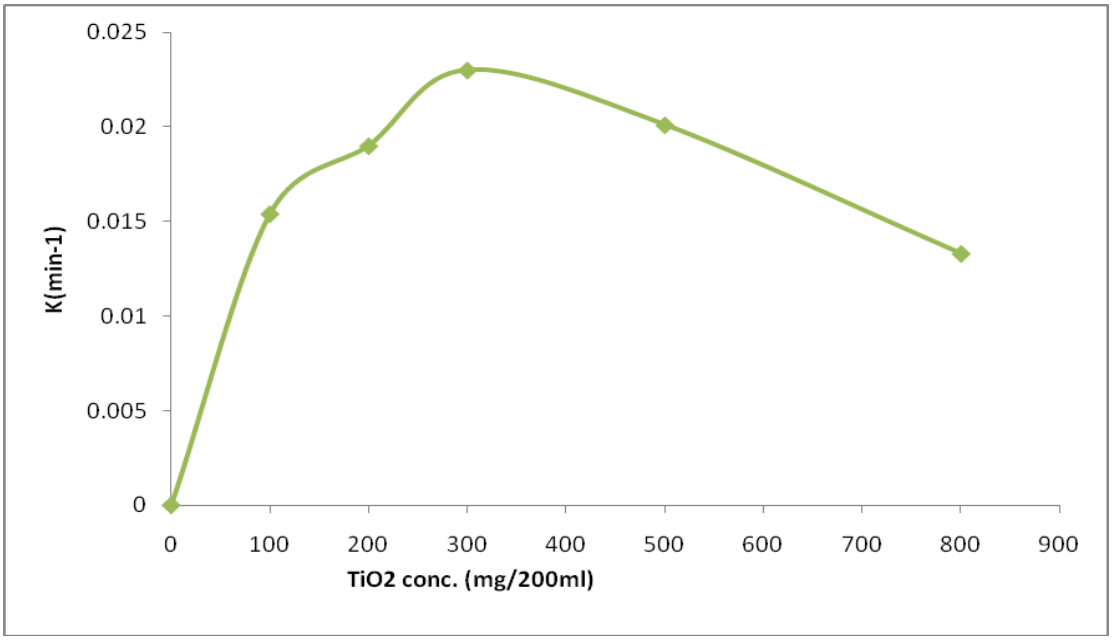

Figure 5.6: Showing the effect of TiO_2 dose on rate constant ,(C_0=150 ppm, pH= 5.8)

5.5.2 Operating pH

The generation of the hydroxyl radicals in AOP's is also effected by pH of the solution which is powerful oxidizing agent. Hence, employing Degussa P25 as Photocatalyst the degradation of compound in the aqueous suspensions of 0.3 gm/200 ml TiO_2 was studied in the pH range between 4 and 9. The effect of the solution pH on the degradation rate can be explained mainly by adsorption of compound on TiO_2 surface. In acidic suspensions, the adsorption of molecules of compound on the TiO_2 particles was significantly increased comparing to the extent of adsorption in alkaline suspensions. This is attributed to the fact that TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. The point of zero charge of the used TiO_2 (Degussa P-25) is widely reported at pH≈6.5. The TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution. Because the compound is negatively charged, the acidic solution favors adsorption of wastewater onto photo catalyst surface. In our study the degradation rate is increasing from pH 4 to 7 but after 7 it will start decreasing and further decreased in alkaline conditions (**Figure-5.7 and Figure-5.8**). The maximum degradation was observed at pH 7.0, moreover, the final pH after photo catalytic treatment was 6.5 which are suitable for biological treatment as well as discharge of compound into the water bodies.

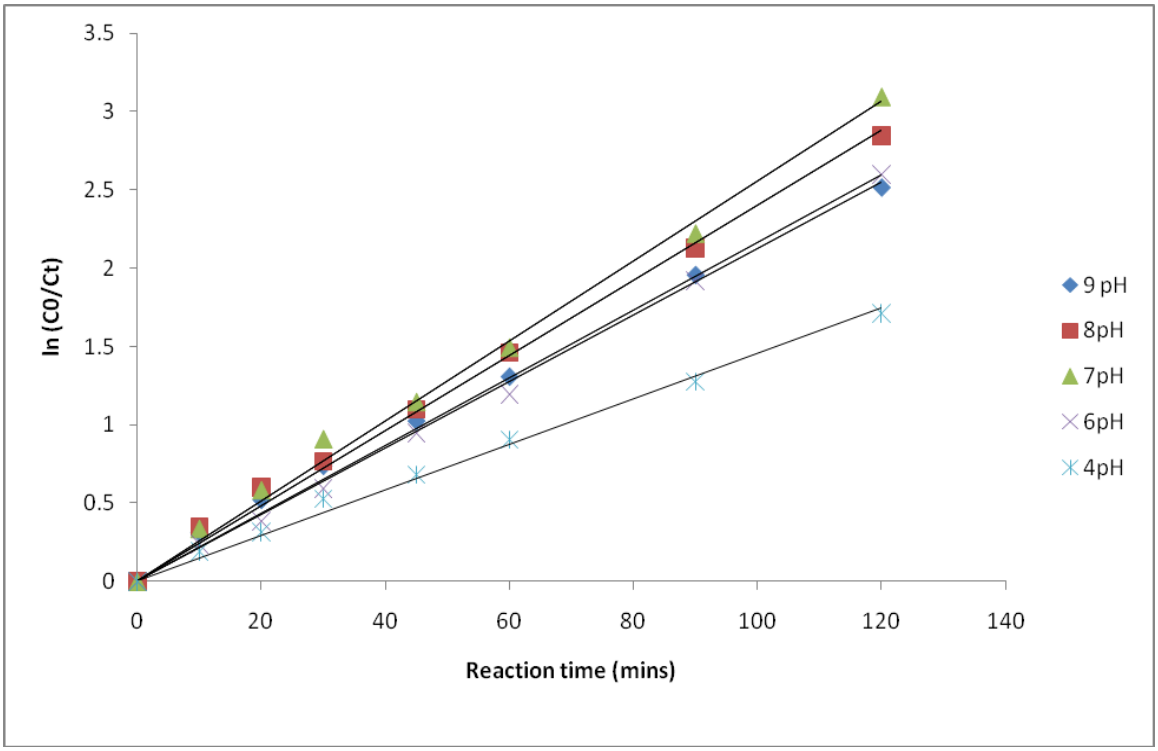

Figure 5.7: First order kinectic pilot showing the varying range of pH {C_0=150ppm, TiO_2 = 0.3g/200ml}

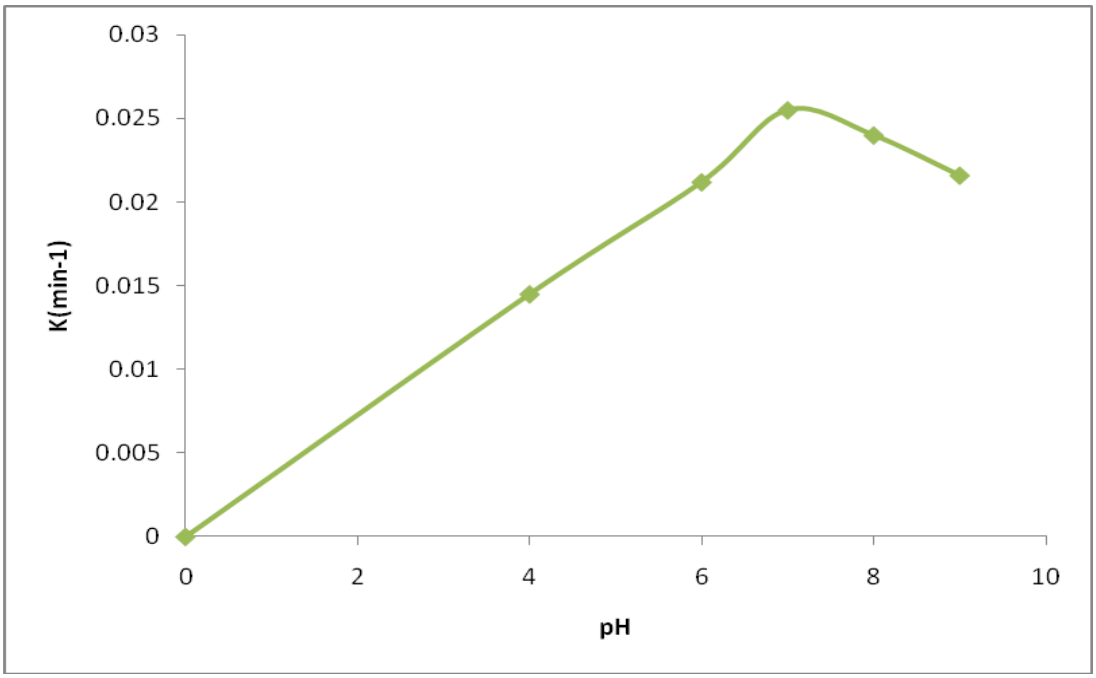

Figure 5.8 : Showing the effect of pH on rate constant K , {C_0=150 ppm, TiO_2 = 0.3g/200ml}

5.5.3 Effect of Oxidant addition

One possible way to increase the reaction rate is to increase the concentration of OH radicals because these species are promoters of photocatalytic degradation. The addition of hydrogen peroxide to the photocatalytic treatment process increases the concentration of OH radical, since it impairs the electron-hole recombination, according to the following equation:

$$TiO_2 (e-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^{\cdot}$$

It accepts the photo generated electron from the conduction band and thus promotes the charge separation, and it also forms OH radicals. However at high concentrations of H_2O_2 it also acts as scavenger as shown in the following equation.

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$$

$$H_2O_2 + OH^- \rightarrow H_2O + O_2$$

In our experiment in order to optimize the oxident dose the concentrations were varied during the photo catalytic treatment from 0.5 to 2.5 ml/200ml at constant pH of 7 and catalyst dose of 0.3g/200ml. It has been observed that best results were obtained when oxidant addition came out to be 1ml/200 ml of the sample and has been taken as the optimum amount required for maximum effective treatment of compound. **Figure 5.9 and Figure 5.10** shows the effect of oxidant clearly indicates maximum degradation at 1ml / 200 ml of the wastewater.

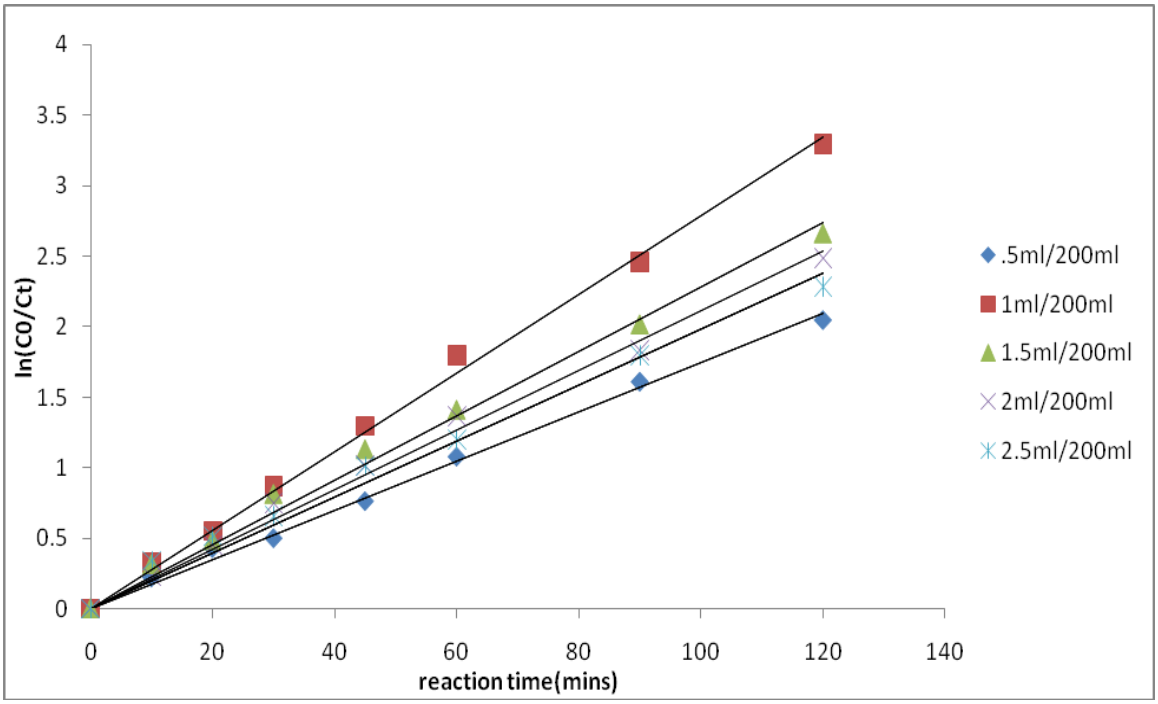

Figure 5.9 :First order kinectic plot showing the varry conc.of H_2O_2 {C_0=150ppm, TiO_2 = 0.3g/200ml, pH=7}

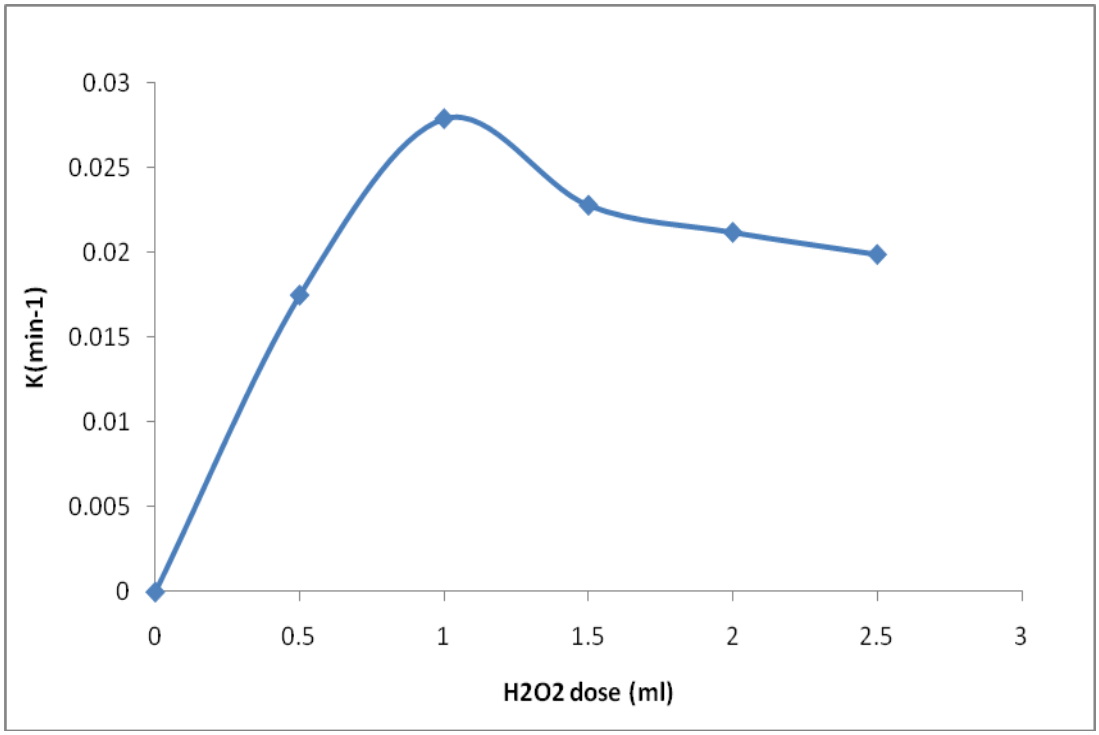

Figure 5.10: Showing the effect of oxidant dose on rate constant K {C_0=150ppm, TiO_2 = 0.3g/200ml, pH =7}

S.K.Kavitha, and P.N.Palanisamy, 2011 have reported the similar behavior during Photocatalytic and Sonophotocatalytic degradation of Reactive Red 120 using Dye sensitized TiO_2 under Visible Light. It show that the degradation rate increases with increases in addition of H_2O_2, becomes maximum at certain level and then starts decreasing with further increase in the concentration of H_2O_2.

5.6 Sonolytic (US) and Sonocatalytic treatment (US+TiO_2)

Sonolysis is the breaking of chemical bonds or formation of radicals using ultrasound. The action of ultrasound allows for the creation of micro bubbles in water at high temperature and pressure, leading to localize transient supercritical conditions. This leads to the production of active radicals ($H^{\cdot}$ and $^{\cdot}OH$) that take part in the degradation of organic matter. The use of photocatalyst and oxidant addition further raises the degradation level and it is clear from the following figures that maximum degradation was achieved with US+ TiO_2+ H_2O_2 then US + TiO_2 and then US.

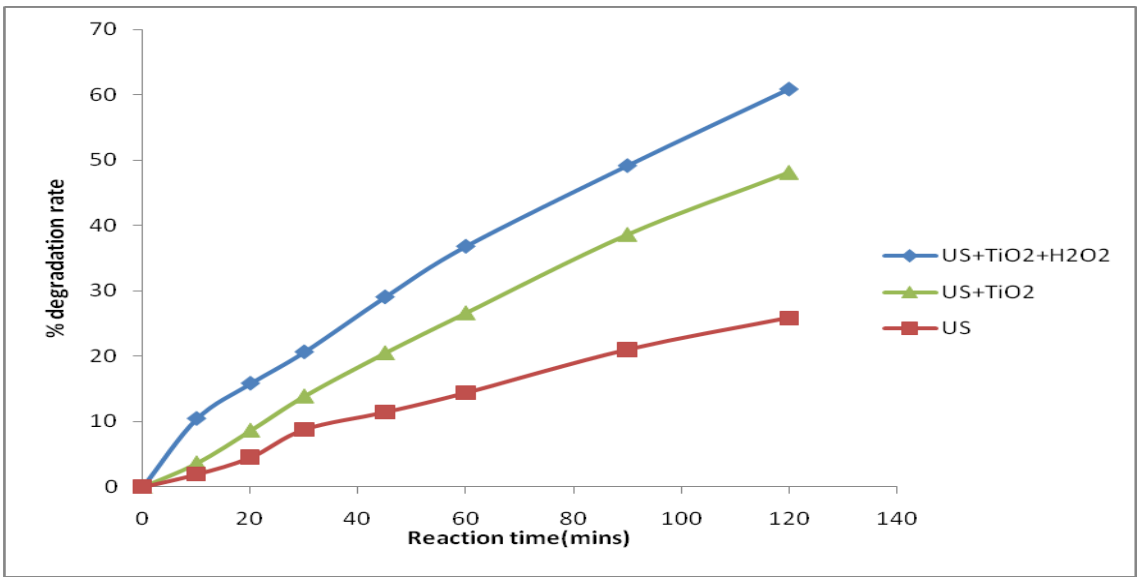

Figure 5.11: % Degradation rate due to Sonolytic and Sonocatalytic and Sonocatalytic + oxidant processes {C_0=150ppm, TiO_2 = 0.3g/200ml, H_2O_2= 1.0ml/200ml}

Figure 5.11 shows Sonolysis with all optimum parameters (i.US+TiO_2+H_2O_2, ii. US+TiO_2) shows better results than alone Sonolysis because ultrasound play a profound role due to substantial increase in the no. of active sites and also the surface area available due to defragmentation of the catalyst agglomerates under the action of turbulence by acoustic streaming along with an increase in the diffusion rates of contaminants.

5.7 Sonophotocatalytic (US+TiO_2+H_2O_2) treatment under UV

Photocatalytic action with the ultrasound has resulted in higher degradation rates of the contaminants. This is because in heterogeneous catalytic systems, the use of ultrasound creates conditions of increased turbulence in the liquid, thus decreasing mass transfer limitation and increasing the surface area available due to catalyst fragmentation and de-agglomeration.

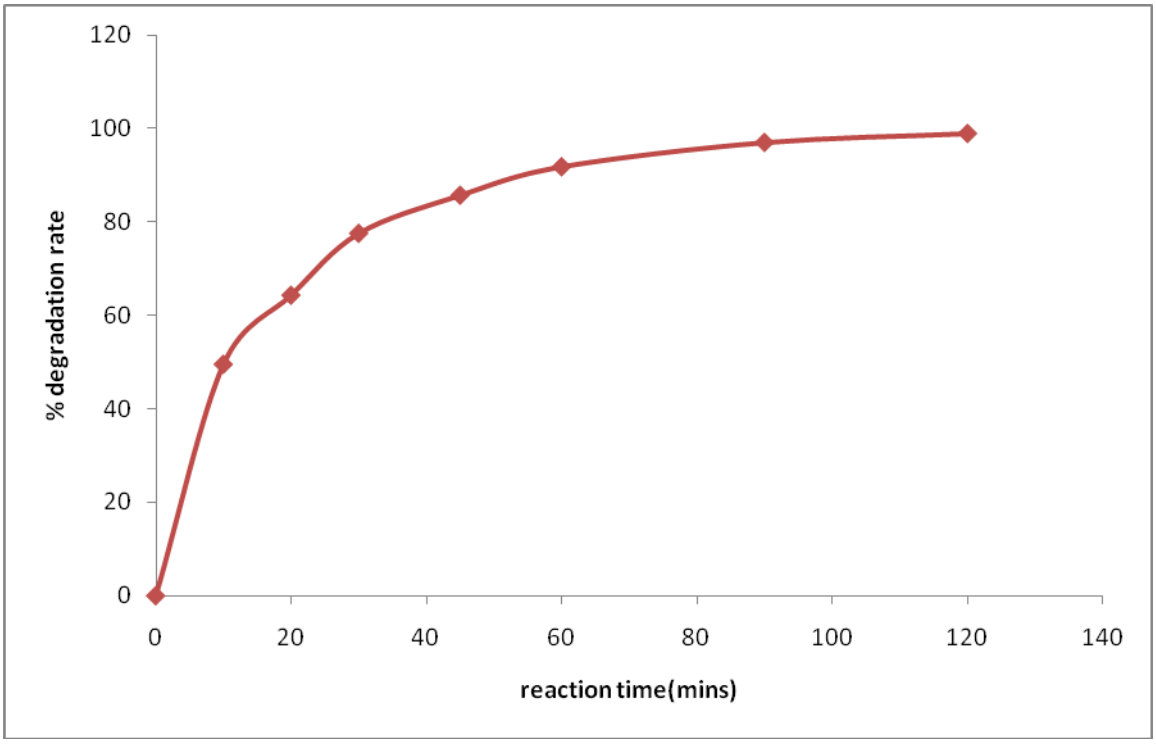

Figure 5.12 Effect of UV on sonocatalytic degradation of wastewater {C_0=150ppm, TiO_2 = 0.3g/200ml, H_2O_2= 1.0ml/200ml}

Figure 5.12 shows that the maximum degradation achieved in under UV light is 98% after 1.5 hour.

5.8 Comparisons of Sonocatalytic, Photocatalytic and Sonophotocatalytic treatment.

The reason for this is that the basic mechanism for both ultrasound and photocatalytic oxidation is generation of free radicals. If these modes of irradiations are operated in combination, more no. of radicals will be available for the reaction. **Figure 5.13** shows that by increasing the rate of reaction max degradation were achieved under Sonophotocatalytic treatment of compound (4C2NP) i.e. 96 % after 1 hours of reaction time. As compared to photocatalytic treatment i.e. 95% after 2 hours and very less under Sonocatalytic process i.e. only 61% after 2 hours.

González A.S and S.S Martínez, 2008 have shown the similar results on the degradation of basic blue 9 industrial textile dyes

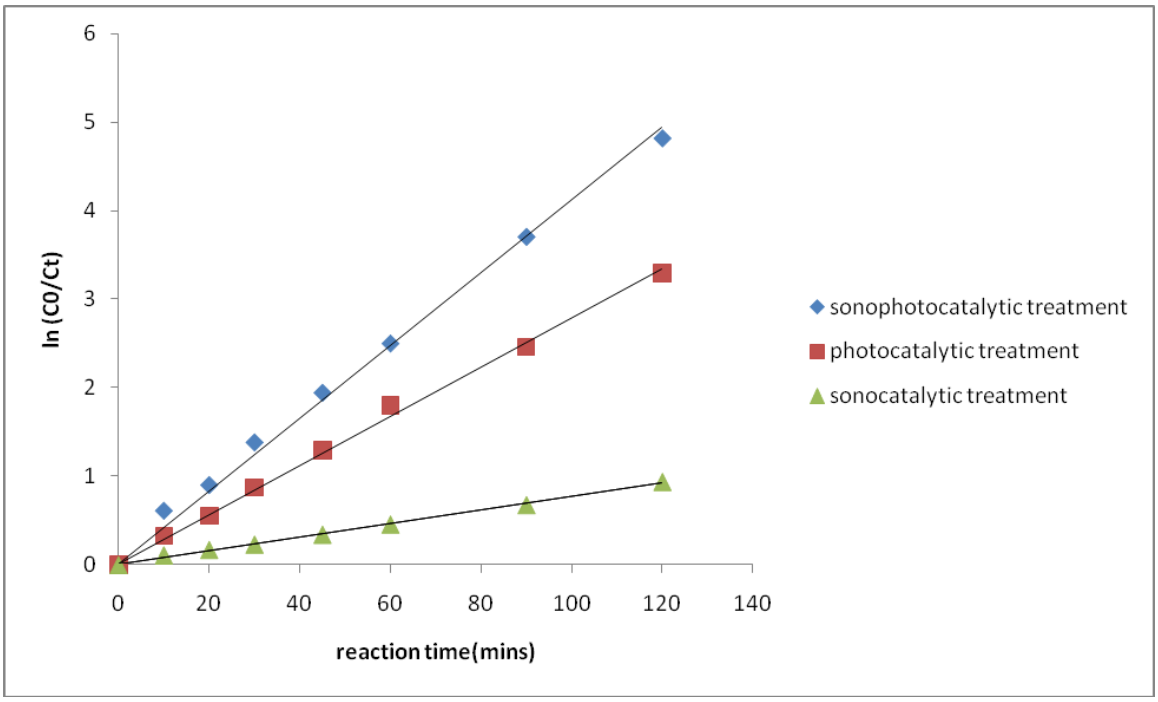

Figure-5.13 First order kinetic plot with 0.3g/200ml TiO_2, 1ml/200ml H_2O_2 and 7 pH under Sonophotocatalysis, photocatalysis and Sonocatalysis as a function of time.

5.9 Mineralization studies

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. COD reflects the degree to which the degradation or mineralization of an organic species has occurred. Therefore, reduction of COD is also monitored along with 4C-2-NP concentration.

Percentage reduction of COD with different AOPs is shown in **Figure 5.14**.Neither sonocatalytic nor could photocatalyitic alone totally remove COD. But both in combination that is sonophotocatalytic process showed considerable reduction in COD (96%).

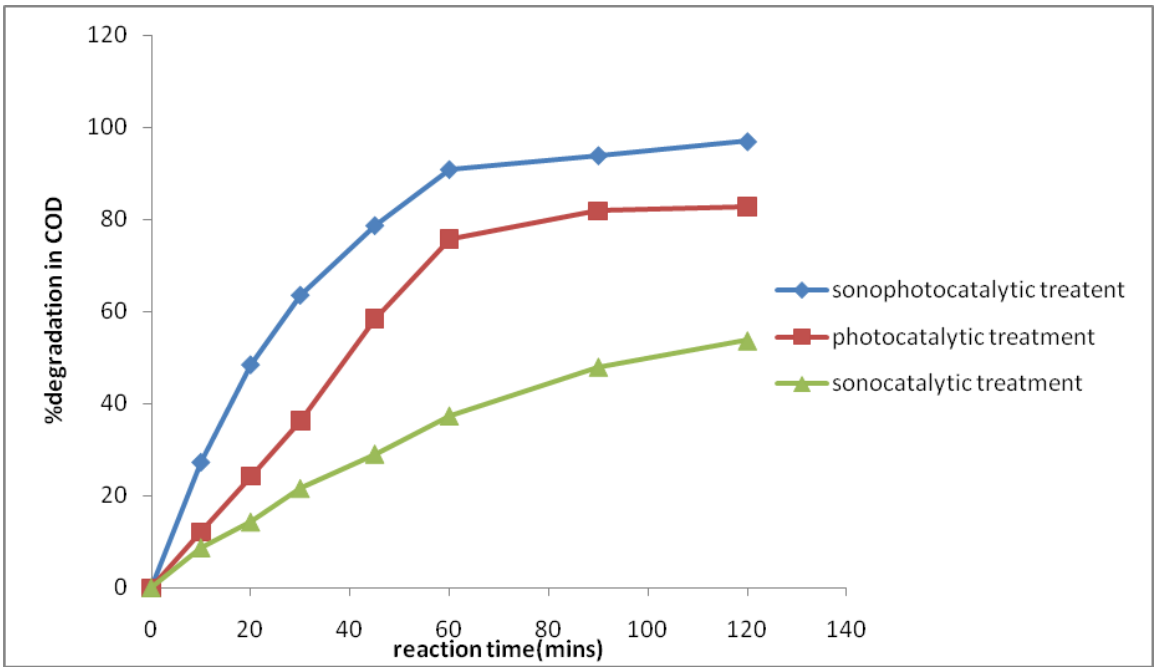

Figure 5.14: Reduction in COD using various processes (C0=150 ppm, pH=7, H_2O_2=1ml/200ml, TiO_2=.3g/200ml)

5.10 Synergy

There appears to be a synergistic effect between ultrasound and ultraviolet irradiation in the presence of semiconductor since rate constants of the combined process ($K_{US+UV+TiO2+H2O2}$) are greater than the sum of the rate constants of the individual processes ($K_{UV+TiO2+H2O2}$ +$K_{US+TiO2+H202}$). The synergy can be quantified as the normalized difference between the rate constants obtained under sonophotocatalysis and the sum of those obtained under separate photocatalysis and sonocatalysis .

$$\% \text{ synergy} = 100 \times \frac{(K_{US+UV+TiO2+H2O2}) - (K_{UV+TiO2+H2O2} + K_{US+TiO2+H2O2})}{(K_{US+UV+TiO2+H2O2})}$$

In our study the rate constant of combined process $(K_{US+UV+TiO2+H2O2})$ is .0411hr^{-1} and rate constant of $(K_{UV+TiO2+H2O2}$ is .0279 hr^{-1} and for $K_{US+TiO2+H2O2}$ is .0077 hr^{-1}

$$K_{UV+TiO2+H2O2} + K_{US+TiO2+H2O2} = .0279 + .0077 = .0356\ hr^{-1}$$

$$K_{US+UV+TiO2+H2O2} = .0411 hr^{-1}$$

So it is clear that rate constants of the combined process are greater than the sum of the rate constants of the individual processes.

$$\% \text{ synergy} = 100 \times \frac{(.0411) - (.0279 + .0077)}{.0411}$$

$$= 13.3\%$$

Therefore % synergy is 13.3%

Berberidou.C et al., 2007 have shown the similar synergistic effect on the degradation of Malachite green in aqueous solution.

5.11 Effluent characteristics after Sonophotocatalytic treatment

After the Sonophotocatalytic treatment in UV reactor under optimized conditions i.e. at TiO_2 dose of 0.3 gm/200ml, operating pH of 7.0 and 1ml/200ml of oxidant, characterization of the treated wastewater was done. **Table- 5.2** showing the parameters analyzed after the 1.5 hrs of Sonophotocatalytic treatment of pharmaceutical wastewater which shows a major reduction in pollution load.

s.no	Parameters	After Sonophotocatalytic treatment (mg. L^{-1}) (Optimized conditions)	Percentage degradation
1	pH	6.5	--
2	COD	40	96

Table 5.2 Characteristics of compound after Sonophotocatalytic (UV) Treatment under Optimized Condition

5.12 Absorbance spectra after Sonophotocatalytic treatment

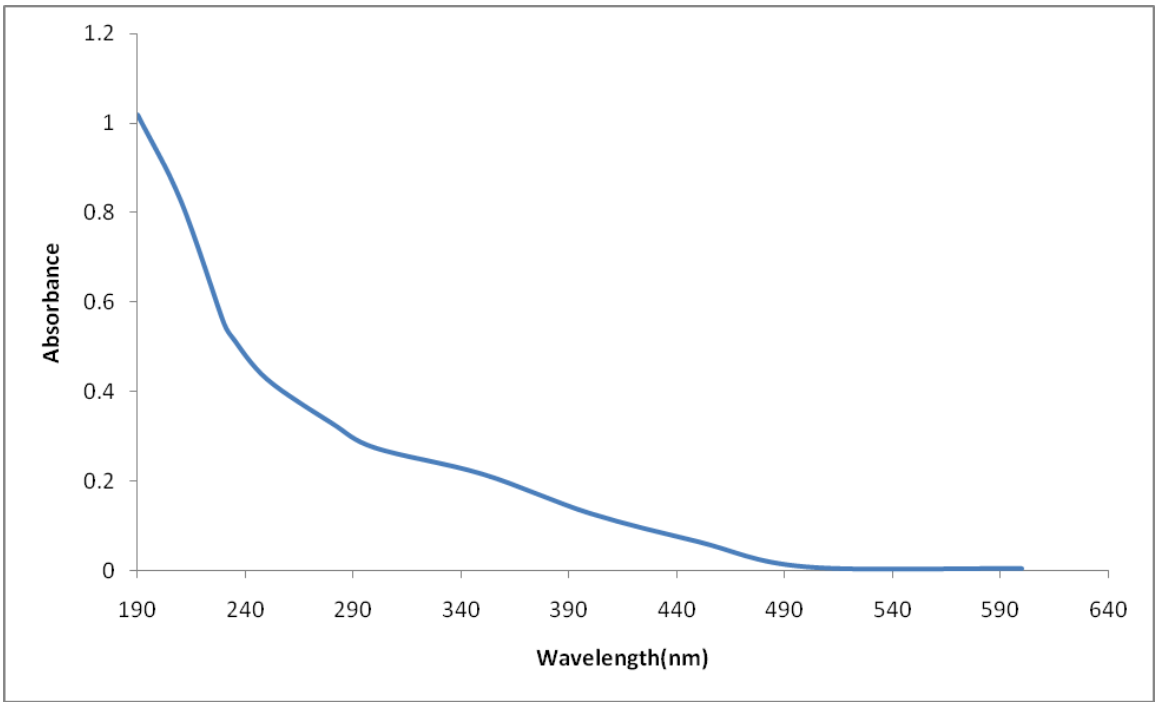

Figure 5.15- Absorption spectra after Sonophotocatalytic treatment.

The primary absorption peaks of the raw pharmaceutical wastewater were at 234 nm. As the reaction proceeds, the peak disappear gradually as shown in **Figure 5.15** and the full scanning spectrum pattern changes obviously after 2 hrs. At the end of the 2 hrs of reaction time, there is no evident absorption peak observed. It proves that compound is fully decomposed in the UV+US+TiO_2 system.

CHAPTER 6

CONCLUSION

Escalating rates of urbanization, industrialization and population growth have aggravated the significance of water pollution as a threat to whole world. And these are some of the factors that are determining the future water demands. So we can't let diminish our natural resources.

Lots of efforts to control and dispose of wastes appropriately are rising. One of the key concerns in waste control is the protection and remediation of the world's finite potable water supply. Although there are various methods for water purification, they are typically dated and inadequate for the removal of the toxins known to be in today's water sources.

Heterogeneous photocatalysis process is eco-friendly way to reduce the pollution load of wastewater. This process has proved its superiority to other conventional methods of wastewater treatments, in the presence of biorecalcitrant compounds. It leads to complete destruction of hazardous contaminants and avoid transfer of pollutants from one phase to another.

4-chloro-2-nitrophenol has been successfully degraded in the presence of TiO_2 photocatalyst. In case of stock solution of 150ppm concentration, degradation was found to be 98% in UV light at the optimized reaction conditions like pH of 7, catalyst dose of 300 mg/200ml and oxidant concentration of 1ml/200ml. Hence, it is deduced that UV can be effectively used for the degradation and decolorization of compound solution. The diminishing of peaks in the UV and visible region of 4-chloro-2-nitrophenol during UV Photocatalytic treatment shows the complete degradation of compound into simpler end products which results in the complete mineralization of resulting solutions.

Sonophotocatalytic treatment has synergy effect on the degradation of pollutants as confirmed by the percentage degradation in this case reaches up to 98% in 90 minutes.

The mineralization studies were done in terms of COD reduction also the degradation of 96% shows that organic compounds are converted into simpler ones.

Results from the study indicate, Advanced Oxidation Process may become most widely used technologies for organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability in the near future. Combination of AOPS as preliminary treatment method with inexpensive biological process seem very promising from an economical point of view. Heterogeneous catalysis using sunlight provides an alternative and effective method for degrading the various organic chemicals. Addition of ultrasound treatment with AOP's can has synergetic effect on the degradation of most priority pollutants.

Hence, it can be concluded from the observations that sonophotocatalysis can be suitably and effectively employed for the degradation of 4-chloro-2-nitrophenol.

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