SONOPHOTOCATALYTIC OXIDATION PROCESS FOR THE TREATMENT OF PHARMACEUTICAL WASTEWATER

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Master of Technology
In
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DECLARATION

I hereby declare that the work embodied in dissertation entitled **"Sonophotocatalytic oxidation process for the treatment of pharmaceutical 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 submitted in part or full, to this or any other University/Institute for any degree or diploma.

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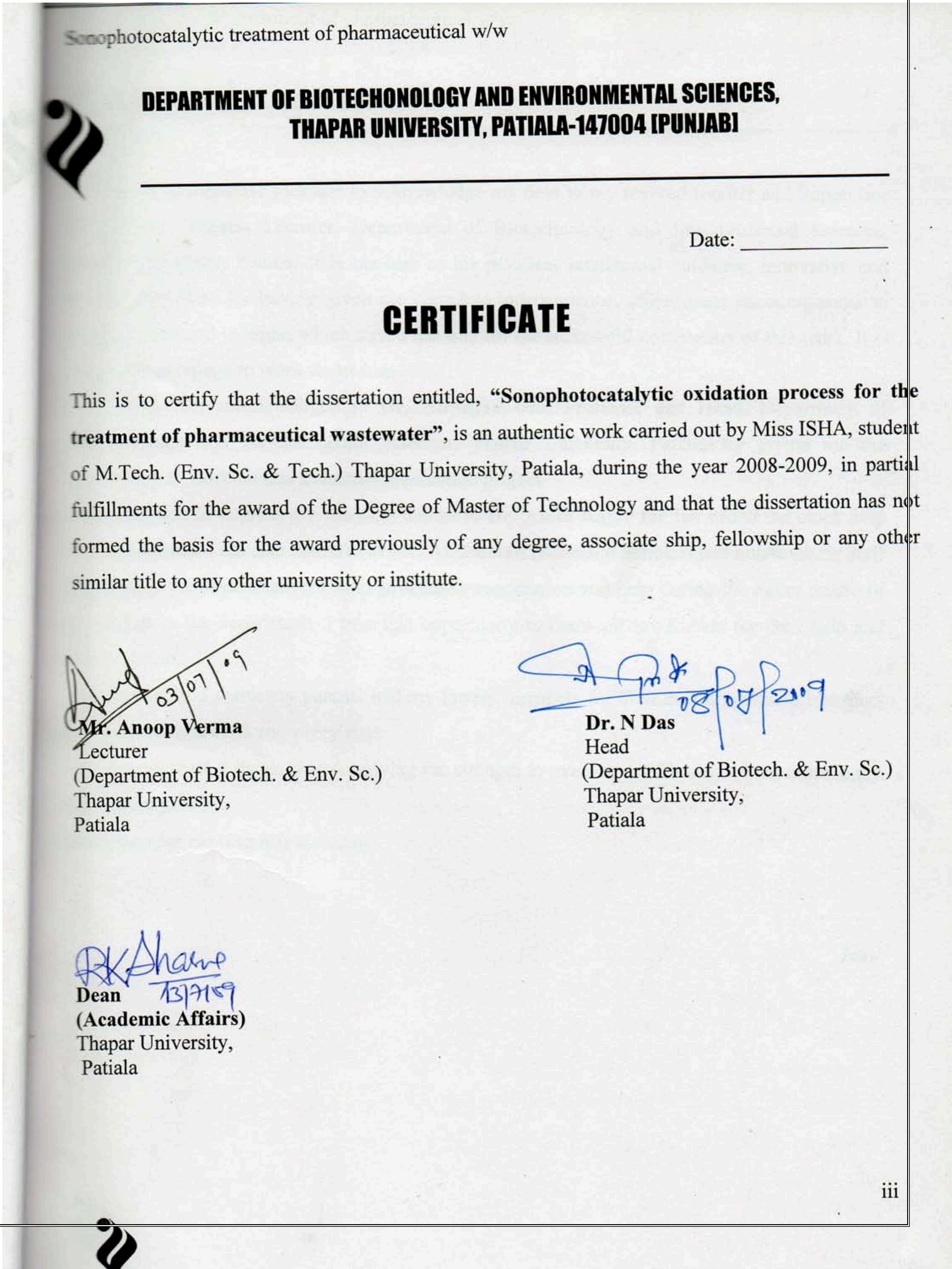

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CERTIFICATE

This is to certify that the dissertation entitled, **"Sonophotocatalytic oxidation process for the treatment of pharmaceutical wastewater"**, is an authentic work carried out by Miss ISHA, student of M.Tech. (Env. Sc. & Tech.) Thapar University, Patiala, during the year 2008-2009, in partial fulfillments for the award of the Degree of Master of Technology and that the dissertation has not formed the basis for the award previously of any degree, associate ship, fellowship or any other similar title to any other university or institute.

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ABSTRACT

Now a day, due to the presence of extremely refractory organic matter in the wastewater stream, the use of conventional wastewater treatment methods are increasingly become challenged. So, now there is a clear need to test and set up the emerging alternative technologies that can deal with highly concentrated and toxic non biodegradable organic matter. So in this way advanced oxidation process (AOP's) has emerged in the last decade especially for the treatment of industrial wastewater. Recently, considerable interest has been shown by researchers all over the world in the application of ultrasound on the photocatalysis i.e. Sonophotocatalysis, to improve 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).

The basic reaction mechanism for both Sonolysis as well as Photocatalysis is the generation of free radicals and subsequent attack by these on the pollutant organic species. If the 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 combining the two modes of irradiations is that it will eliminate the drawbacks of individual process.

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 recalcitrant compounds. So, we can say that Sonophotocatalysis has large capability for the water treatment.

The scope of this project is to see Sonophotocatalysis as a viable treatment option in case of pharmaceutical industry wastewater. The experiments and analysis work is done with actual industrial wastewater. Titanium dioxide was used as photocatalyst. Experiments were performed in slurry mode in both UV and solar light at optimized condition. The degradation of wastewater has been investigated in terms of reduction in COD. Various process parameters like catalyst dose, pH, concentration of oxidant, initially pollutant concentration were varied and their effects

have been analyzed. In this case the catalyst concentration was optimized at 0.2g/100ml, pH at 4 and oxidant concentration at 0.5ml/100ml of the sample.

The results obtained were quit appreciable as it reduced COD by 99%, BOD by 98.8%, Sulfate by 93.7%, Chloride by 98.7% and TDS 99.5%.

The results of Sonophotocatalytic degradation of wastewater 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, pre-requisite for life and key resource of humanity is in abundance on earth. The total water that exists on the Earth surface is present as a water of oceans, lakes, rivers and glaciers **(Figure-1.1)**. The small cube corresponds roughly to 9000 km^3 of drinkable water per year.

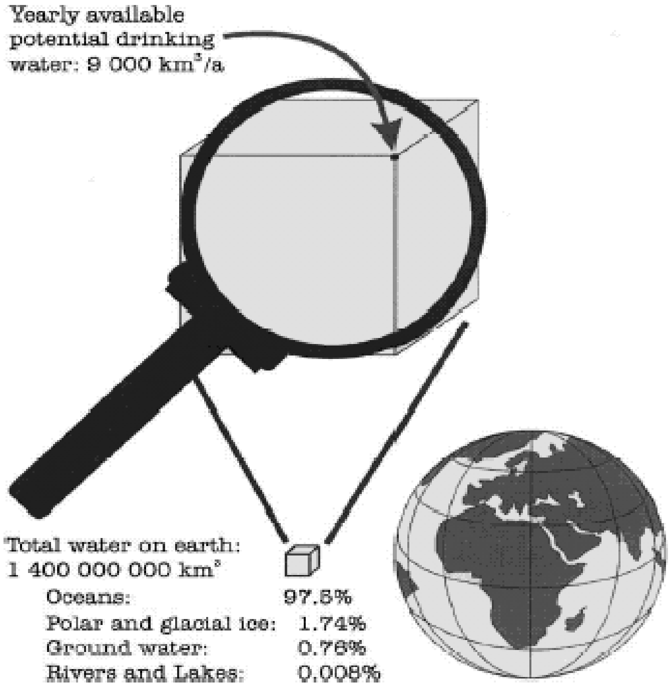

Figure- 1.1 Total water exists on earth (Aitali M.K, 2002)

It is estimated that:

* 1, 2 billion people (a quarter of the world population) have no direct access to drinking water.

* 1, 4 billion people are without effective evacuation of waste water.

* More than 80 countries (> 40% of the world population) lacking tap water. **(Aitali M.K, 2002)**

1.2 Water pollution

Water pollution is of widespread national concern. Industrial activities generate a large number and variety of waste products. The nature of industrial waste depends upon the industrial processes in which they originate. The problem of adequately handling industrial waste waters is more complex and much more difficult because industrial waste water vary in nature from relatively clean rinse waters to waste liquors than are heavily laden with organic or mineral matter or with corrosive ,poisonous, inflammable or explosive substances.

As a result of rapid industrial growth following World War II, the amount of waste material generated by industries has increased manifold and the treatment/removal of these contaminants from the natural resources such as air and water in which they are released has progressed into a special science, involving chemical, mechanical and biological processes. The impure water containing inorganic salts, organic compounds, microbial contamination and turbidity disturbing the natural hydrologic cycle (water cycle). The hydrologic cycle can be maintained by the removal of toxic chemicals by many scientifically simple yet sometimes technologically very complex methods.

Our environment is delicately balanced. It is a system of complex global chemical cycles working in harmony 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)**

In front of this critical situation, wastewater treatment is a must.

1.3 Wastewater treatment processes

In general, the numerous unit operations and processes to remove wastewater contaminants are grouped together to provide various levels of treatment.

The treatment of water is divided into 3 parts:

1. **Physical** - primary methods are referred to physical or physical-chemical unit Operations. e.g. filtration, adsorption, air flotation, flocculation and sedimentation.

2. **Biological** - secondary referred to biological operations. e.g. aerobic, anaerobic and activated sludge.

3. **Chemical** - advanced or tertiary referred to chemical or to combinations of all three e.g. Thermal oxidation (combustion), Chemical oxidation, Ion exchange, Chemical precipitation, incineration.

The use of conventional water and wastewater treatment processes becomes increasingly challenged with the identification of more and more contaminants, rapid growth of population and industrial activities, and diminishing availability of water resources. **(Zhou.H and D.W. Smith, 2001)**

The actual state performance of conventional methods is clearly not suitable to treat toxic, non-biodegradable organic pollutants and new improved treatments have to be developed and tested. To overcome the inconveniences of conventional treatment methods, Advanced Oxidation Techniques (AOP’s) have emerged in the last decades, in particular for the treatment of industrial wastewaters.

1.4 Emerging Technologies

The emerging wastewater treatments methods like advanced oxidation processes are increasingly gaining popularity since they have shown the potential of converting harmful organic pollutants into innocuous compounds such as carbon dioxide and water. The emerging treatment technologies have been already demonstrated to successfully remove various potentially harmful compounds that could not be effectively removed by conventional treatment processes. **(Paradowska M.A, 2004).** These advanced oxidation processes helps in conversion of organic wastes into inorganic form, which is required in order to have a more stable and inert form for final disposal. **(Prasad T.L et al, 2001)**.

The major advantage of this technology is that it can completely or partially destroy organics at ambient temperature by converting them into various harmless intermediates and end products, such as carboxylic acids, carbon dioxide and halide ions. The major oxidants of AOP are hydroxyl radicals and ozone which can react with organic compounds at very high reaction rates. In particular, hydroxyl radicals can attack most organics non-selectively through hydrogen atom abstraction or by addition of the hydroxyl radical. Advanced oxidation processes (AOP) combine ozone (O_3), ultraviolet, hydrogen peroxide (H_2O_2) and/or catalyst to offer a powerful water treatment solution for the reduction (removal) of residual organic compounds as measured by COD, BOD or TOC. All AOP are designed to produce hydroxyl radicals. It is the hydroxyl radicals that act with high efficiency to destroy organic compounds**. (Sacco A.R and R.J Coin, 2002).**

Recently the technique of ultrasound has received much attention as advanced oxidation process for treating wastewater. When ultrasound is combined with other AOPs, the combination would lead to faster degradation rates when compared to either method alone. The use of ultrasound has been recognized, for many years, in a wide variety of processes such as cleaning, floatation, drying, degassing, plastic welding filtration, emulsification, biological cell disruption, extraction and crystallization and stimulus for chemical reactions. By using ultrasound the complicated reactions are performed with inexpensive equipment and often in fewer steps than the conventional methods. 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 WASTEWTER

1.5 Overview

Pharmaceutical manufacturers use water for process operations, as well as for other non-process purposes. However, the use and discharge practices and the characteristics of the wastewater will vary depending on the operations conducted at the facility. Additionally, in some cases, water may be formed as part of a chemical reaction. Process water includes any water that, during manufacturing or processing, comes into direct contact with or results from the use of any raw material or production of an intermediate, finished product, byproduct, or waste. Process wastewater includes water that was used or formed during the reaction, water used to clean process equipment and floors, and pump seal water. Non-process wastewater includes noncontact cooling water (e.g., used in heat exchangers), noncontact ancillary water (e.g., boiler blowdown, bottle washing), sanitary wastewater, and wastewater from other sources (e.g., storm water runoff).

Based on the responses from 244 facilities to a 1990, 308 Questionnaire, EPA estimated the average daily wastewater generation by the pharmaceutical manufacturing industry to be 266 million gallons. Additionally, EPA learned that more than half of the responding facilities have implemented water conservation measures. Such measures include: careful monitoring of water use, installation of automatic monitoring and alarm systems or in-plant discharges, implementation of alternative production processes, reuse of non-contact water as process makeup water and treatment of contact cooling water to allow reuse.

Pharmaceutical manufacturers generate process wastewater containing a variety of conventional parameters (e.g., BOD, TSS, and pH) and other chemical constituents. The top ten chemicals discharged by the pharmaceutical industry are provided in **Table 1.1**. Of these compounds, two are “priority pollutants”. The top four compounds are oxygenated organic solvents (e.g., methanol, ethanol, acetone, and isopropanol).

In recent years, several studies have indicated the presence of a new kind of pollutant in water: pharmaceutical and personal care products (PPCPs) -and its metabolites- have been founded in the effluents of sewage treatment plants (STPs) and in the next discharge points like rivers, lakes and other superficial water. The biological oxidation in the STPs is not enough to achieve a complete degradation of this kind of pollutants. The ecotoxicological consequences for the microorganisms present in the aquatic environment have been already reported **(Richard et al., 2006).**

Advanced Oxidation Processes specially sonophotocatalysis are a treatment alternative for a wide variety of recalcitrant micro pollutants.

Constituent Name	Quantity Discharged (lbs/yr)
Methanol	15,388,273
Ethanol	6,802,384
Acetone	4,573,766
Isopropanol	4,565,370
Acetic acid	4,328,691
Methylene chloride	3,590,640
Formic acid	2,136,059
Ammonium hydroxide	1,365,741
N1N-Dimethylacetamide	1,046,333
Toluene	783,364

Table 1.1 Chemicals Discharged in Wastewater by the Pharmaceutical Manufacturing Industry

1.6 Occurrence and Fate of Pharmaceuticals in the Environment

Until recently pharmaceutical compounds in the environment have drawn very little attention. Although their presence in sewage treatment plant effluents was reported by **Richardson and Bowron, (1985)**, it had been anticipated that these compounds were easily biodegradable in environment as most of them could be metabolized and transformed to some extent in humans**.** However, a large number of recent studies have demonstrated persistence of these pharmaceuticals in the aquatic environment. 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, Brazil, Italy and the United States **(Kolpin 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 mg/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 1 mg/L **(Clara et al., 2004).** There are several possible sources and routes for the occurrence of pharmaceutical compounds in the aquatic environment **(Figure 1.2)**. For human pharmaceuticals, on-prescription drugs and some prescription drugs are consumed in households, and other prescription drugs are consumed in healthcare facilities such as hospitals and clinics. These drugs are partially metabolized and excreted in the urine and faeces and go into a wastewater collection system**.** Some unused, surplus, or expired drugs may be disposed into toilets, although this kind of practice is not recommended nowadays. Wastewater from the hospitals may be treated separately or combined with municipal wastewater and then treated at sewage treatment plants. Some of the pharmaceuticals and (human) metabolites in wastewater are degraded completely or partially, giving rise to a mixture of parent compounds and a variety of microbial metabolites. Some pharmaceuticals such as ibuprofen and bezafibrate are relatively biodegradable, while others such as carbamazepine and diazepam are practically non-biodegradable **(Larsen et al., 2004).** It is also known that some drug conjugates such as glucoronides can be cleared by microbial degradation resulting in a release of parent compounds**.** Effluent from sewage treatment plants may be released to surface water or be subjected to groundwater recharges, so that the mixture of compounds enters the aquatic environment. In some cases, biologically treated municipal wastewater may be treated further to produce various reclaimed waters for different purposes including portable re-use.

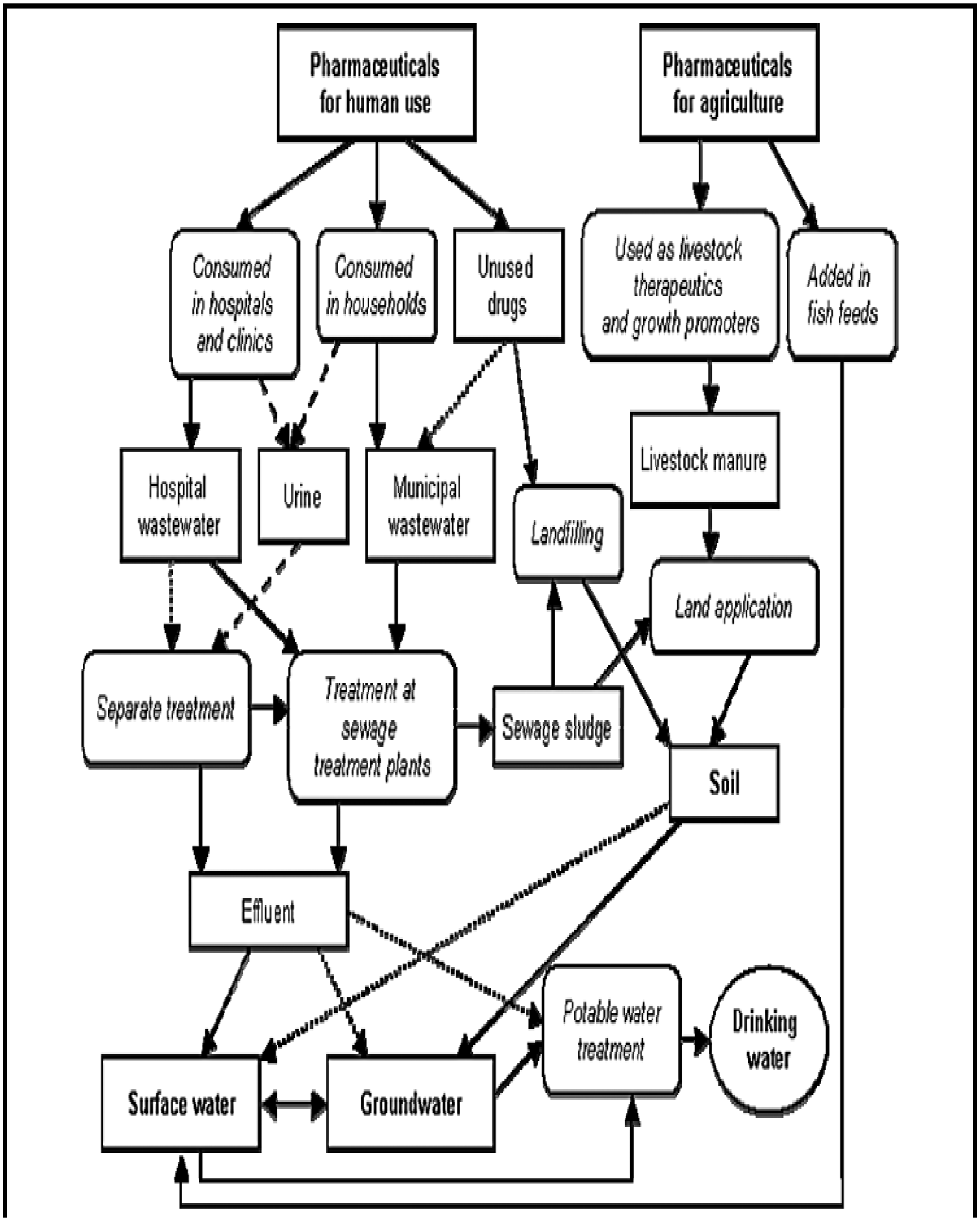

Figure-1.2 Occurrence and Fate of Pharmaceuticals in the Environment

1.7 Environmental impacts of pharmaceuticals effluent

As the Pharmaceutical residues have been detected in environmental samples including groundwater, surface water, and municipal wastewater. Pharmaceutical drugs given to people as well as to domestic animals include antibiotics, hormones, pain relievers, tranquilizers, and chemotherapy chemicals given to cancer patients. Many drugs are designed to be persistent and lipophilic, so that they can retain their chemical structure long enough to do their therapeutic work. These drugs are excreted and distributed into the environment by flushing toilets as well as by spreading manure and sewage sludge onto soil.

These chemicals persist in the environment, enter the food chain, bioaccumulate, biomagnify, and cause harmful effects in wildlife and humans. Because of aquatic contamination by these chemicals, bacteria and other microbes in the aquatic environment can become more resistant to these chemicals. This results in the development of more antibiotic resistant and virulent pathogens in the environment. Therefore, the persistence of pharmaceutical chemicals in the environment has become a global problem. **(Jones O.A et al, 2005b)**

OBJECTIVES OF PRESENT STUDY

Main objective of the study is to treat pharmaceutical wastewater containing recalcitrant /non-biodegradable compounds which cannot be completely treated by conventional treatment technologies/ biological methods employed in industry. In an attempt to increase the efficiency of degradation of the impurities present in the wastewater and to improve the economics of the treatment, the work was carried out on the degradation of untreated wastewater of Pharmaceutical industry using heterogeneous 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:

- **Characterization of wastewater**
- **Sonophotocatalytic treatment of real pharmaceutical wastewater**
- **Effect of variables on degradation efficiency and its optimization**

CHAPTER-2

TREATMENT TECHNOLOGIES (ADVANCED V/S EMERGING)

2.1 General overview

Advanced oxidation processes involve the production of highly reactive radicals such as hydroxyl radicals which have the ability to oxidize almost all complex organic molecules into smaller molecules. Complete mineralization of the compounds into CO_2, water and inorganic structures such as $SO_4^{2-,}$ NO_3^- and N_2 is possible. These treatment processes are considered as very promising methods for the remediation of contaminated ground, surface, and wastewaters containing non-biodegradable organic pollutants. Hydroxyl radicals are extraordinarily reactive and non-selective and for this reason it reacts with all surrounding chemicals, organic pollutants and inhibitors as well. That attacks most of the organic molecules. AOPs involve the two stages of oxidation:

1) The formation of strong oxidants (e.g., hydroxyl radicals) and

2) The reaction of these oxidants with organic contaminants in water.

However, the term advanced oxidation processes refer specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals. Hydroxyl radicals are known to be the second strongest oxidants after fluorine. The oxidation potential of the most powerful oxidants is summarized in **Table 2.1**.

Oxidizing Agent	**Electrochemical oxidation potential (EOP),V**
Fluorine	3.06

Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen Peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

Table 2.1 - Oxidation potential of common oxidizing agents (Metcalf and Eddy, 2003, page no.-1197).

Hydroxyl radicals are characterized by a little selectivity of attack, attractive feature for an oxidant to be used in wastewater treatment. Several and different organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals, as it is shown in **Table 2.2 (Ozencilh.H, 2007)**

Acids	Formic, gluconic, lactic, malic, propionic, tartaric
Alcohols	Benzyl, *tert*-butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutyraldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, trichlorophenol, xylene,

	trinitrotoluene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine
Dyes	Anthraquinone, diazo, monoazo
Ethers	Tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone

Table2.2 - Oxidizable compounds by hydroxyl radicals (Rodríguez.M, 2003)

Advanced oxidation processes differ from the other treatments processes because wastewater compounds are degraded rather than concentrated or transferred into a different phase. Because secondary waste materials are not generated, there is no need to dispose of or regenerate materials. **(Metcalf and Eddy, 2003)**

There are many oxidation processes or combination of processes which can produce hydroxyl radicals.

2.2 Homogenous photocatalysis

The application of homogeneous photo degradation (single-phase system) to treat contaminated waters, concerns the use of UV/ozone and UV/H_2O_2. The use of UV light for photo degradation of pollutants can be classified into two principal areas.

(1) Direct photo degradation, which proceeds following direct excitation of the pollutant by UV light and
(2) Photo-oxidation, where light drives oxidation processes principally initiated by hydroxyl radicals.

The latter process involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. Three major oxidants used are:

- hydrogen peroxide

- ozone
- photo-Fenton system ($fe^{3+/}H_2O_2$) **(Verma.A,2004)**

2.2.1 H_2O_2/UV Process

This system involves the formation of $OH^{\bullet}$ radicals by hydrogen peroxide photolysis and subsequent propagation reactions. The mechanism most commonly accepted for the photolysis of H_2O_2 is the cleavage of the molecule into hydroxyl radicals.

$$H_2O_2 \rightarrow 2\ {}^{\bullet}OH \qquad \text{(UV <300 nm)}$$

UV/H_2O_2 process is a widely used process for the decolouration of dye contaminated wastewater.The effectiveness of the UV/H_2O_2 system in the treatment of aromatic compounds such phenol and NB (nitrobenzene) has been widely studied (e.g. **García et al., 1989** and **Lipczynska- Kochany, 1992). Alaton and Balcioglu (2002)** show the effectiveness of H_2O_2/UV system as pretreatment or in combination with other advanced oxidation process in the treatment of textile wastewater.

2.2.2 UV/ozone

The AOP with UV radiation and ozone is initiated by the photolysis of ozone. The Photodecomposition of ozone leads to two hydroxyl radicals.

$$O_3 + H_2O \rightarrow \square O_2 + H_2O_2 \qquad \text{(UV<300 nm)}$$

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

This system contains three components to produce OH radicals and/or to oxidize the pollutant for subsequent reactions: UV radiation, ozone and hydrogen peroxide.

Several authors have studied the efficiency of this process with different aromatic compounds. **Gurol and Vatistas (1987)** studied the photolytic ozonation of mixtures of phenol, p-cresol, 2, 3-xylenol and catechol at acidic and neutral pH. **Guittoneau et al. (1990)** reported that the O_3/UV process was found to be more efficient than the UV/H_2O_2 system for the degradation of p-chloronitrobenzene. Some articles have been found as well in the literature regarding the degradation of NB by means of the O_3/UV process. **Beltrán et al. (1998)** have studied the effect of ozone feed rate, pH and hydroxyl radical scavengers in the removal of NB by this combination. Besides, **Contreras et al. (2001)** have studied the effect of pH and ozone in the oxidation of NB by this process.

2.2.3 UV/O_3 /H_2O_2 process

In this process again $HO^{\cdot}$ 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 H□ $^{\cdot}$□radicals generation. This is a very powerful methot 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

2.3.1 Photocatalysis or UV/TiO_2

The process is heterogeneous because there are two active phases, solid and liquid.

The word photocatalysis is composed of two parts:

1. The prefix *photo,* defined as "light",
2. *Catalysis* is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy.

The definition of photocatalysis is basically the acceleration of a photoreaction by the presence of a catalyst. A more in depth approach would include that the catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction.

Principle (Figure 2.1 shows the principle of photocatalysis)

1. **Exposure to ultraviolet rays (UV)**

The electron jumps up from the surface when light (Ultraviolet rays) hits the photo catalyst (titanium dioxide). At this time the hole which the electron jumped up from is called the positive hole, and has worn the charge of the plus.

2. **OH radical appearance**

The positive hole has the strong oxidation power and takes the electron from OH^-(hydroxide ion) in water. At this time OH^-, that was taken the electron, becomes OH radical of very unstable condition.

3. **Decomposition of organic compound**

OH radical takes the electron by the strong oxidation from the nearby organic compound to become stable oneself. In this way the organic compound is decomposed by loss of the electron and finally becomes carbon dioxide and water, and emanated to an atmosphere.

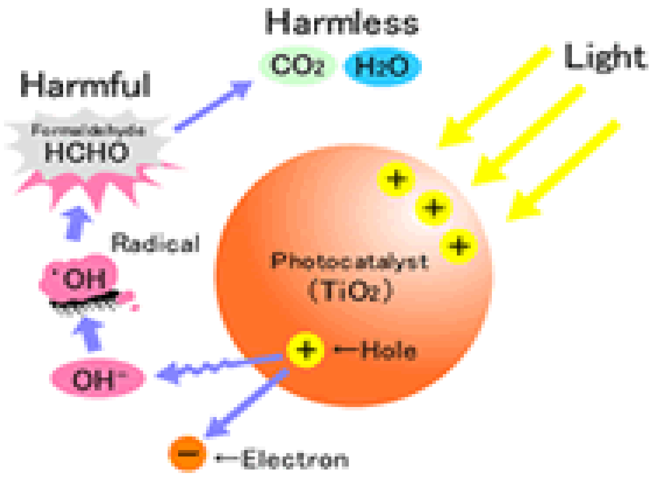

Figure - 2.1 Showing the principle of photocatalysis

Following are the reactions involving in photo catalysis:-

- Concerning photocatalysis with titanium dioxide as the catalyst, electrons in conduction band (e_{cb}^{-}) and holes in the valence band (h_{vb}^{+}) are produced when the catalyst is irradiated with light energy higher than its band gap energy E_{bg} ($h\nu > E_{bg}$).

TiO_2 +hν (UVl < 400nm) → TiO_2 ($e_{cb}^{-} + h_{vb}^{+}$) (1)

$H_{vb}^{+} + H_2O \rightarrow H^{+} + HO\cdot$ (2)

$H_{vb}^{+} + HO^{-} \rightarrow HO\cdot$ (3)

Organic molecule +h_{vb}^{+} → oxidation products (4)

$E_{cb}^{-} + O_2\,O \rightarrow O_2^{\cdot-}$ (5)

$O_2^{\cdot-} + H^{+} \rightarrow HO_2\cdot$ (6)

Organic molecule +e_{cb}^{-} + reduction products (7)

Radicals ($HO^{\cdot}$, $HO_2\cdot$) + organic compounds → degradation products (8)

Today, semiconductors are usually selected as photo catalysts, because semiconductors have a narrow gap between the valence and conduction bands. In order for photo catalysis to proceed, the semiconductors need to absorb energy equal to or more than its energy gap. This movement of electrons forms e^-/h^+ or negatively charged electron/positively charged hole pairs. The hole can oxidize donor molecules **(Fig. 2.2).**

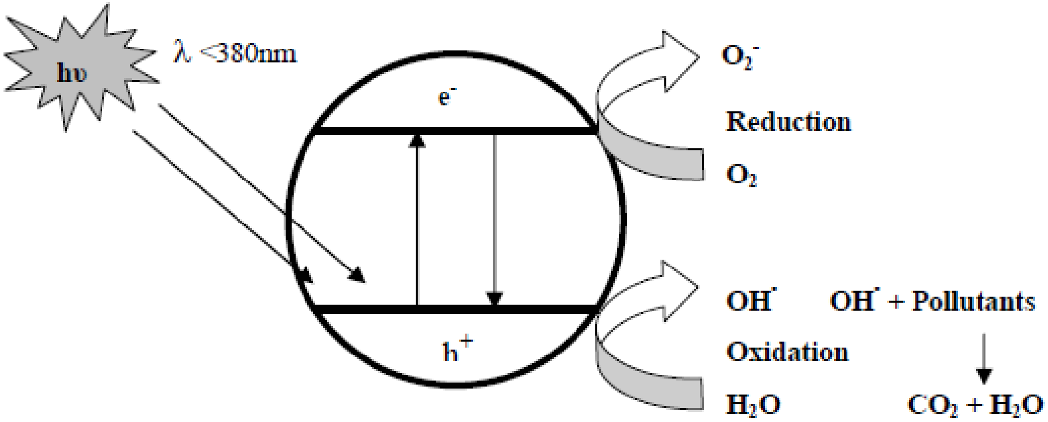

Figure 2.2 - Showing the working principle of TiO_2 catalyst.

Among the possible semiconductors, TiO_2, or Titanium Dioxide, (E_g = 3.2 eV) is most extensively used because it has many advantages that are shown in **Table 2.3**.

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 = -0.1 eV)
8	Absorbs in near UV light (<387 nm) (i.e., natural (solar) energy)

Table 2.3 Showing the advantages of TiO_2

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; Curcó et al., 1999b; Minero, C. et al., 1993**). Few studies have been found in the literature regarding the photocalytic oxidation of textile wastewaters.

The technique of ultrasound has received much attention as advanced oxidation process for treating wastewater. When ultrasound is combined with other AOPs, the combination would lead to faster degradation rates when compared to either method alone. By using ultrasound the complicated reactions are performed with inexpensive equipment and often in fewer steps than the conventional methods. 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.

2.4 Ultrasonic Cavitation / Sonication

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. **(Amarnath R.K, 1998)**

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 the formation, growth and collapse of bubbles in the liquid. **(Ravazzini.A et al, 2002)**. 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. Thus, cavitation serves as a means of concentrating the diffuse energy of sound into micro reactors. 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, $HO_2{}^{\bullet}$ radicals and H_2O_2 are formed. In this molecular environment, organic compounds are decomposed and inorganic compounds are oxidized or reduced.

Ultrasound has been widely known to induce radical reactions. This useful property has found its applications in sonolysis of water, sonolytic degradation of aqueous organic pollutants, and sonochemical synthesis of chemicals. The underlying phenomena include cavitation, microstreaming, and localized supercritical conditions. These phenomena lead to sonolytic splitting of water as well as pyrolysis of a vaporized molecule. **(Chen Y.C, 2002)**

Figure 2.3 shows that liquids irradiated with ultrasound can produce bubbles. These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions these bubbles can undergo a violent collapse, which generates very high pressures and temperatures. This process is called cavitation. The compression of cavities when they implode in irradiated liquids is so rapid that little heat can escape from the cavity during collapse. The surrounding liquid, however, is still cold and will quickly quench the heated cavity.

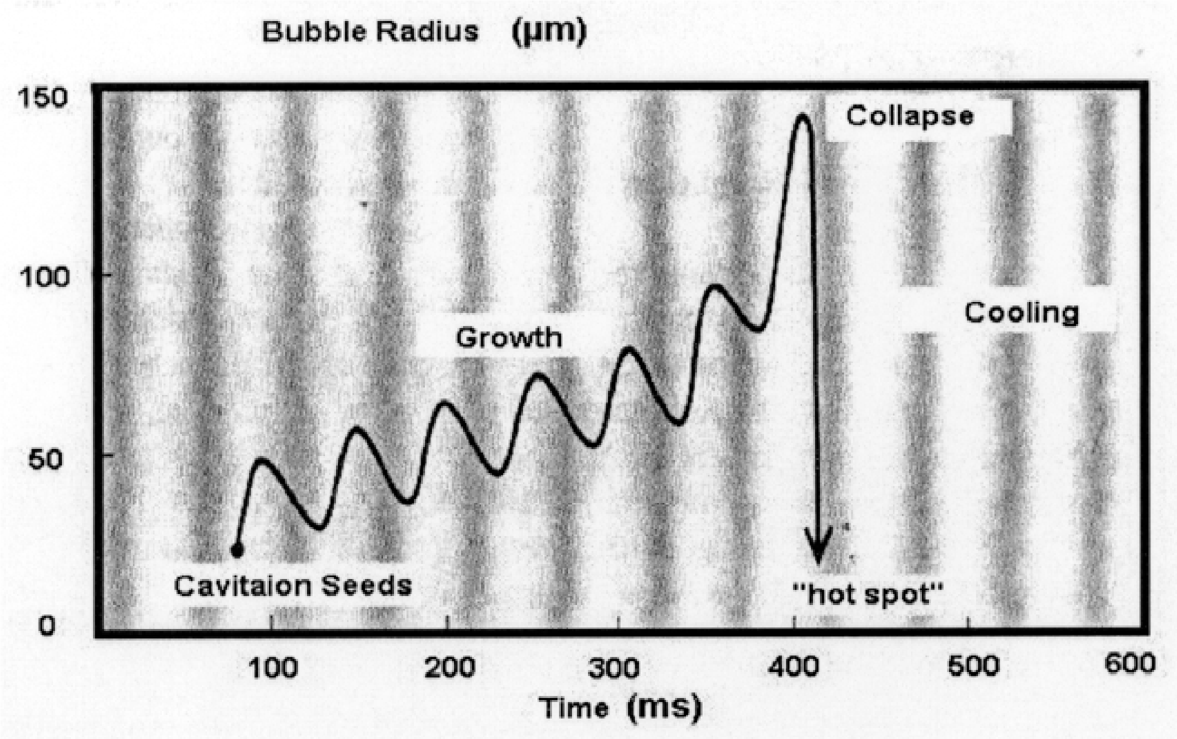

Figure -2.3 Cavitation and Implosion phenomen (Dehghani M.H and F.ChanganiI, 2006)

Thus, one generates a short-lived, localized hot spot in an otherwise cold liquid. It has a temperature of roughly 5000° C (9,000° F), a pressure of about 1000 atmospheres, a lifetime considerably less than a microsecond, and heating and cooling rates above 10 billion° C per second.**(Dehghani M.H and F.ChanganiI, 2006).**

In aqueous phase sonolysis, there are three potential sites for Sonochemical activity, namely:

(I) The gaseous region of the cavitation bubble where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving the participation of hydroxyl radicals with the latter being formed through water sonolysis:

$H_2O \rightarrow H^{\cdot} + OH^{\cdot}$

(II) The bubble–liquid interface where hydroxyl radicals are localized and, therefore, radical reactions predominate although pyrolytic reactions may also, to a lesser extent, occur and

(III) The liquid bulk where secondary sonochemical activity may take place mainly due to free radicals that have escaped from the interface and migrated to the liquid bulk. It should be pointed out that hydroxyl radicals can recombine yielding hydrogen peroxide which may, in turn, react with hydrogen
to regenerate hydroxyl radicals:

$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$

$H_2O_2 + H^{\cdot} \rightarrow H_2O + OH^{\cdot}$ **(Berberidou.C et al, 2007)**

Following are the advantages of Sonication (Table 2.4).

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.

Table2.4 Showing the advantages of sonication.(Roselló I.R, 1999)

2.5 Sonophotocatalytic process

It is the combination of two advanced oxidation processes i.e. sonication and photocatalysis. Both these technologies are discussed in detail previously.

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. Also in the case of photocatalytic oxidation, the most common problem associated is the reduced efficiency of photocatalyst with continuous operation possibly due to the adsorption of contaminants at the surface and blocking of the UV activated sites, which makes them unavailable for the destruction. Moreover photocatalytic oxidation technique is also affected by severe mass transfer limitations especially in the case of immobilized catalyst type of reactors, which are generally preferred over slurry reactors to avoid solid catalyst separation problems. The turbulence induced by the cavitation phenomena can aid in eliminating the drawbacks associated with photocatalytic oxidation.

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 (9)–(14)

(i) Water sonolysis (reactions (9) and (10)),

(ii) Reaction of hydrogen peroxide with the hydrogen atoms formed from water sonolysis (reaction (11)),

(iii) Hydrogen peroxide photolytic dissociation (reaction (12)),

(iv) Reaction of hydrogen peroxide with the super oxide radical anions formed during

Photocatalysis (reaction (13)),

(v) Reaction of hydrogen peroxide with conduction band electrons (reaction (14))

$H_2O + \text{ultrasound} \rightarrow H^{\cdot} + HO^{\cdot}$ (9)

$H_2O + \text{ultrasound} \rightarrow \frac{1}{2} H_2 + \frac{1}{2} H_2O_2$ (10)

$H_2O_2 + H^{\cdot} \rightarrow \mathrm{H2O} + HO^{\cdot}$ (11)

$H_2O_2 + hv \rightarrow 2HO^{\cdot}$ (12)

$H_2O_2 + O_2^{\cdot -} \rightarrow HO^{\cdot} + HO^{-} + O_2$ (13)

$H_2O_2 + e_{cb}^{-} \rightarrow HO^{\cdot} + HO^{-}$ (14)

(Silva A.M.T et al, 2007*)***

There have been many studies depicting the observed synergism and the enhanced rates of degradation for the combinatorial operation of sonochemical reactors and photocatalytic oxidation. (**Adewuyi Y.G, 2005)** have given an extensive overview of different studies depicting the use of Sonophotocatalytic oxidation for treatment of pollutant wastewaters. It has been generally observed that the rates of degradation for the combination of ultraviolet and ultrasonic irradiation are at times order of magnitude higher as compared to individual operation. It should be noted that in the situations where the adsorption of pollutants at the specific sites is the rate controlling step, ultrasound will play a profound role due to substantial increase in the number of active sites and also the surface area available due to defragmentation of the catalyst agglomerates under the action of turbulence generated by acoustic streaming along with an increase in the diffusion rates of the contaminants.

CHAPTER-3

LITERATURE REVIEW

Extensive air and water pollution has plagued the planet for a long time. As a response to the looming threat, the humankind has been expediting its efforts in pollution abatement. Several approaches are used: to utilize environmentally benign processes, to provide *in situ* destruction of pollutants during the process, and to decontaminate the air or water stream emanating from the high throughput production facility.

The treatment of industrial wastewater before discharge to prevent the quality of natural water body from deterioration and to meet regulatory requirements continues to be a significant challenge of environmental protection. In the field of wastewater treatment, many kinds of technologies in the areas of chemistry, physics, and even biochemistry have been applied under the considerations of economics and practicability.

Recently, considerable interest has been shown by researchers all over the world in the application of ultrasound to improve the performance of photocatalytic degradation of organic and inorganic contaminants in aqueous streams.

The chemical effects of ultrasound enhance chemical reactivity through the phenomenon of cavitation which involves the nucleation, growth and collapse of bubbles in a liquid. 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:

Suzuki.Y et al, (1999) investigated Photo-catalytic oxidation of surfactant (polyoxyethylenealkyl-ether,$C_{14}H_{29}O(CH_2CH_2)_7H$, hereinafter 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 the stirring speed largely influenced the degradation efficiency. It is considered that the catalyst particles might be localized by ultrasonic standing wave, and caused inhibition to the decomposition in the degradation process. However, by high stirring speed, the inhibition could be overcome.

The study of Utilization of Ultrasonic Energy in a Photocatalytic Oxidation Process for Treating Waste Water Containing Surfactants has also been done by **Maezawa.A et al**, **(2000)**

Decomposition efficiency of 1, 4-dioxane in water by Sonophotocatalytic method through comparison of TiO_2 and HF-treated TiO_2 has been done by **Nakajima.A et al, (2004)** and shows decomposition behavior of 1,4-dioxane by US, UV + TiO_2, UV + HF–TiO_2, US + UV + TiO_2, and US + UV + HF–TiO_2. The order of the degradation rate of 1, 4-dioxane is US < UV + TiO_2 < UV + HF–TiO_2 < US + UV + TiO_2 < US + UV + HF–TiO_2. This synergistic effect is attributable to effective enhancement of photo catalysis by sonolysis .HF treatment of TiO_2 surface enhances its absorption capabilities for 1, 4-dioxane.

Selli.E et al, (2008) have worked on the rate of 1, 4-dichlorobenzene (1, 4-DCB) degradation and mineralization in the aqueous phase either under direct photolysis or photocatalysis in the presence of TiO_2, or under sonolysis at 20 kHz with different power inputs. Photocatalysis ensured faster removal of 1, 4-DCB with respect to sonolysis and direct photolysis. The highest degradation and mineralization rate was attained with the combined use of photocatalysis and sonolysis, i.e. under Sonophotocatalytic conditions.

The degradation of malachite green (MG) in water by means of ultrasound irradiation and its combination with heterogeneous (TiO_2) photocatalysis was investigated by **Berberidou.C et al, (2007)**. Eighty-kilohertz of ultrasound irradiation was provided by a horn-type sonicator, while a 9 W lamp was used for UV-A irradiation. The extent of sonolytic degradation increased with increasing ultrasound power (in the range 75–135 W) and decreasing initial concentration (in the range 2.5–12.5 mg L/1), while the presence of TiO_2 in the dark generally had little effect on degradation. Sonolysis under argon was substantially faster than under air, oxygen or helium leading to complete MG degradation after 120 min at 10 mg L/1 initial concentration and 135 W ultrasound power. On the other hand, TiO_2 photocatalysis led to complete MG degradation in 15–60 min with the rate increasing with increasing catalyst loading (in the range 0.1–0.5 g L/1 for TiO_2). TiO_2 Sonophotocatalytic was always faster than the respective individual processes due to the enhanced formation of reactive radicals as well as the possible ultrasound-induced increase of the active surface area of the catalyst. The complete degradation of MG can be achieved in less than 20 minutes in case of Sonophotocatalytic treatment.

Vajnhandl and Marechal, (2005) in his paper reviewed some fundamentals of ultrasound, its broad applications and gathered some new research regarding its applications in textile wet processes, with the emphasis on textile dyeing and the decoloration/mineralization of textile wastewaters

Jiang et al., (2006) investigated the sonolysis of 4-chlorophenol (4-CP) in oxygen saturated aqueous solutions for a variety of operating conditions with the loss of 4-CP from solution following pseudo-first-order reaction kinetics. He concluded that the degradation takes place in the solution bulk at low reactant concentrations**.**

Zeng and James (2006) studied the degradation of pentachlorophenol (PCP) in aqueous solution by audible-frequency sonolytic ozonation. The first-order rate constant of PCP degradation by ozonation with sonication was found to be 15 times faster than that with bubbling ozone alone, while the rate constant with mechanical stirring was only four times faster**.**

Tezcanli-Guyer and Ince (2004) investigated a comparative degradation of azo dyes by 520 kHz ultrasonic irradiation and its combinations with ozone and/or ultraviolet light was investigated using a probe dye Acid Orange 7. He concluded that the overall degradation process was most rapid under simultaneous operation of the three (UV/US/O_3) in the presence of a continuous flow of a gas mixture made of argon and oxygen.

The hybrid effect of the irradiation by light and ultrasonic waves in conjunction with H_2O_2 was first confirmed to achieve the complete mineralization of propyzamide by **Yano et al., (2005). Fung et al., (2000)** reported the decolorization of reactive dye wastewater with UV radiation and ultrasonic vibration in the presence of hydrogen peroxide by a batch operation system. He found that the degradation of the reactive dye followed a pseudo-first-order kinetic model at different pH and peroxide dosages. **Harada et al., (2001)** investigated the role of a photocatalyst in the sonophotocatalytic reaction of water splitting using TiO_2 photocatalyst.

Selli (2002) in another paper reported that photocatalysis and sonolysis exhibit the synergistic effects in the degradation of Acid Orange 8 in aqueous suspensions, when low ultrasound frequency is used.

A comparative study between the sonolytic, photocatalytic and Sonophotocatalytic oxidation processes of aqueous solutions of malachite green was also carried out by **Pe´rez N.J.B and M.F Herrera, (2007)** and showed the same results that the highest degradation was achieved in case of Sonophotocatalytic treatment.

Gogate and Pandit (2005) in a review reflected the current status of the hydrodynamic cavitation reactors discussing the bubble dynamics analysis and optimum design considerations illustrating the utility of these reactors.

Several other authers have also done the work on the Sonophotocatalytic treatment of dyes like **Maezawa.A et al, (2006), Entezari M.H and Z. S Al-Hoseini, (2006), Pérez N.J.B and S. Herrera MF,(2006), Sistla.S and S. Chintalapati, (2008), Selli.E, (2002), An T. et al, (2003).**

Kulkarni A.K et al, (2000) have also concluded that the Photocatalytic action with the ultrasound has resulted in higher degradation rates of the contaminants. This is due to the mechanical effects of cavitation involving photocatalyst surface cleaning and increased mass transfer of the polluting species to the powdered catalyst surface.

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 TiO2 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.

Chen Y.C, (2002) studied the enhancement on Photocatalytic Degradation of Phenol by Ultrasound and showed that under the presence of ultrasound at the frequency of 20 kHz, a certain degree of conversion (about 10%) of phenol occurred within 3 hours. Only 76% photocatalytic decomposition of phenol within 3 hours using UV only means that phenol was not completely removed by photocatalysis within 3 hours. However, when the application of ultrasound was combined with the above photocatalytic degradation of phenol, the result showed that a significant enhancement on the degradation rate occurred in our reaction system and the elimination of phenol was achieved at about 150 min. The reaction rate in the photocatalytic decomposition of phenol with ultrasound increased about 63% in comparison with that without ultrasound and he also concluded that there was dramatic promotion of synergistic effect from the combination of UV and US by reducing the reaction volume. A relative enhancement of 29% was found at the volume of 300 ml; the enhancements observed for 200 ml and 100 ml were 70% and 82%, respectively. The possible explanation for the enhancement due to ultrasound in our study lies on the effects of deagglomeration and continuous surface cleaning from ultrasound.

Mechanistic aspects of the role of 20 kHz ultrasonication in photocatalytic oxidation of dimethyl methylphosphonate (DMMP), a simulant for nerve chemical warfare agents, were studied in a batch reactor by **Chen Y.C, (2003)**. They found that DMMP did not undergo mineralization under low frequency (20 kHz) ultrasonic irradiation. The increase of the rate of DMMP photocatalytic mineralization in the presence of ultrasound was not due to deagglomeration of TiO**2**, but was associated with enhanced mass transport of reagents. The same intermediate non-volatile products were detected in photocatalytic and sonophotocatalytic degradation. A kinetic model involving all stable intermediate species detected was introduced. Apparent rate constants of all stages of DMMP mineralization increase under sonication. A reaction route of DMMP mineralization without the formation of intermediate products appeared under ultrasonication. Such behaviour was attributed to enabling mass transport of DMMP into micropores and to the surface of TiO_2.

The study of Sonophotocatalytic/H_2O_2 degradation of phenolic compounds in agro-industrial effluents has been done by **Silva A.M.T et al, (2007)** and gave following conclusions

(1) Sonophotocatalytic treatment of a synthetic solution containing several phenolic compounds typically found in agro-industrial effluents over Degussa TiO_2 suspensions proved efficient in terms of specific pollutants removal and solution mineralization. Interestingly, the combined process was considerably more effective than the respective individual treatments, i.e. Sonolysis and photocatalysis. Process efficiency was further enhanced in the presence of H_2O_2 acting as hydroxyl radical source.

(2) TiO_2 characterization before and after use showed that composition and morphology of the catalyst were not considerably affected during the Sonophotocatalytic treatment. However, the BET surface area of the used catalyst was much higher than that of the fresh one, suggesting possible particle de-aggregation induced by the ultrasound.

(3)The synergistic action of ultrasound may be associated with an increase in the production of hydroxyl radicals via water Sonolysis and H_2O_2 cleavage as well as an increase in catalyst surface area. Moreover, the ultrasound may accelerate mass transfer of reagents onto the TiO_2 surface as well as remove any impurities from its surface.

Same work has also been done by **Gogate PR. (2008), Zhiming Dai et al, (2005)**

Bahena C.L et al, (2008) worked on the photocatalytic degradation of alazine and gesaprim commercial herbicides was carried out in aqueous TiO_2 suspensions under UV light. Degradation of these herbicides was also observed by the combined effects of photocatalysis with sonolysis (sonophotocatalysis) using an ultrasound source of 20 kHz.

Degradation profiles were recorded by measuring the concentration of the active compounds present in the alazine (alachlor and atrazine) and gesaprim (atrazine) and It has been shown that the alazine resulted in a complete mineralization and a high mineralization for the gesaprim (90-95%) was accomplished by the employment of sonophotocatalysis over TiO_2 suspensions in the presence of UV light as source of energy. 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.

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 recalcitrant compounds but very less on the wastewater treatment of pharmaceutical industry. So work was done on the Sonophotocatalytic treatment of pharmaceutical wastewater.

CHAPTER-4

MATERIALS AND METHODS

Raw effluent was collected from a pharmaceutical industry. The samples were checked for some initial parameters and then treatment was done.

4.1 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 with a BET surface area of 50± m^2g^{-1} and average particle size of 30 nm). 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. For determination of BOD phosphate buffer, Calcium chloride, Ferric chloride, Magnesium sulfate, Magneous sulphate, Potassium iodide, Sulphuric acid, Sodium thiosulphate and starch as indicator were used. For Sulphate determination Barium chloride was used and for Chloride content Silver nitrate and K_2CrO_4 indicator were used.(standard method). In all experiments distilled water was used. Different normality of HCl and NaOH were used for adjustment of pH of wastewater.

4.2 Instruments used

4.2.1 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 4and 9) from time to time throughout study. **(Figure-4.1)**

4.2.1 COD Digester

COD Digester was used for the digestion of samples in the process of COD determination.

Figure - 4.1 pH meter

Figure -4.2 COD Digester

4.2.2 Spectrophotometer The spectrum was taken with UV- vis. Spectrometer (Hitachi V- 500 UV/VIS (Japan) double- beam spectrometer. **(Figure-4.3)**

Figure -4.3 Spectrophotometer

4.2.3 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-4.4 and Figure-4.5)**

Figure-4.4 Two Photocatalytic reactors

Figure -4.5 UV bulb of 125 watts

4.2.4 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-4.6)**

Figure -4.6 Ultrasonic bath

4.2.4 Sonophotocatalytic reactor

The immersion type photocatalytic reactor was placed in sonicator bath thus making sonophotocatalytic reactor. **(Figure 4.7)**

Figure 4.7- Sonophotocatalytic reactor

4.2.5 Magnetic Stirrer

Magnetic stirrer was used during experimentation to solve the problem of mixing and titanium dioxide remains in suspension. **(Figure-4.8)**

Figure -4.8 Glass bowl reactor magnetic stirrer under sun light

4.2.6 Air sparger

Air is continuously supplied during experiments in UV reactor as well as solar experiments in order to oxidize the organic matter.

4.3 Methods

4.31 Collection and storage of sample

Sample was collected from the core process of industry. Sampling vessel was cleaned and rinsed carefully with distilled water and rinsed carefully with distilled water and then washed with sample during sample collection. Then effluent was stored in cold store at 4.C.

4.3.2 Characterization of Wastewater sample

Wastewater sample was analyzed for the COD, BOD, TS, TSS, TDS, Chloride, Sulfate, pH etc. the entire experimental setup was repeated to get the reproducibility of results. Parameters were analyzed by methods given in standard methods for the examination of water and wastewater 1989(17th edition) and single distilled water was used throughout the study. The methods used are follows:

Estimation of COD

COD was estimated as per the standard method no. 5220 C, page no. 5-14 from Standard Methods for the examination of water and wastewater, 1989 (17th edition). Samples were digested in COD digester.

Estimation of BOD

BOD was estimated as per standard method no. 5210 B, page no. 5-4 from Standard Methods for the water and wastewater, 1989(17th edition). Tests were repeated for getting the reproducibility of the results.

Estimation of Total Solids

TS were estimated by method no. 2540 B, page no. 2-72 of Standard Methods for the examination of water and wastewater.

Estimation of Total Dissolved solids

TDS were estimated as per the standard method no. 2540 C, page no. 2-74 of the Standards Methods for the examination of water and wastewater.

Estimation of Suspended Solids

TSS was estimated by method no. 2540 D, page no. 2-75 of Standard Methods for the examination of water and wastewater.

Estimation of sulfate

TDS were estimated as per the standard method no.4500-D, page no. 4-206 of the Standards Methods for the examination of water and wastewater.

Estimation of Chloride

TDS were estimated as per the standard method no.4500-B, page no.4-68 of the Standards Methods for the examination of water and wastewater.

4.3.3 Treatment

Preparation of sample:

Wastewater collected from the pharmaceutical industry was highly concentrated. So to get the values within range, the sample was diluted. Distilled water was used for the dilutions. Initial pH was checked and varied to get the optimized value of the pH. Catalyst was added in a wide range from 0.1 to 0.7 gm/100 ml to optimize the process for maximum pollutant degradation. H_2O_2 was added in the range of 0.25-3 ml/100 ml to check optimum volume for the process. The concentration of H_2O_2 used was 30% in all experiments.

Procedure:

Sample was treated in UV, US and UV+US for seven hours. Samples were withdrawn after one hour and filtered from 0.45 micron syringe filter. COD of the samples were then measured as per the standard methods. Results were then optimized regarding catalyst addition, pH and oxidant addition. Tests were repeated for the getting the reproducibility of results.

After Sonophotocatalytic treatment (with optimized conditions), water was filtered and checked for COD. BOD, TSS, pH, Sulfate, Chloride etc.

CHAPTER-5

RESULTS AND DISSCUSSIONS

5.1 Wastewater characteristics

Raw wastewater sample was collected from a Pharmaceutical industry. Wastewater was taken from core process and analyzed for its various parameters. The values of the various parameters are shown in **Table 5.1** before the treatment of the sample water.

S.No.	Parameter	Prevailing Range (mg. L^{-1})
1	pH	3.75
2	COD	32000
3	BOD	12800
4	TS	25200
5	TDS	23900
6	TSS	1300
7	Sulfate	3716
8	Chloride	7526

Table 5.1 Characteristics of raw pharmaceutical effluent

All these parameters shows that the wastewater to be highly polluted. So some sort of treatment is required to satisfying prescribed limits.

5.2 Absorption spectra for raw effluent

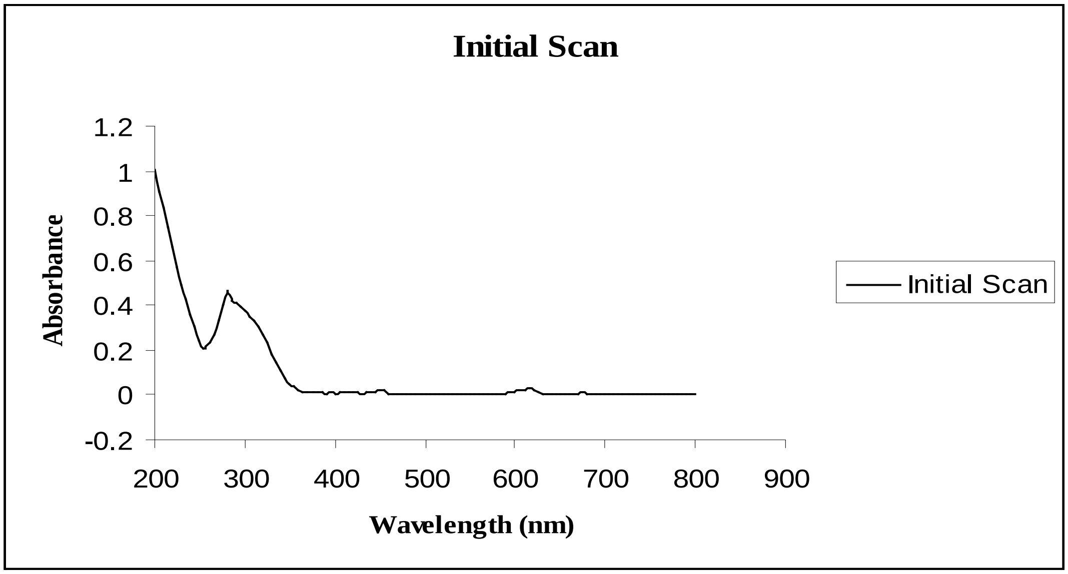

Figure 5.1 Absorption spectra for raw Pharmaceutical wastewater

The photocatalytic experiments were conducted under both UV as well as solar light. The degradation was recorded in term of change in intensity of characteristics peaks. Pharmaceutical wastewater shows the absorption peaks at 280 and 616 nm. **Fig. 5.1** shows the UV-Vis. Spectra of raw pharmaceutical wastewater. The rate of degradation was recorded with respect to change in intensity of absorption of peaks at 280 nm.

5.3 Dark adsorption studies

Dark adsorption studies were carried out to know that how much adsorption was resulted from TiO_2 instead of UV light. As soon as the catalyst was added, pollutants from solution adsorbed on the surface and lead to decrease in concentration of pollutant in the solution but 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 COD was observed. Thus results observed from adsorption experiment confirmed that decrease in concentration of pollutant was due to adsorption i.e. no degradation of the wastewater was confirmed.

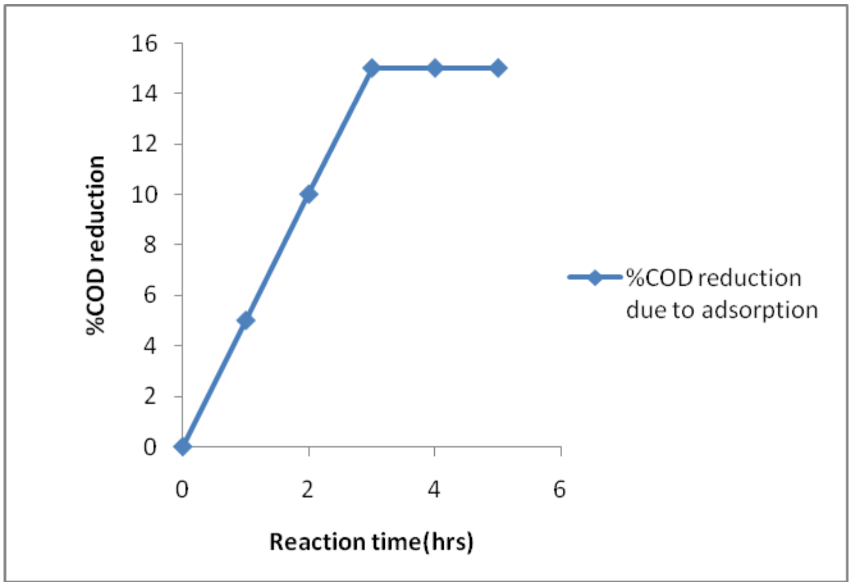

Figure-5.2 % COD reduction due to adsorption phenomena

As it is clear from the **Figure-5.2** that the rate of decrease in pollutant concentration was very less i.e. only 15% from adsorption process thus suggesting some other alternative advanced methods that are capable of complete degradation of wastewater.

5.4 Photolysis (UV) of wastewater

Wastewater is able to absorb part of the emitted 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, wastewater 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.

Kuo W.S and P.H.Ho, 2006 have reported the similar behavior during the photolysis of dye under ultraviolet irradiation. **Figure-5.3** shows that there is only 12.5 % degradation due to photolysis.

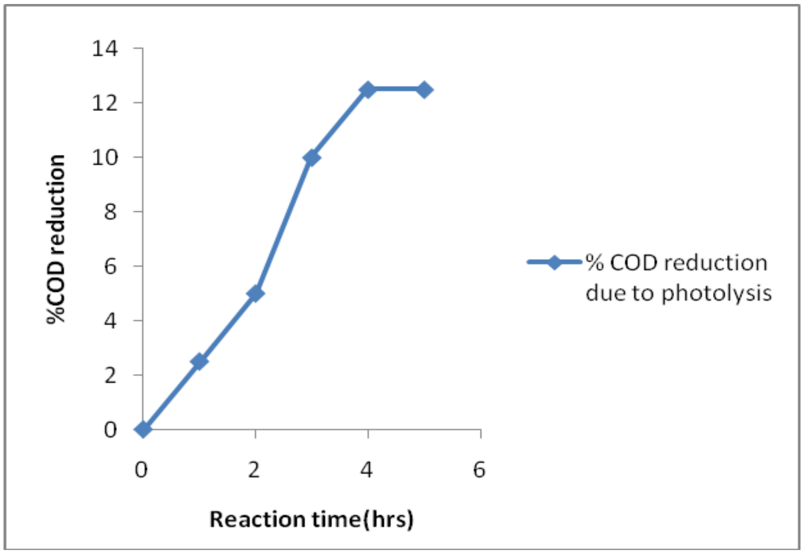

Figure-5.3 % COD reduction due to Photolysis

5.5 Photocatalytic (UV+TiO_2) Treatment

As it was clear from the results of adsorption and photolysis processes that the rate of degradation in pollutant concentration was very less. Therefore some sort of treatment was required to degrade the pollutants present in wastewater. Photocatalytic treatment in UV light with TiO_2 showed promising results with decrease in COD value up to 85% after six hours **(Figure 5.4**).

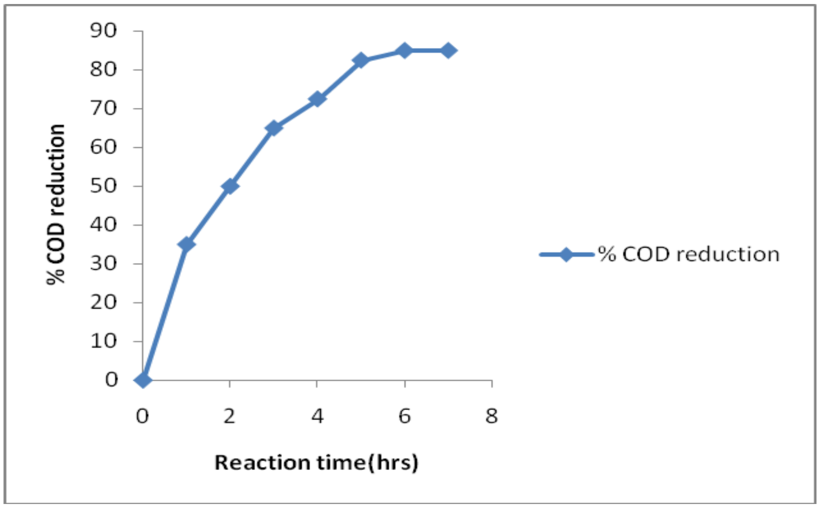

Figure -5.4 % COD reduction due to photocatalysis

5.6 Process Optimization

After the characterization of the raw wastewater, 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 deciding factors and these optimized conditions were used for the further actual treatment of the wastewater.

So the Photocatalytic treatment process was optimized for the following deciding factors and these optimized conditions were used for the further actual treatment of the wastewater.

Photocatalytic reactions can usually be described by a pseudo-first order kinectic expression.i.e.

$$-dCOD/dt = K_{UV}COD$$

$$\text{Or} \quad \text{In } COD_0/COD = k_{UV}t$$

Where k_{UV} is an apparent reaction rate constant and COD_0 and COD are initial and final COD respectively.

5.6.1 Concentration of photocatalyst

Photocatalyst used was Degussa P-25 TiO_2 in varying concentrations ranging from 0.1gm/100ml to 0.7gm/100ml during the photocatalytic treatment process for the optimization of the concentration. 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 pollutant molecules absorbed on the surface of catalyst are increased owing to an increase in rate of photocatalytic reaction. Above a certain level, the pollutant 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, Figure 5.6 and Figure 5.7 depicts that the maximum COD reduction was achieved with 0.2g/100ml concentration of photocatalyst. So an amount of 0.2g/100ml of TiO_2 has been taken for the subsequent experiments for the optimization of the operating pH and concentration of oxidant to be added.

Faisal et. al., (2005) have documented the effect of catalyst dose on two dyes acridine orange and ethidium bromide and observed that the degradation rate for the decomposition of both the dyes in the presence of TiO_2 Degussa P25 increases with the increase in catalyst concentration and a further increase in catalyst concentration leads to a decrease in degradation rate.

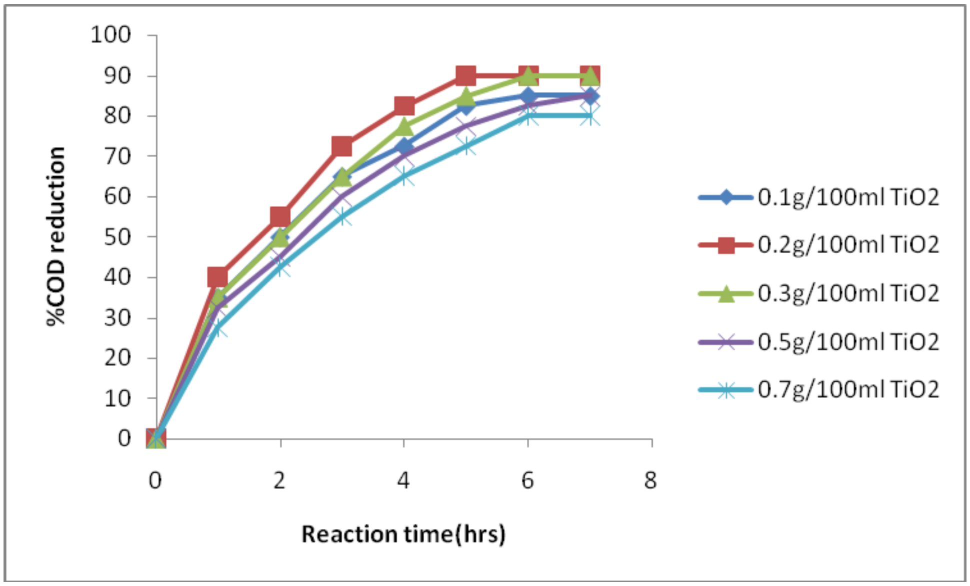

Figure -5.5 % COD reduction with varying concentration of TiO_2

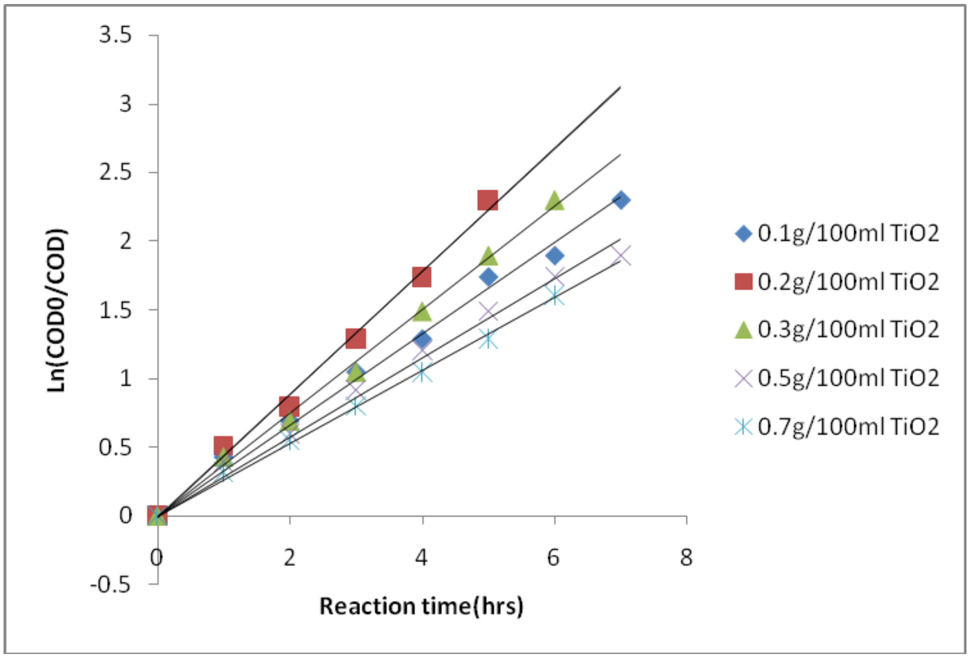

Figure-5.6 First order kinetic plot showing varying concentration of TiO_2

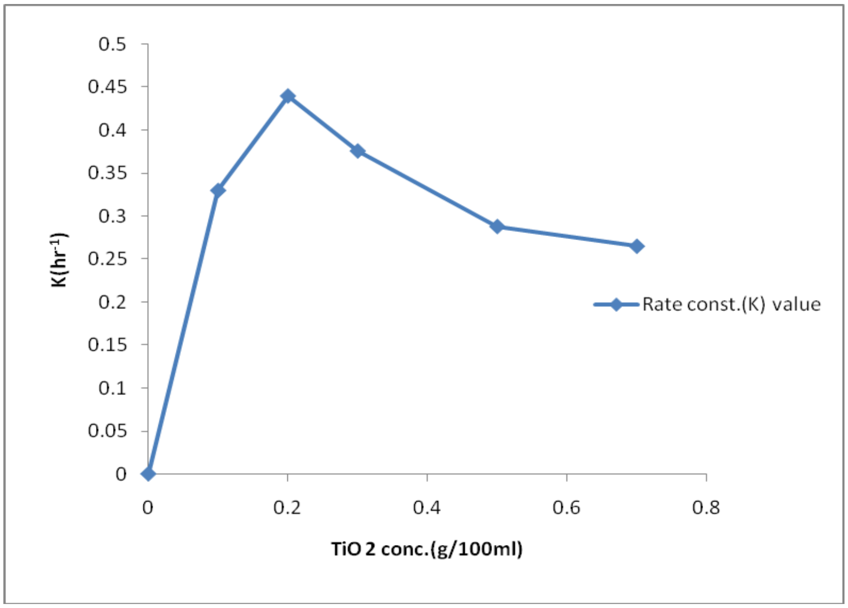

Figure- 5.7 Showing the effect of TiO_2 dose on rate constant K

5.6.2 Operating pH

The Pharmaceutical wastewater sample in question has pH 3.75 which was collected from core process. The generation of the hydroxyl radicals in AOP’s is also effected by pH of the solution. Thus pH plays an important role in generation of hydroxyl radicals which is powerful oxidizing agent. Hence, employing Degussa P25 as Photocatalyst the degradation of wastewater in the aqueous suspensions of 0.2 gm/100 ml TiO_2 was studied in the pH range between 2 and 10.

The effect of the solution pH on the degradation rate can be explained mainly by adsorption of wastewater pollutant on TiO_2 surface. In acidic suspensions, the adsorption of pollutant 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 (pzc) 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 wastewater is negatively charged, the acidic solution favors adsorption of wastewater onto photo catalyst surface.

Figure-5.8, Figure-5.9 and Figure-5.10 shows that the degradation rate is better at acidic pH and increasing from pH 2 to 4 but after 4 it will start decreasing and further decreased in alkaline conditions. The maximum degradation was observed at pH 4.0 and the final pH after photo catalytic treatment was 7.1 which is suitable for biological treatment as well as discharge of wastewater into the water bodies.

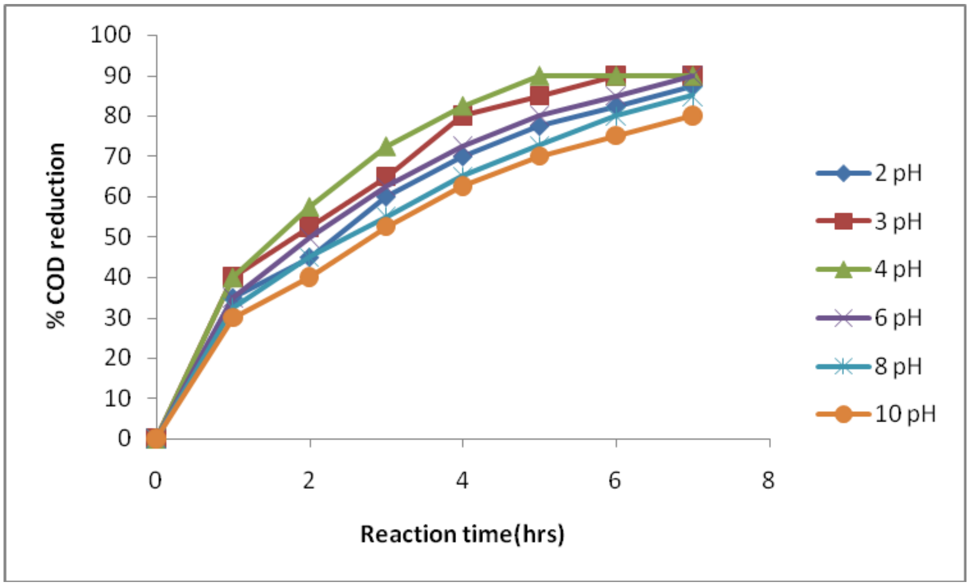

Figure-5.8 % COD reduction with varying pH range

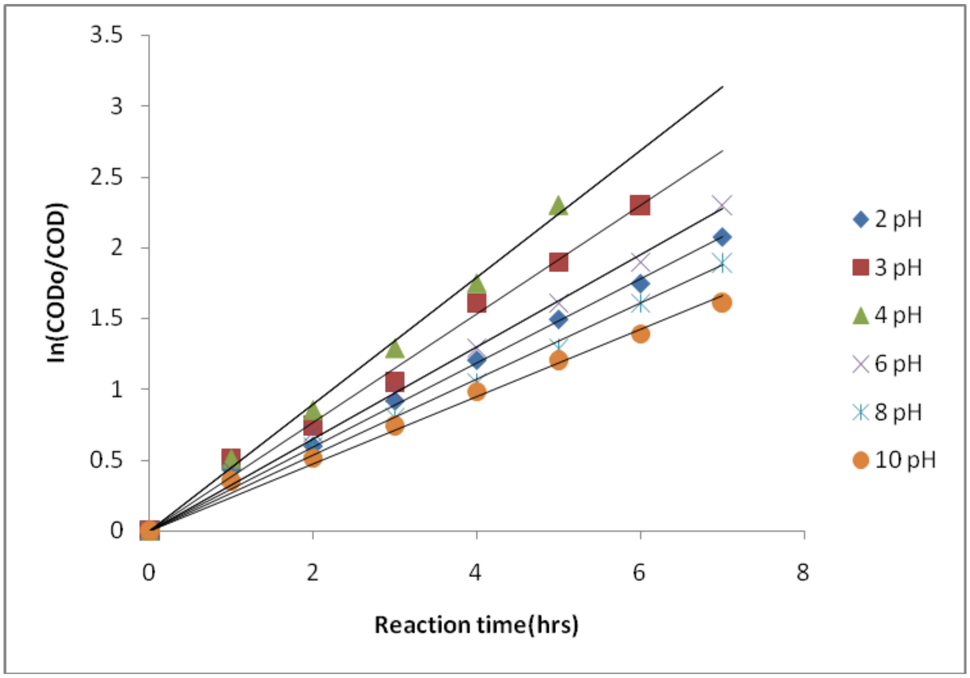

Figure 5.9 First order kinetic plot showing the varying range of pH.

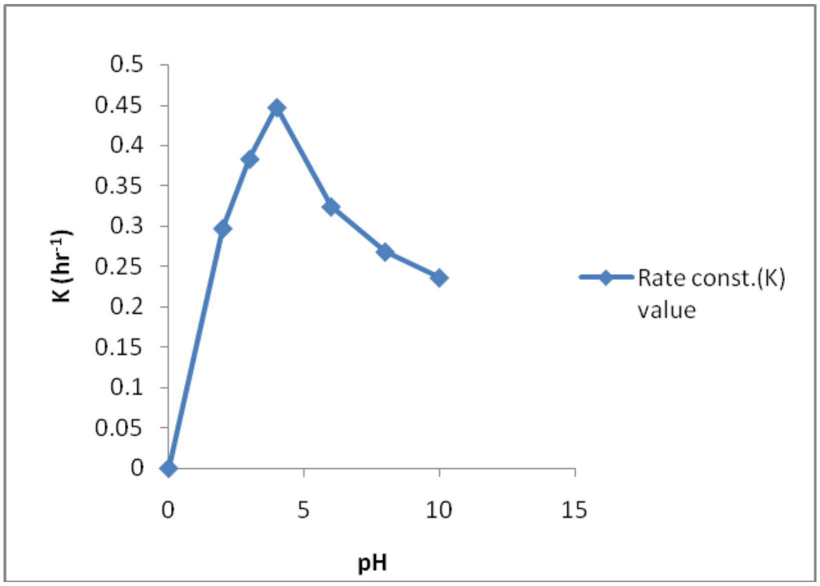

Figure 5.10 Showing the effect of pH on rate constant K.

5.6.3 Effect of Oxidant addition

One possible way to increase the 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:

$$TiO_2\ (e-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^\bullet$$

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 concentration of H_2O_2, it also acts as a scavenger as shown in the following equations.

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

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

In our experiment in order to optimize the catalyst dose the concentrations were varied during the photo catalytic treatment from 0.25 to 3 ml/100ml at constant pH of 4 and catalyst dose of 0.2gm/100ml. It has been observed that best results were obtained when oxidant addition came out to be 0.5ml/100 ml of the sample and has been taken as the optimum amount required for maximum effective treatment of pollutant

Figure 5.11, Figure 5.12 and Figure 5.13 shows the effect of oxidant of COD reduction of sample wastewater and clearly indicates maximum removal of COD at 0.5 ml / 100 ml of the wastewater.

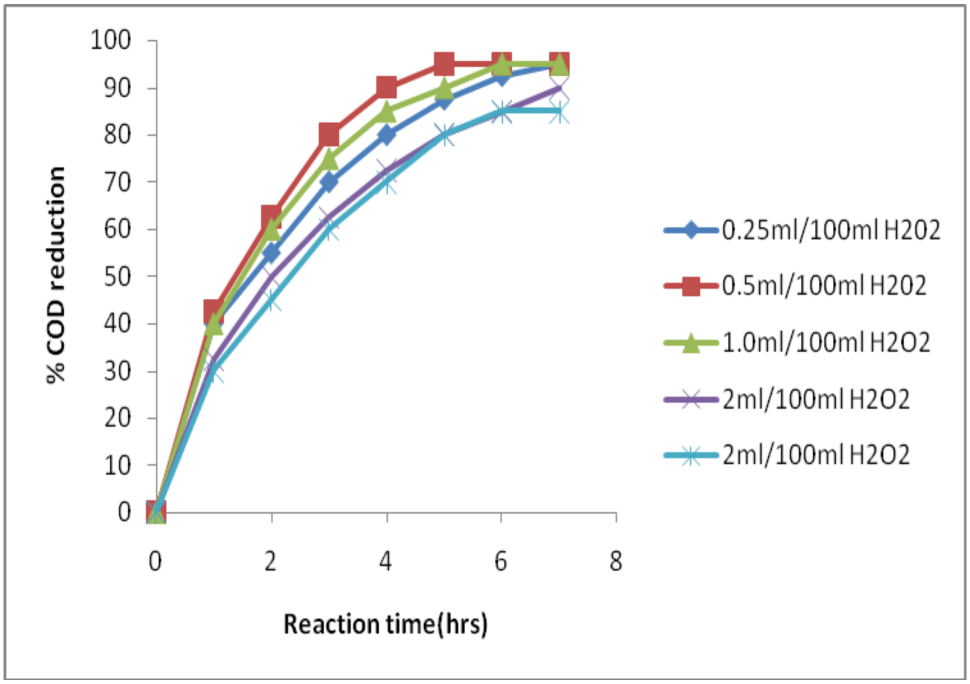

Figure -5.11 % COD reduction with varying H_2O_2 concentrations

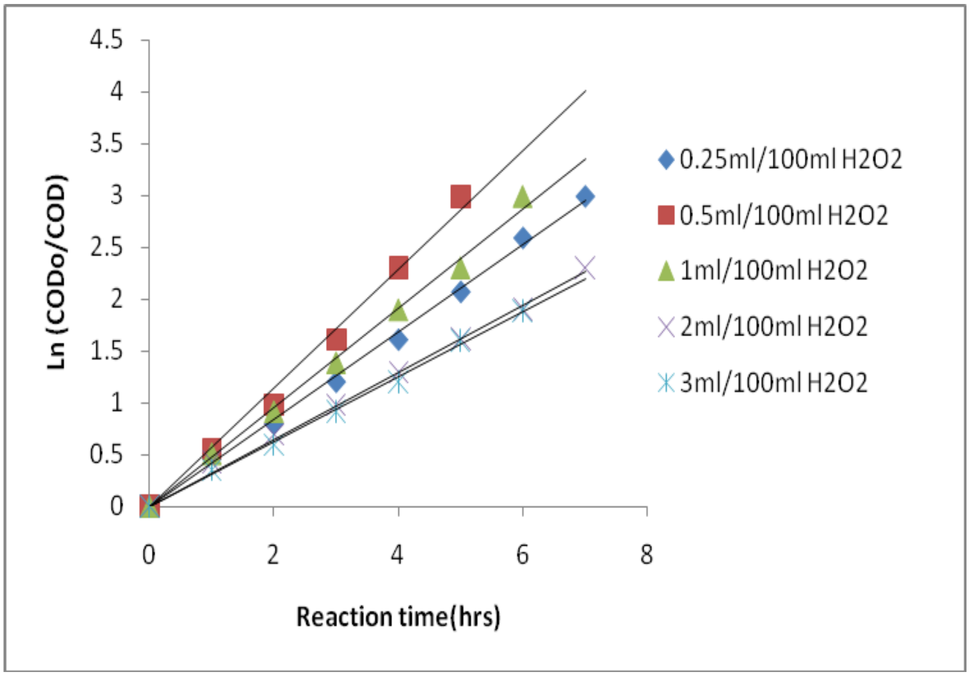

Figure- 5.12 First order kinetic plot showing the varying concentration of H_2O_2

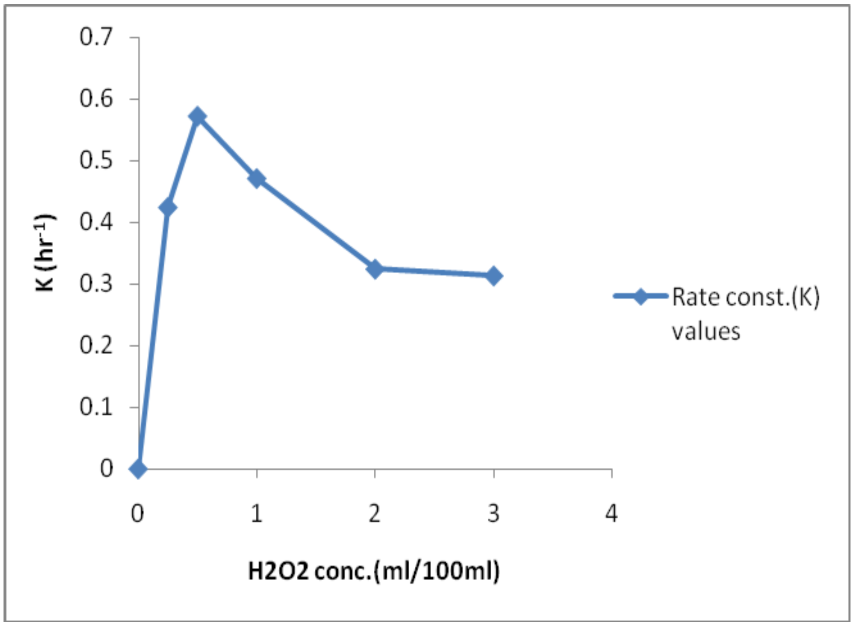

Figure - 5.13 Showing the effect of oxidant dose on rate constant K

5.7 Photocatalytic treatment using sun light and its comparison with treatment under UV light.

The effect of UV light on the degradation of Pharmaceutical industry wastewater by photocatalytic process has been investigated. The comparative study has been carried out for the degradation of wastewater in Solar and UV light. The aqueous suspensions of TiO_2 (0.2 gm/100ml) containing wastewater was exposed to Solar and UV at pH 4.0

Figure 5.14 shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of wastewater under sunlight and UV light source, respectively. The rate of degradation was found to be slightly more in the UV light in comparison to solar light. The maximum degradation achieved in sun light is 90% after 5 hrs of reaction time and the maximum degradation achieved under UV light is 95% after 5 hours. It is evident from the graph that percentage degradation of solar light is very close to UV light degradation so solar light can be efficiently used for the photocatalytic degradation of wastewater. India being a tropical country, there is a free availability of sunlight so for industrial applicability sunlight is preferred for the wastewater treatment.

Faisal et. al., 2005; Muruganandham. M et. al., 2006; Kuo W.S et. al., 2006 have studied the aqueous suspensions of TiO_2 containing dye derivatives to solar radiation. It was found that the degradation of the model compounds proceeds more rapidly in the presence of UV/TiO_2 light source as compared to Solar/TiO_2.

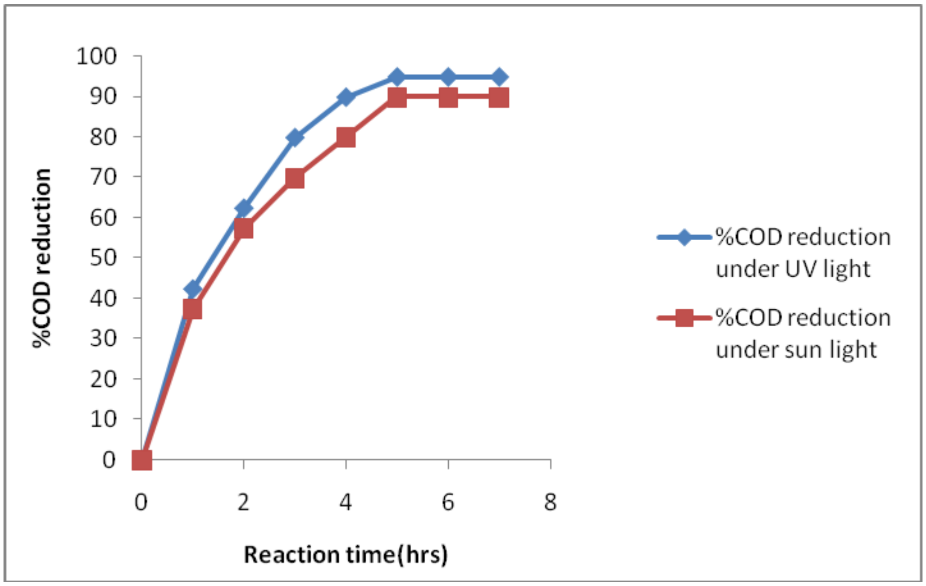

Figure 5.14 Effect of UV/Solar light on photo catalytic degradation of wastewater at 4 pH, [TiO_2] = 0.2gm/l00ml and 0.5ml H_2O_2/100ml

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

Sonolysis is the breaking of chemical bonds or formation of radicals using ultrasound. The use of ultrasound has recently been attraction as advanced oxidation process for wastewater treatment. 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 ($H^\bullet$ and $^\bullet OH$) 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.

Same effect have been shown by **Zhiming D et al, (2005)** on the degradation of 4-Chlorophenol.

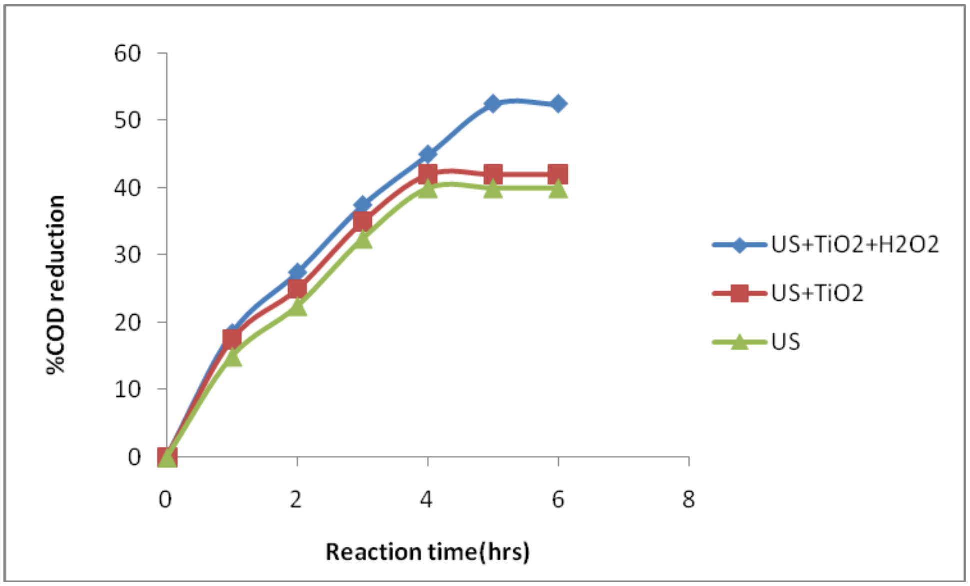

Figure 5.15 % COD reduction due to Sonolytic and Sonocatalytic and Sonocatalytic + oxidant processes at 4 pH, [TiO_2] = 0.2gm/l00ml and 0.5ml H_2O_2/100ml

Figure 5.15 shows Sonolysis with all optimum parameters 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.

5.9 Sonophotocatalytic (UV+US+TiO_2) treatment under UV and sunlight.

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.

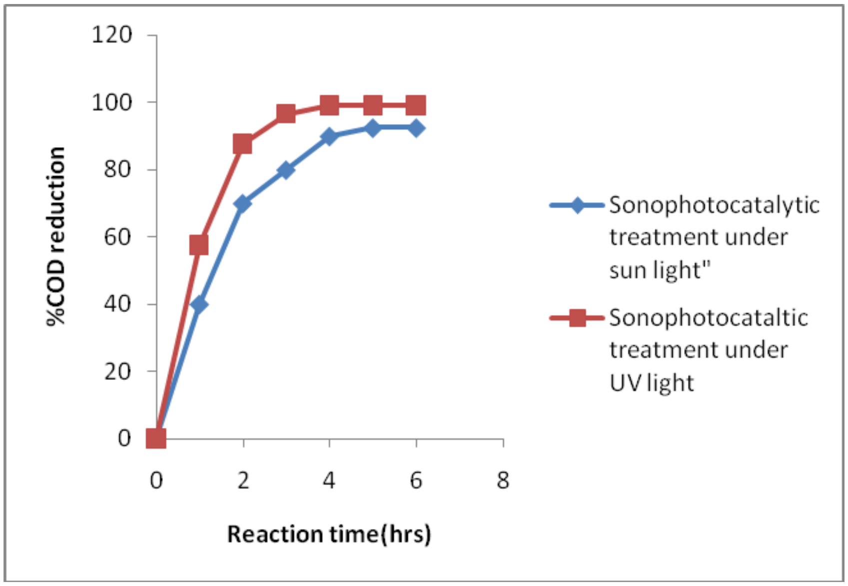

Figure 5.16 Effect of UV/Solar light on photo catalytic degradation of wastewater at 4 pH, [TiO_2] = 0.2g/l00ml and 0.5ml H_2O_2/100ml

Figure 5.16 shows that the rate of degradation was found to be more in the UV light in comparison to solar light. The maximum degradation achieved in sun light is 92.5% after 5 hrs of reaction time and the maximum degradation achieved under UV light is 99% after 4 hours.

5.10 Comparisons of Sonocatalytic, Photocatalytic and Sonophotocatalytic treatment.

Figure 5.17 and **Figure 5.18** shows that the max degradation was achieved under Sonophotocatalytic treatment of wastewater i.e. 99 % after 4 hours of reaction time. The reason for this is that the basic mechanism for both ultrasound and photocatalytic oxidation is generation of free radicals. if these mode of irradiations are operated in combination, more no. of radicals will be available for the reaction there by increasing the rate of reaction followed by photocatalytic treatment i.e. 95% after 5 hours and very less under Sonocatalytic process i.e. only 52.5% after 5 hours. **González A.S and S.S Martínez, (2008)** have shown the same results on the degradation of basic blue 9 industrial textile dyes.

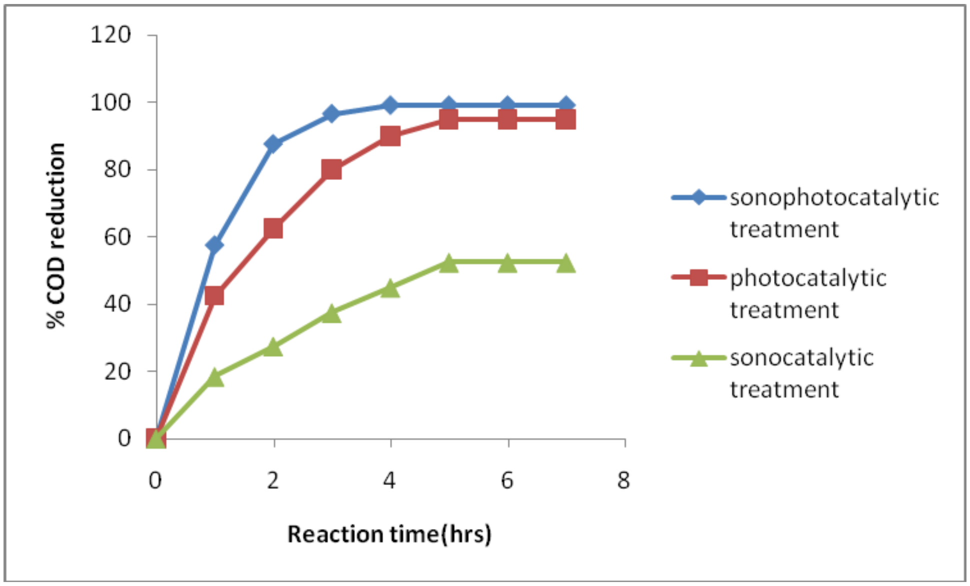

Figure 5.17 Showing % degradation of wastewater under Sonocatalytic, photocatalytic and Sonophotocatalytic process at optimum condition i.e. 0.2g/100ml TiO_2, 0.5ml/100ml H_2O_2 and at pH 4

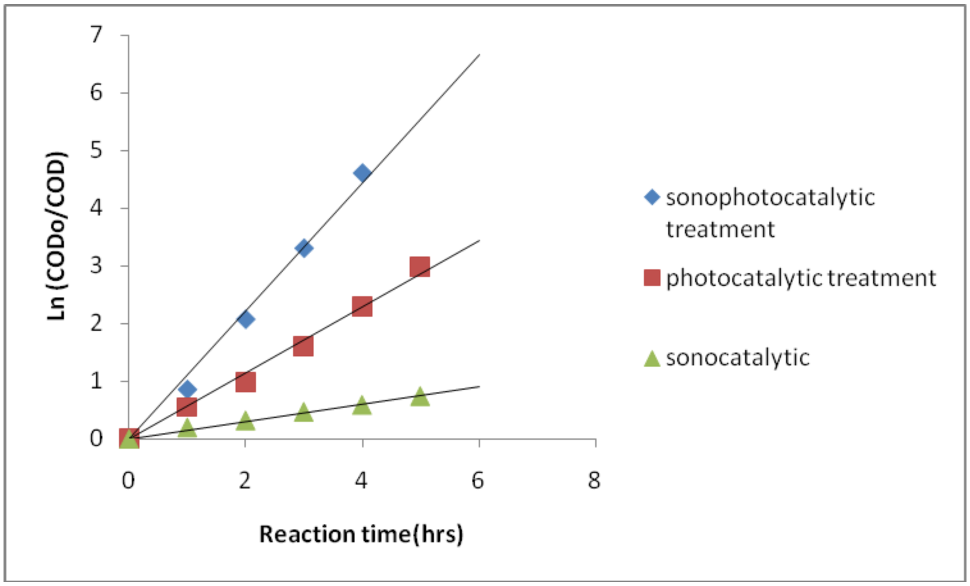

Figure-5.18 First order kinetic plot with 0.2g/100ml TiO_2, 0.5ml/100ml H_2O_2 and 4 pH under Sonophotocatalysis, photocatalysis and Sonocatalysis as a function of time.

5.11 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 .

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

In our study the rate constant of combined process ($K_{US+UV+ TiO2+H2O2}$) is 1.1 hr^{-1} and rate constant of $K_{UV+TiO2+H202}$ is .57 hr^{-1} and for $K_{US+TiO2+H2O2}$ is .15 $hr^{-1.}$

$K_{UV+TiO2+H202} + K_{US+TiO2+H2O2}$ = .57 +.15 = .72 hr^{-1}

$K_{US+UV+ TiO2+H2O2 =}$ 1.1 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.

$$\% \text{ synergy} = 100 \times \frac{(1.1) - (.57 +.15)}{1.1}$$

Therefore % synergy is 34.5.

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

5.12 Effluent characteristics after Sonophotocatalytic treatment

After the Sonophotocatalytic treatment in UV reactor under optimized conditions i.e. at TiO_2 dose of 0.2 gm/100ml, operating pH of 4.0 and 0.5ml/100ml of oxidant, characterization of the treated wastewater was done. **Table- 4.2** showing the parameters analyzed after the 4 hrs of Sonophotocatalytic treatment of pharmaceutical wastewater which shows a major reduction in pollution load.

S.No.	Parameter	After Sonophotocatalytic treatment (mg. L^{-1}) (Optimized conditions)	Percentage degradation
1	pH	7.1	–
2	COD	320	99
3	BOD	150	98.8
4	TDS	102	99.5
5	Sulfate	232	93.7
6	Chloride	92	98.7

Table 4.2 Characteristics of Wastewater after Sonophotocatalytic (UV) Treatment Under Optimized Condition

5.13 Absorbance spectra after Sonophotocatalytic treatment

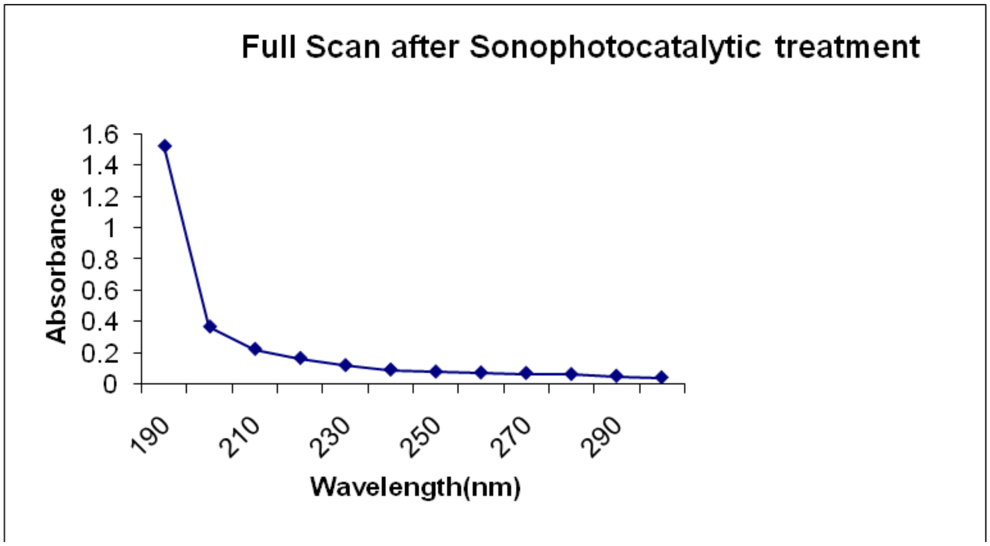

Figure 5.19- Absorption spectra after Sonophotocatalytic treatment.

The primary absorption peaks of the raw pharmaceutical wastewater were at 280 nm and 616 nm. As the reaction proceeds, the two peaks disappear gradually as shown in **Figure 5.15** and the full scanning spectrum pattern changes obviously after 4 hrs. This may be the evidence of the intermediate byproduct. At the end of the 4 hrs of reaction time, there is no evident absorption peak observed. It indicates that the pollutants are destroyed with the Sonophotocatalytic reaction and proves that wastewater is fully decomposed in the UV+US+TiO_2 system.

CHAPTER-6

CONCLUSION

Heterogeneous photocatalysis process and sonophotocatalysis are 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. These processes differ from the other treatments processes because wastewater compounds are degraded rather than concentrated or transferred into a different phase. Because secondary waste materials are not generated, there is no need to dispose of materials.

Pharmaceutical wastewater has been successfully degraded in the presence of TiO_2 photocatalyst. First of all we did photocatalytic treatment under UV light and sun light respectively at the optimized reaction conditions i.e. pH of 4.0, catalyst dose of 0.2g mg/100ml and oxidant concentration of 0.5 ml/100ml. The rate of degradation was found to be slightly more in the UV light in comparison to solar light. The maximum degradation achieved in sun light is 90% after 5 hrs of reaction time and the maximum degradation achieved under UV light is 95% after 5 hours. As the percentage degradation of solar light is very close to UV light degradation so solar light can be efficiently used for the photocatalytic degradation of wastewater. India being a tropical country, there is a free availability of sunlight so for industrial applicability.

Then the Sonolysis treatment was done with all optimized conditions and the maximum degradation achieved was 52.5% after 5 hours of reaction time. Sonolysis alone is not that much capable of degradation the pollutant as it is when combined with other AOP, s like photocatalysis.

So after that we did Sonophotocatalysis treatment (i.e. Sonolysis + photo catalysis) with all the optimized condition like pH of 4.0, catalyst dose of 0.2gm/100ml and oxidant concentration of 0.5 ml/100ml. The results obtained are very good i.e. degradation achieved is 99% after 4 hours. This is because Photocatalytic action with the ultrasound has resulted in higher degradation rates of the contaminants 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. And by combining these two modes of irradiations (US + UV) more number of hydroxyl radicals are produces.

And now it is clear from the results obtained that the max degradation was achieved with Sonophotocatalytic treatment of wastewater i.e. 99% after 4 hours of reaction time followed by photocatalytic treatment i.e. 95% after 5 hours and very less under Sonocatalytic process i.e. only 52.5% after 5 hours.

After Sonophotocatalytic treatment the results obtained were quit appreciable as it reduced COD by 99%, BOD by 98.8%, Sulfate by 93.7%, Chloride by 98.7% and TDS 99.5%.

The results of Sonophotocatalytic degradation of wastewater 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. It is differ from the other treatments processes because wastewater compounds are degraded rather than concentrated or transferred into a different phase. Because secondary waste materials are not generated, there is no need to dispose of materials. So, we can say that Sonophotocatalysis has large capability for the water treatment.

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